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PRACTICAL CHEMISTRY

BY

LYMAN C. NEWELL, Ph.D. (JOHNS HOPKINS)

PROFESSOR OF CHEMISTRY, BOSTON UNIVERSITY, BOSTON, MASS.

AUTHOR OF

"EXPERIMENTAL CHEMISTRY," "DESCRIPTIVE CHEMISTRY"

"GENERAL CHEMISTRY," "INORGANIC CHEMISTRY FOR

COLLEGES," "LABORATORY MANUAL OF

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PREFACE

A TEXTBOOK intended for the first year of chemistry should meet certain requirements. Both pupil and teacher must be considered. The pupil needs a book which is written plainly, illustrated fully, and applied practically; which stimulates interest in chemistry, and which can be studied profitably. The teacher needs a book in which the text is carefully selected, judiciously apportioned, and properly arranged; which provides teaching material, and which can be taught successfully. The author believes his PRACTICAL CHEMISTRY meets these requirements.

The text includes the facts and principles suitable for beginners. No important topic has been omitted. The selection is varied, permitting the use of the book in different kinds of classes. The topics suggested by the College Entrance Examination Board and the Board of Regents (New York) have been incorporated.

The style and arrangement are clear — short sentences, brief paragraphs, explanatory examples, lettered subdivisions, numbered sections, instructive topical headings. Unusual care has been taken to write clearly such topics as symbols, formulas, equations, atomic weights, molecular weights, and valence.

The exercises, which are placed at the end of the chapters, have been prepared to meet the real needs of pupils. The author believes that a class should be drilled on fundamentals as well as provided with opportunities to answer test questions. Hence, numerous exercises have been provided for review, home study, practical experience, and themes. Teachers are urged to examine these exercises and assign those best adapted to the needs of the class. The list of books incorporated in the Appendix, § 5, will be serviceable in connection with home study and other assignments.

The problems emphasize fundamental principles and processes; many require original thinking. The liberal selection will meet the requirements of different kinds of classes.

An examination of the book will show that it is a PRACTICAL CHEMISTRY — practical in several ways. The more vital applications of chemistry are described in connection with the appropriate facts or principles. Moreover, the major applications of chemistry are so fully described and illustrated that a pupil can obtain from the book itself an accurate and adequate account of modern chemical indus-

tries. Teachers are referred to such topics as purification of water (69), nitric acid (196), sulphur (250), sulphuric acid (268, 270), fuel oil and gasolene (311, 312, Fig. 112), sodium silicate (387), glass (394), cast iron (490), steel (494, 495), and copper (528, Fig. 193).

Certain features of this book should not be overlooked.

(1) The study of carbon is begun in Chapter III, thereby introducing a familiar element and its striking applications at the start. This element is reviewed (with extensions) in Chapter XXI, and its useful compounds are studied in Chapters XXII (Fuels and Illuminants), XXIII (Other Carbon Compounds), and XXIV (Food). No apology is offered for devoting so much space to carbon. It is a fundamental element, and the practical applications of this element and its compounds are indispensable and conspicuous.

(2) The portion of the text that deals with theory is thoroughly adequate. The material is strategically distributed among several chapters (VII, VIII, X, XV, XVI, XVII). This distribution, as well as the simple treatment, will make the theory of chemistry less formidable to beginners.

(3) Certain metals are treated rather fully and placed in the first part of the text devoted to metals. These are sodium, calcium, iron, aluminium, and copper (Chapters XXIX-XXXIII). By this arrangement the essential principles of metallurgy, the characteristics of metals, and the applications of metals and their compounds are available for study before the hurried work at the close of the year.

(4) Half-tone illustrations have been liberally used because they tell a story which is often more complete than verbal description. The author trusts they will be made indispensable adjuncts to instruction. The portraits of chemists, which were made from originals in the author's private collection, have been inserted to arouse interest in those chemists who have contributed conspicuously to the founding and progress of chemistry.

(5) The drawings of processes and apparatus are likewise intended as a supplement to the text. Especial care has been taken to draw them accurately and to represent salient features without confusing details. These drawings, with minor exceptions, were made by Harold C. Spencer, Boston University, 1914. The author is deeply indebted to him for commendable patience and skillful coöperation.

The author is grateful for suggestions and assistance received from members of the faculty of Boston University and from former students who are teaching chemistry in high schools.

L. C. N.

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CONTENTS

CHAPTER		
I.	CHEMICAL CHANGE — ELEMENTS — COMPOUNDS —	
	LAW OF CONSTANT COMPOSITION	1
II.	OXYGEN	12
III.	CARBON AND ITS OXIDES — LAW OF MULTIPLE PRO-	
	PORTIONS	28
IV.	HYDROGEN	39
V.	MEASUREMENT OF GASES	50
VI.	WATER — LAW OF GAS VOLUMES — HYDROGEN	
	PEROXIDE	59
VII.	ATOMIC THEORY — ATOMS AND MOLECULES	87
VIII.	SYMBOLS AND FORMULAS	96
IX.	NITROGEN — AIR — ARGON — HELIUM — LIQUID AIR	102
X.	REACTIONS AND EQUATIONS	115
XI.	CHLORINE — HYDROCHLORIC ACID	129
XII.	ACIDS — BASES — SALTS — NEUTRALIZATION	142
XIII.	AMMONIA — AMMONIUM COMPOUNDS	148
XIV.	NITRIC ACID — NITROGEN OXIDES	159
XV.	MOLECULAR WEIGHTS AND FORMULAS	171
XVI.	ATOMIC WEIGHTS	182
XVII.	VALENCE	192
XVIII.	IONS AND IONIZATION	201
XIX.	SULPHUR — SULPHIDES	218
XX.	SULPHUR OXIDES, ACIDS, AND SALTS	229
XXI.	CARBON — CARBONIC ACID — CARBONATES —	
	OXIDES — CARBIDES	244
XXII.	FUELS — ILLUMINANTS — FLAME	260
XXIII.	OTHER CARBON COMPOUNDS	289

CHAPTER	PAGE
XXIV. FOOD	307
XXV. SILICA — SILICATES — GLASS	316
XXVI. METALS AND NON-METALS — PERIODIC CLASSIFICATION	329
XXVII. FLUORINE — BROMINE — IODINE	337
XXVIII. PHOSPHORUS — PHOSPHATES — ARSENIC — ANTIMONY — BISMUTH	346
XXIX. SODIUM — POTASSIUM	360
XXX. CALCIUM CARBONATE — LIME — CEMENT	376
XXXI. IRON AND STEEL	391
XXXII. ALUMINIUM — CLAY — PORCELAIN	415
XXXIII. COPPER	426
XXXIV. MAGNESIUM — ZINC — MERCURY	439
XXXV. TIN — LEAD	452
XXXVI. SILVER — PHOTOGRAPHY — GOLD	464
XXXVII. CHROMIUM — MANGANESE — PLATINUM — NICKEL — COBALT	474
XXXVIII. RADIUM AND RADIOACTIVITY	482
APPENDIX	
Metric System	493
Thermometers	493
Weights of Gases	493
Vapor Pressure	494
Books	494
INDEX	497

PRACTICAL CHEMISTRY

CHAPTER I

CHEMICAL CHANGE — COMPOUNDS — ELEMENTS

1. **What is chemistry?** — If we light a candle and let it burn, the candle wax slowly disappears — “burns away.” Let us study this change carefully. By holding a cold, dry bottle over the burning candle (Fig. 1), a film of water gathers on the inside. Now if we remove the bottle, pour in some clear limewater, and shake the bottle, the clear liquid becomes cloudy. This cloudiness is caused by a gas called carbon dioxide. Hence, the candle wax did not really “burn away.” By burning in the air, the wax changed into water and carbon dioxide.



Fig. 1. — Studying a chemical change

The experiment just studied is an example of chemical change. **Chemistry** is the science devoted largely to a study of chemical changes.

2. **Substances and properties.** — The different materials involved in a chemical change are called **substances**. We are able to recognize and distinguish substances by characteristics called **properties**. Some properties are readily detected, *e.g.* color, taste, odor, hardness, and the physical state (*i.e.* if solid, liquid, or gaseous). Other

properties are found by measurement or special experiment, and are usually expressed by numbers, *e.g.* boiling point, melting point, conductivity of heat or electricity, and specific gravity (*i.e.* relative weight). These properties, often called **physical properties**, are important, and we often use them in describing and recognizing substances.

Very important, also, are **chemical properties**—the characteristics of substances revealed in chemical changes. Thus, iron rusts in the air but gold does not, copper dissolves readily in nitric acid but platinum does not. Chemical properties are the different items, so to speak, in the

chemical conduct of substances. In chemistry we pay special attention to **chemical conduct**.



Fig. 2. — Heating a mixture of iron and sulphur in a test tube

3. What is the first characteristic of chemical change? — Let us answer this question by an experiment. Iron and sulphur are readily recognized. Besides their conspicuous properties, sulphur dis-

solves in carbon disulphide, and iron is attracted by a magnet. If we heat a mixture of iron powder and sulphur in a test tube (Fig. 2), the mass soon glows, and the glow often spreads and continues after the tube is removed from the flame. If we break the test tube and examine the product, we find that it is a hard, black solid, quite unlike either iron or sulphur. If we grind it in a mortar, and add a few drops of acid to a little of the

powder, a gas with a bad odor is liberated. No such gas is produced when acid is added to the iron, the sulphur, or the mixture. Moreover, this black solid is not attracted by a magnet nor does it dissolve in carbon disulphide.

Clearly a new substance has been formed. We may describe the chemical change in chemical language. Two different substances, iron and sulphur, each with characteristic properties, have disappeared and a new substance called iron sulphide has been produced with properties different from the properties of the original substances. All chemical changes, however complicated, involve transformation of substances. So we may say: —

The first characteristic of chemical change is the formation of one or more new substances from the original substance or substances.

4. What is the second characteristic of chemical change?

— The experiment just considered may be done with more care. If we take the right proportions of iron and sulphur (7 of iron and 4 of sulphur), weigh each substance accurately, and heat the mixture until the chemical change is complete, we find that the weight of the iron sulphide is the same as the weight of the iron and sulphur together. Precise study has shown that this striking observation is true of all chemical changes. Hence,

The second characteristic of chemical change is unchanged weight.

5. An important law. — We see, then, as a result of our study, that in a chemical change substances are transformed but this transformation involves no change in the total weight of all the substances involved. This general fact about chemical change is often stated as the **law of the conservation of matter**: —

No weight is lost or gained in a chemical change.

6. What is a substance? — The word substance is often used in ordinary language to designate various kinds of materials. Thus, wood, cloth, paper, flour, soil, sugar, iron, and water are substances. But in chemistry the word **substance** means a kind of material which is alike throughout, *i.e.* all parts have the same properties. Moreover all specimens of a given substance have the same set of properties. Sulphur is a substance. That is, every particle of sulphur is like every other particle, and different samples of sulphur are alike. Anything found in a specimen of sulphur that has different properties is another substance. It is called an impurity and the specimen of sulphur is called impure sulphur.

7. What is a mixture? — If we examine certain materials, we find that they consist of two or more substances, which can be easily recognized with the eye (or a magnifying glass) or can be separated by sifting, dissolving, or filtering. A material which consists of substances merely mixed or stuck together is called a **mixture**. Paint, milk, soil, granite, and muddy water are examples of mixtures.

Mixtures have certain unmistakable characteristics. First, the ingredients of a mixture may vary in kind and proportion. Thus, soil may be largely sand, or clay, or organic matter. Indeed, the kind and proportion of ingredients may vary widely and the mixture still have the same name. Second, the ingredients can be readily separated. For example, the preparation of flour consists mainly in separating the starch from the other parts of the ground kernel. Third, when we compare a mixture with a (chemical) substance, we find a marked difference. Every specimen and each part of a substance has the same properties. But the properties of a mixture vary with the kind

and proportion of the ingredients. Obviously, a mixture of iron and sulphur may consist of any proportion of the ingredients, and the properties will depend on the proportion; whereas iron sulphide is always alike throughout.

8. Compounds and elements. — There are two classes of substances — compounds and elements. How are they related? If we heat strongly some red powder, called mercury oxide, in a test tube (Fig. 2), the powder turns dark and soon minute silvery drops collect on the upper part of the test tube. Now if we push well down into the test tube a joss stick with a glowing end, the glow increases and the end of the joss stick bursts into a flame. Clearly a gas is being produced which differs from ordinary air.

The new substances formed from the red powder are the liquid, mercury, which can be seen, and the colorless gas, oxygen, which mingles with the air. Both substances are quite different from the original red solid, mercury oxide. Therefore, by heating we have transformed the substance, mercury oxide, into two different substances, mercury and oxygen. A chemical change has taken place. Mercury oxide has been decomposed into mercury and oxygen. Moreover, these new substances, mercury and oxygen, differ from mercury oxide in one fundamental property, viz. they cannot be decomposed.

The relation of mercury and oxygen to mercury oxide is clear. Mercury and oxygen are the fundamental constituents of mercury oxide. We can decompose mercury oxide into its constituents, but there the decomposition stops. We have reached the end, chemically speaking. These two substances, mercury and oxygen, are not only simpler than mercury oxide, but they are examples of the simplest sub-

stances. Substances which have not yet been decomposed by chemists into simpler substances are called **elements**, whereas substances which can be decomposed into elements are called **compounds**. Obviously the compound mercury oxide consists of the elements mercury and oxygen.

9. What are the characteristics of compounds? — Compounds have several essential characteristics.

(1) The **elements** in compounds are **chemically united**. That is, the constituents of a compound are not merely mingled or lying side by side as in a mixture. They are held together by a force which is sometimes called chemical attraction. To separate a compound into its elements, this attraction must be reduced or overcome chemically. Only by a chemical change can we decompose a compound into its elements or unite elements into a compound. Whereas a mixture can usually be separated into its ingredients by some simple mechanical operation (7).

(2) The **properties of compounds differ** — often conspicuously — **from the properties of the elements** that compose them. Thus, the blue solid copper sulphate is composed of three elements — the red metal copper, the yellow solid sulphur, and the colorless gas oxygen.

(3) The most important characteristic of chemical compounds is their **constant composition**. This means that any given chemical compound always consists of an unvarying per cent of the same elements. For example, the compound water always contains 88.82 per cent of the element oxygen and 11.18 per cent of the element hydrogen. This is an important fact in chemistry, so important that it is stated as the **law of constant composition** : —

A chemical compound has a constant composition by weight.
This law will be studied again (98).

10. There is a large number of compounds. — The number of compounds formed by various combinations of the elements is very large indeed, — too large for one person to study profitably. Fortunately, we can learn much about the essentials of chemistry by confining our study to the important elements and the best representatives of a few classes of compounds.

11. More about elements. — There is only a small number of elements — about eighty-five. A complete table of the elements will be found on the inside of the back cover of this book.

Important elements are shown in the accompanying table.

TABLE OF IMPORTANT ELEMENTS AND THEIR SYMBOLS

ELEMENT	SYMBOL	ELEMENT	SYMBOL	ELEMENT	SYMBOL
Aluminium	Al	Gold	Au	Oxygen	O
Barium	Ba	Hydrogen	H	Phosphorus	P
Bromine	Br	Iodine	I	Potassium	K
Calcium	Ca	Iron	Fe	Silicon	Si
Carbon	C	Lead	Pb	Silver	Ag
Chlorine	Cl	Magnesium	Mg	Sodium	Na
Chromium	Cr	Manganese	Mn	Sulphur	S
Copper	Cu	Mercury	Hg	Tin	Sn
Fluorine	F	Nitrogen	N	Zinc	Zn

Less than half of the elements are common. About 98 per cent of the outer shell of the earth's crust consists of compounds derived from eight elements. The per cent of these elements is shown in the accompanying table.

TABLE OF THE COMPOSITION OF THE EARTH'S CRUST

Oxygen.....47.07	Iron.....4.43	Sodium.....2.43
Silicon.....28.06	Calcium.....3.44	Magnesium.....2.40
Aluminium.....7.90	Potassium.....2.45	Remainder.....1.82

Compounds in the ocean likewise consist of but few elements, as appears from the following:—

TABLE OF THE APPROXIMATE COMPOSITION OF THE OCEAN

Oxygen.....85.79	Sodium1.14	Calcium0.05
Hydrogen10.67	Magnesium....0.14	Bromine.....0.008
Chlorine..... 2.07	Sulphur.....0.09	Carbon..... 0.002

The human body is a complicated structure, and yet the compounds in it are composed of but few elements; and some of these elements are in very small proportions. This fact is apparent from the illustrative table.

TABLE OF THE AVERAGE COMPOSITION OF THE HUMAN BODY

Oxygen..... 65.00	Phosphorus.... 1.00	Magnesium..... 0.05
Carbon..... 18.00	Potassium..... 0.35	Iron..... 0.004
Hydrogen.... 10.00	Sulphur 0.25	Iodine..... trace
Nitrogen..... 3.00	Sodium..... 0.15	Fluorine..... trace
Calcium..... 2.00	Chlorine..... 0.15	Silicon..... trace

It is evident from these tables that only a dozen elements are abundant. As a matter of fact a few elements by their various combinations furnish most of the substances studied in this book. The elements given in the above tables, indeed most elements, do not occur free. That is, they do not occur singly but are combined with other elements in the form of compounds. Only a very few elements are found in the free, native, or uncombined state, *e.g.* sulphur, copper, gold, and carbon in the earth's crust, and oxygen and nitrogen in the atmosphere.

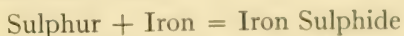
12. Each element has a symbol.—Each element is designated by an abbreviation called a **symbol** (11). Symbols are usually the first letter, or the first and a significant one, of the common name of the element. Thus, O is the symbol

of oxygen, C of carbon, Cl of chlorine, Zn of zinc. In some cases the symbol is an abbreviation of a Latin name, e.g. Cu for copper (*cuprum*), Fe for iron (*ferrum*), Ag for silver (*argentum*). All symbols, as we shall see later (105), have a very explicit meaning. They are used constantly, not only to designate elements and compounds but also to express the relations of elements and compounds in chemical change. The symbol of each important element should be learned early in the study of chemistry. (See Exercise 11 at the end of this chapter.)

13. Each compound has a formula. — Just as each element is designated by a symbol, so each compound is represented by a formula. A formula is a group of symbols — the symbols of the elements of which the compound is composed. Thus, FeS is the formula of the compound iron sulphide, HgO of mercuric oxide, CO₂ of carbon dioxide, and H₂O of water. Later we shall learn how formulas are derived.

14. How chemical change, elements, and compounds are related. — In the chemical change involving iron and sulphur (3), these elements unite to form the compound iron sulphide. So also in the chemical change illustrated by the behavior of mercuric oxide (8), this compound decomposes into the elements mercury and oxygen. We cannot have a chemical change without involving one or more compounds. And in many cases elements, too, are directly concerned.

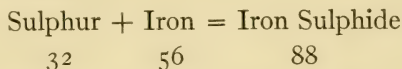
Chemical change is sometimes called chemical action. The term **reaction**, or **interaction**, is usually applied to a single chemical change. A reaction may be represented in a condensed form, thus: —



Such a condensed expression is called an **equation**. In

these simple equations, the plus sign may also be read *and* and the equality sign *form(s)*. Thus, sulphur and iron form iron sulphide. Or in full, the elements iron and sulphur under suitable conditions undergo a chemical change which results in the formation of the compound iron sulphide.

Since no weight is lost or gained in a chemical change (5), an equation can be used to represent this fundamental fact. Experiment shows that 32 parts of sulphur always unite with 56 parts of iron. This fact is expressed as an equation thus:—



This equation is read; 32 parts of sulphur and 56 parts of iron form (or equal) 88 parts of iron sulphide. By parts we mean any denomination by weight, *e. g.* grams, kilograms, pounds, tons.

EXERCISES

1. State characteristic properties of (a) glass (b) gasoline, (c) water, (d) paper, (e) air, (f) lead.
2. Define the term *substance* as used in chemistry.
3. Give three illustrations of chemical change you have observed.
4. State and illustrate the two characteristics of chemical change.
5. State the law of the conservation of matter. What does the word *conservation* mean?
6. Name (a) five elements and (b) five compounds.
7. What are some characteristics of a mixture? Name three familiar mixtures.
8. How can water be distinguished from gasoline? Copper from iron? Glass from sand? Air from illuminating gas? Sugar from starch?
9. Name the eight most abundant elements in the earth's crust in their order. Give the symbol of each.
10. What is an element? A compound? In what fundamental way do elements and compounds differ? Could you prepare (a) a compound from elements, (b) elements from a compound, (c) compounds from compounds, (d) elements from elements?

11. Learn the symbol of each element mentioned in this chapter. What is the formula of iron sulphide, water, mercury oxide, carbon dioxide?

12. What is a reaction? An equation? Give an example of each.

13. Interpret this equation: Mercury Oxide = Mercury + Oxygen.

14. Make a list of all the new words in this chapter and define each.

15. State practical uses of chemistry in (a) the school building, (b) your home, (c) agriculture, (d) manufacturing processes in your city or town.

PROBLEMS

(The Metric System of Weights and Measures is constantly used in Chemistry and it should be learned or reviewed at once. See Appendix, §1.)

1. What is the abbreviation of gram, centigram, liter, meter, cubic centimeter, decimeter, milligram, millimeter?

2. Express (a) 1 liter in cubic centimeters, (b) 2 l. in cc., (c) 1 meter in centimeters, (d) 250 cm. in dm., (e) 1 kg. in grams, (f) 250 gm. in mg., (g) 56.75 l. in cc., (h) 1250 cc. in l., (i) 1 cc. in cu. m.

3. How many cc. in (a) 1 liter, (b) 1 cu. dm., (c) 1 cu. m.?

4. If 1 m. of magnesium ribbon weighs 4 dg., how many mg. will 5 cm. weigh?

5. Into how many pieces 5 cm. long can a glass tube 1 m. long be cut?

6. A flask holds 750 cc. Express its capacity in (a) l., (b) cu. dm.

7. A bottle holds exactly 1250 cc. (a) How many grams of water will fill it? (b) How many kg.? (c) How many l.?

8. Suppose exactly 3.5 gm. of iron and 2 gm. of sulphur are heated until the chemical change is complete. What weight of iron sulphide is produced? (*Suggestion.* See 5.)

9. Suppose 5 gm. of iron and 2 gm. of sulphur are heated until the chemical change is complete. (a) What weight of iron sulphide is produced? (b) Is any sulphur or iron left over? (c) If so, which and how much?

10. What per cent of iron sulphide is sulphur? Iron?

11. When mercury oxide is made, 25 parts by weight of mercury and 2 of oxygen unite. What is the per cent of (a) mercury and (b) oxygen in mercury oxide?

12. How many grams of (a) hydrogen and (b) oxygen can be obtained from 150 gm. of water? (*Suggestion.* See 9 (3).)

CHAPTER II

OXYGEN

15. Oxygen is an abundant and important element. — It forms nearly 21 per cent (by volume) of the atmosphere. Combined with hydrogen, it constitutes 88.82 per cent (by weight) of water; combined with silicon and certain

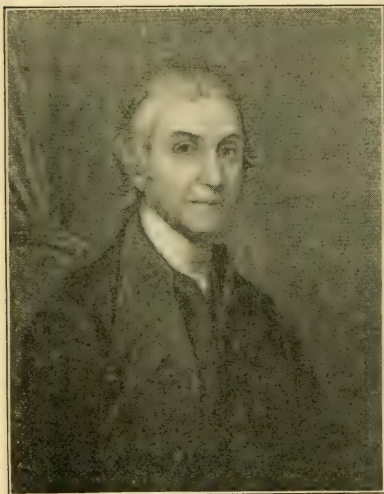


Fig. 3. — Priestley (1733-1804)

metals, it makes up nearly half of the earth's crust (11). Combined with carbon, hydrogen, nitrogen, and other elements, it forms a large part of animal and vegetable matter. Thus, the human body contains about 65 per cent of combined oxygen, while vegetable matter contains about 40 per cent.

If the elements were to be named in order of importance, oxygen would be first. Without free oxygen animal life is impossible. It is also necessary in the familiar process of burning.

16. Preparation of oxygen. — Among the first to prepare oxygen was the English scientist, Priestley (Fig. 3). He prepared it in 1774 by heating mercury oxide in much the same way as previously described (8).

The gas can be prepared by decomposing other compounds of oxygen, such as potassium chlorate (KClO_3), lead oxide (PbO_2), or barium oxide (BaO_2). Thus, potassium chlorate — a compound of oxygen, chlorine, and potassium — when heated to a moderately high temperature yields all its oxygen, and a compound, potassium chloride (KCl), remains.

Oxygen can also be prepared from water (H_2O). When an electric current is passed through water which contains sulphuric acid or sodium hydroxide, two gases, oxygen

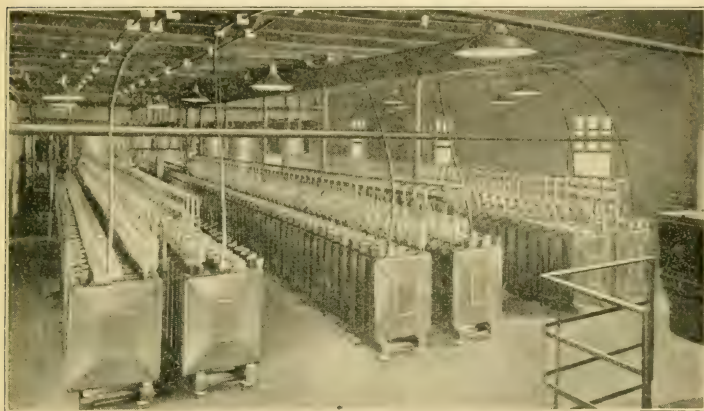


Fig. 4. — A plant for manufacturing oxygen (and hydrogen) by passing an electric current through water containing sodium hydroxide

and hydrogen, are liberated in separate tubes or compartments. This method is used to prepare oxygen (and hydrogen) on a large scale (Fig. 4). When a small quantity is needed, it is prepared by dropping water upon sodium peroxide.

17. Preparation of oxygen in the laboratory. — Oxygen is conveniently prepared in the laboratory by heating a mixture of potassium chlorate and manganese dioxide in the apparatus shown in Fig. 5. A mixture of about four

parts of potassium chlorate and one part of manganese dioxide is put in the test tube *A* and gently heated.

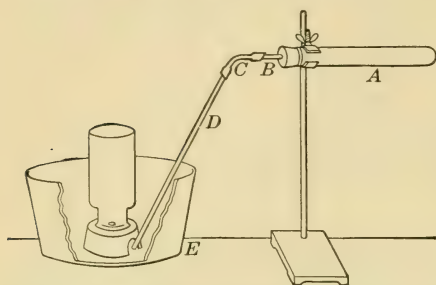
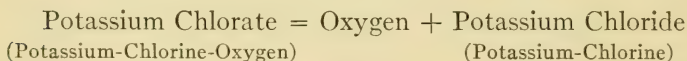


Fig. 5. — Apparatus for preparing oxygen in the laboratory

The oxygen escapes through the delivery tube *D* into bottles previously filled with water and inverted over the end of the tube in the pneumatic trough. The oxygen bubbles up into the bottle and displaces the water.

18. The preparation of oxygen illustrates chemical change. — The chemical change consists in the decomposition of the compound potassium chlorate into the element oxygen, and the compound potassium chloride. This chemical change may be expressed by this equation:—



Chemical changes like this are common, and the term *decomposition* is applied to them. **Decomposition** is chemical change in which a compound is separated chemically into other substances which are elements or compounds.

19. Properties of oxygen. — Pure oxygen has no color, odor, or taste; certain impurities may give a slight odor and taste to the gas prepared in the laboratory. It is not very soluble in water, and for this reason can be collected over water. Oxygen is slightly heavier than air. One liter of oxygen weighs 1.43 grams, if carefully measured and weighed at the temperature of 0 degrees as registered by a centigrade

thermometer and also under a pressure of 760 millimeters as registered by a barometer (or briefly at 0° C. and 760 mm.). This value — 1.43 grams — should be remembered.

20. The chemical conduct of oxygen is conspicuous. — Oxygen forms compounds with most elements. It also interacts chemically with many compounds. This combining or interacting is often striking on account of the accompanying light and heat. At ordinary temperatures oxygen unites slowly with many elements. Thus, metals, such as lead, zinc, and copper, tarnish or rust slowly, *i.e.* they combine slowly with the oxygen of the air. With phosphorus, however, the chemical action is quite rapid, as may be seen by the glow and fumes when the end of a phosphorus-tipped match is rubbed, especially in the dark.



Fig. 6. — Sulphur burning in a bottle of oxygen

The chemical activity of oxygen at temperatures above the ordinary is readily shown by putting burning or glowing substances into the gas. The action, scarcely noticeable in air, becomes energetic, and the substances burn rapidly and brilliantly. Thus, a glowing splint of wood or piece of charcoal when put into a bottle of oxygen bursts immediately into flame. Sulphur burns in air with a feeble bluish flame, but in oxygen the flame becomes large and brilliant (Fig. 6). Iron can hardly be made to burn in air, but if steel wool (matted strands of iron) is merely heated and thrust into a bottle of oxygen, the iron burns, sends off a shower of sparks, and often forms drops of molten iron which crack the bottle (Fig. 7).

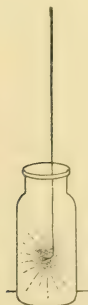


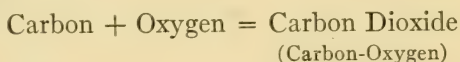
Fig. 7. — Iron burning in a bottle of oxygen

In the experiments just described, we should note especially that the oxygen itself

does not burn. Rather it assists burning. So if we were to state briefly the chemical conduct of oxygen, we would say oxygen does not burn but assists the burning of other substances. The chemical conduct of oxygen described above is sometimes called its chief chemical property.

21. Test for oxygen. — The critical examination made to establish the identity of an element or compound is called testing or making a test. The behavior of a substance under stated conditions is called the test for the substance. Thus, the **test for oxygen** is its chief chemical conduct, viz. the gas does not burn, but assists burning at elevated temperatures.

22. The chief chemical property of oxygen illustrates chemical change. — In the experiments described in 20, one feature is conspicuous, viz. the disappearance of the original substances and the formation of new substances. The chemical change in the case of the carbon, sulphur, and iron is the combining of oxygen with these elements. The oxygen unites with each element, and the product is a compound of the two elements. This kind of chemical change illustrates combination, and can be expressed by an equation. Thus: —



Combination is chemical change in which compounds are formed by the union of two or more substances.

23. Oxidation and oxides. — The special term *oxidation* is applied to those cases of combination in which oxygen is the combining element. Substances which furnish the oxygen are oxidizing agents. Free oxygen and air are oxidizing agents, though the oxygen for oxidation is often provided by compounds of oxygen, especially those that yield oxygen readily, such as potassium chlorate. The

compound formed by the union of oxygen and another element is called an **oxide** of that element. Thus, carbon forms carbon dioxide.

Oxides of different elements are distinguished by placing the name of the element (or a slight modification of it) before the word oxide, *e.g.* magnesium oxide, nitric oxide. Sometimes di-, or a similar numerical syllable, is prefixed to the word oxide, *e.g.* manganese dioxide (MnO_2), sulphur trioxide (SO_3), phosphorus pentoxide (P_2O_5). Many familiar substances are oxides, *e.g.* water is hydrogen oxide (H_2O), lime is calcium oxide (CaO), sand is silicon dioxide (SiO_2), red lead is lead tetroxide (Pb_3O_4), and the most abundant iron ore is iron oxide (Fe_2O_3).

24. Oxidation of compounds. — Oxidation is by no means limited to elements. Many *compounds* burn readily, *i.e.* combine as a whole with oxygen. Thus, carbon monoxide (CO) unites directly with oxygen to form carbon dioxide (CO_2).

Oxidation is an important chemical change. Later we shall find that the term includes other kinds of chemical action.

25. Combustion is oxidation. — During oxidation heat is liberated, and if the heat is intense, light is also produced. Different substances react with oxygen, *i.e.* oxidize, at different rates. If oxidation is slow, as in the rusting of some metals, the temperature may not rise appreciably, because the heat escapes about as fast as it is liberated. If oxidation is rapid, heat is liberated quickly, the temperature rises suddenly, and the substance burns, often with dazzling light. This rapid oxidation that produces heat and light is called **combustion**. In ordinary language combustion means fire or burning; in chemical language it is rapid oxidation.

Sometimes the heat liberated during slow oxidation cannot escape readily, but accumulates, hastens the oxidation, and finally the temperature rises to such a point that the substance takes fire. Thus, oily rags carelessly thrown aside by painters, moist hay stored in a poorly ventilated barn, and soft coal kept in a pile a long time in the air or in the warm hold of a ship sometimes take fire without apparent cause. Such fires, often unexpected and disastrous, are said to be due to **spontaneous combustion**, though they are simply cases of slow oxidation which becomes accelerated by accumulated heat.

26. Combustion was first interpreted by Lavoisier.

— Simple as it is, the answer to the question “What happens when a substance burns?” was not made quickly. Indeed, several famous chemists tried to answer this fascinating question and their combined work extended over about a century. The answer was delayed many years by a false theory called the **phlogiston theory**. The advocates of this theory believed that “combustible substances contain a principle called phlogiston, and that when

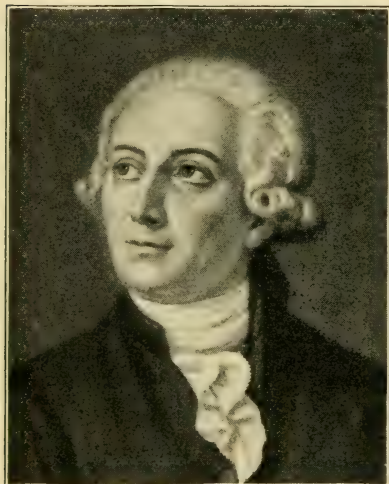


Fig. 8. — Lavoisier (1743–1794)

a substance burns, phlogiston escapes.” This is false. But it was not until about 1775 that the French chemist Lavoisier (Fig. 8) proved by his own and others’ experiments: (1) that phlogiston did not exist, and (2) that ordinary combustion is a process of combining with “a certain substance contained in the air.” Soon after, he showed that this “substance” is identical with the gas discovered by

Priestley in 1774. In 1778 Lavoisier named the gas oxygen.

So important is Lavoisier's discovery we must consider it in detail.

Previous to Lavoisier's time it had been shown that air is necessary for combustion. It had also been shown that when a substance burns in air, the product weighs more than the original substance. Lavoisier himself verified this second observation by careful experiments. He knew, then, these two simple facts about combustion: (1) air is necessary and (2) the weight increases. Still, the

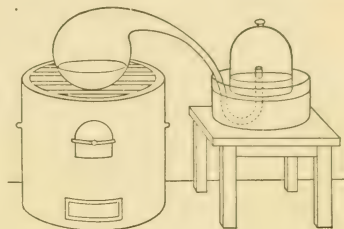


Fig. 9. — Apparatus used by Lavoisier in his famous experiment on combustion

question to be answered was, "What happens when a substance burns?" Lavoisier answered the question by a conclusive experiment (Fig. 9).

He put mercury in the retort having a long neck which communicated with the jar. The jar contained air confined over mercury in the larger lower vessel. Having arranged the apparatus so that the mercury in the retort was in contact with the air in both the retort and jar, he heated the retort by means of the furnace and kept the mercury in the retort just below the boiling point for twelve days. When the apparatus was cold, he noticed two things: (1) A red powder had accumulated on the surface of the mercury in the retort, and (2) the air in the retort and jar had decreased in volume about one fifth.

He collected the red powder, put it in a glass vessel, heated it intensely, collected the gas, and measured its volume. He found the volume was the same as the decrease in the volume of the original air inclosed in the apparatus. He tested this gas, and found it had the properties of the gas previously obtained by Priestley, especially the property of making a lighted candle burn vigorously. Also he tested the gas left behind in the retort and jar and found that it ex-

tinguished a lighted candle. From these facts Lavoisier concluded: (1) that air contains a gas which is removed by heating substances in it, (2) that this gas is about one fifth of air, (3) that this gas unites with substances in the process called combustion or burning, and (4) that this gas is identical with the gas obtained by Priestley from his "red precipitate of mercury."

We might summarize Lavoisier's work thus: oxygen is the gas in the air that is necessary for combustion.

27. Oxygen is essential to life. — Free oxygen is essential to all forms of animal life. If human beings or animals are deprived of air, they die. In breathing, air is drawn into our lungs; here the oxygen of the air is taken up by the blood, which distributes it to all parts of the body. This oxygen slowly oxidizes the tissues of the body. By this slow oxidation, waste products are formed and heat is supplied to the body. Two of these waste products are carbon dioxide gas and water vapor, which are exhaled from the lungs; water vapor is also given off through the skin. New tissue is built up from the food we eat.

The human body resembles a steam engine. In each, the oxygen of the air helps burn fuel largely composed of carbon. In the engine, the products escape through a chimney, and the heat produced by the chemical change is used to form steam, which moves parts of the machine. In the body, the products escape through the lungs and other organs, and the heat keeps the body at the temperature at which it can best perform its functions.

28. Manufacture and uses of oxygen. — Oxygen for industrial and scientific use is manufactured by decomposing water by an electric current (16) or by separating air into its components (128). The gas is stored under pressure in strong metal tanks (Fig. 10).

A mixture of oxygen and hydrogen or acetylene, if burned in a suitable apparatus, produces an intensely hot flame. The oxy-hydrogen flame is used to melt certain

metals and to produce the intense light of the stereopticon, while the oxy-acetylene flame finds application in welding and in burning apart heavy steel structures, *e.g.* girders of bridges (57, 334).

Oxygen is often administered to persons who are too ill or weak to inhale the ordinary volume of air. In submarine boats the oxygen of the air used up is replaced by oxygen released from tanks. Airplanes are often equipped with an oxygen tank and breathing apparatus to supply quickly the oxygen needed by the aviator at elevations where the air is rarefied.

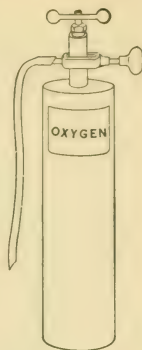


Fig. 10. — A tank of oxygen

29. Saving lives by oxygen apparatus. —

Oxygen is used in various forms of breathing apparatus for rescue work. The **pulmotor**, or lung-motor, is essentially a pump by which air rich in oxygen can be forced into the lungs at intervals approximating the normal rate of breathing. The pulmotor is used to resuscitate persons who have been overcome by smoke or poisonous gases (*e.g.* illuminating gas) or who have been rendered unconscious by drowning or by an electric shock. Fire departments, police officials, and public health officers are supplied with pulmotors for emergencies.

Another form of rescue apparatus can be hung from the shoulders like a knapsack. The man's head in one type is covered with a leather helmet; in a more recent type the man's nose is clipped so he must breathe through his mouth (Fig. 11). Flexible tubes connect his mouth with a breathing bag (right), a cylinder of compressed oxygen gas and a regenerating can (left); the latter contains potassium hydroxide to absorb the water vapor and carbon dioxide exhaled from the lungs. The amount of oxygen

needed by the wearer (as well as the circulation of the gases) can be regulated by a valve on the cylinder; the nitrogen originally inhaled and in the apparatus at first is



Fig. 11. — Man equipped with oxygen-breathing apparatus. He breathes through his mouth from the gas bag carried on his chest (*right*). The tank of oxygen and the regenerating can are carried on his back (*left*)

breathed over and over. The cylinder contains enough oxygen for about two hours.

A man provided with an oxygen-breathing apparatus can safely enter places where the air contains smoke or poisonous gas, and make repairs, extinguish fires, or rescue workmen who have been overcome. Extensive use is made of this kind of rescue apparatus in mine disasters.

30. Ozone. — Ozone is a gas related to oxygen. It is formed from oxygen when electric sparks pass through air, *e.g.* during a thunder storm. It is also formed near electrical machinery, and is prepared on a commercial scale by a silent electrical discharge, *i.e.* in a special kind of machine which permits a discharge without sparks.

Ozone changes back into oxygen — slowly at ordinary temperatures and rapidly at high temperatures. Hence ozone is a good oxidizing agent. It is sometimes used to bleach (*i.e.* whiten) flour, starch, oils,

waxes, and wool. Its main use is to destroy bacteria in drinking water, especially in certain European cities.

EXERCISES

1. Prepare a brief summary of this chapter.
2. What is the characteristic chemical property of oxygen?
3. If air contains a large proportion of another gas besides oxygen, how must the general properties of this other ingredient compare with those of oxygen?
4. Make a list of the new chemical words in this chapter and define each.
5. (a) Make a list of the name and symbol of each element mentioned in studying oxygen. (b) Make a list of the compounds mentioned in this chapter and the elements in each. (c) Learn the formula of each compound (as given).
6. What general chemical change is involved in ordinary burning? What class of chemical changes is illustrated by (a) preparation of oxygen from mercuric oxide, (b) burning of sulphur in oxygen?
7. Cite cases of spontaneous combustion of which you have heard or read. Suggest methods to prevent spontaneous combustion of (a) oily rags, (b) coal, (c) hay.
8. Devise an experiment to show that air contains oxygen.
9. Topics for home study. (a) Why does a draft of air make a fire burn well? (b) A draft of air often extinguishes a candle flame. Why? (c) What oxides are found in the home? (d) How do fish obtain oxygen?
10. What chemical part does oxygen take in: (a) respiration, (b) burning, (c) combustion, (d) oxidation, (e) kindling a fire?
11. Define (a) oxidation and (b) oxide. Name five oxides.
12. Essay topics: (a) Uses of oxygen. (b) Discovery of oxygen. (c) Priestley. (d) Oxygen and life. (e) Combustion. (f) Lavoisier. (g) Extinguishing fires.

PROBLEMS

1. (a) What is the weight in gm. of 35 l. of oxygen? (b) Of 35,000 cc.? (c) Of 35 cubic decimeters?
2. How many gm. of oxygen are in a bottle holding 2.5 l. (at 0° C. and 760 mm.)?
3. A pupil prepared enough oxygen to fill a tank holding 1 cu. m. (at 0° C. and 760 mm.). How many gm. were prepared?
4. (a) How many liters (at 0° C. and 760 mm.) will 25 gm. of oxygen occupy? (b) How many gm. will 25 l. of oxygen weigh?

5. How many gm. of oxygen (at 0° C. and 760 mm.) in a cylindrical gas holder which is 1 m. high and 30 cm. in diameter?

6. If air contains 21 per cent of oxygen by volume, how many gm. of oxygen can be extracted from 950 l. of air?

7. A pupil prepared five bottles of oxygen, each holding 250 cc. (at 0° C. and 760 mm.). How many gm. of oxygen were prepared?

8. Water contains 88.82 per cent of oxygen. Suppose 0.5 kg. was decomposed, how many liters of oxygen (at 0° C. and 760 mm.) were formed?

9. A room is 10 m. long, 5 m. wide, and 4 m. high. How many gm. of water must be decomposed to furnish enough oxygen (at 0° C. and 760 mm.) to fill the room?

10. Potassium chlorate contains 39.18 per cent of oxygen. If 35 gm. are heated, (a) how many gm. of oxygen are liberated, and (b) how many bottles each containing 250 cc. will the gas fill?

CHAPTER III

CARBON AND ITS OXIDES

31. Carbon is an important and useful element. — Like oxygen, the element carbon is found both free and combined. Free carbon is familiar as the black solid that makes up the greater part of the common substances **coal**, **charcoal**, **coke**, and **lampblack**. The soft, slippery, shiny solid called **graphite** is also largely carbon. And, strange as it may seem, the valuable gem called **diamond** is also carbon — pure crystalline carbon.

Coal, charcoal, and coke are fuels. Lampblack is made into printing ink and black paint. The various varieties of these three forms of carbon are used in many chemical industries, *e.g.* the manufacture of iron and steel. Graphite is made into the “lead” of lead pencils, stove polish, lubricants, crucibles (for melting metals), and electrodes (for electric furnaces and electrolytic cells (**497**, **512**)). Impure diamond is used to polish pure diamond and other gems, to cut glass, and as the cutting part in the diamond drill that is used to bore wells for oil and water and to drill hard rocks.

32. Carbon forms an extraordinarily large number of compounds. — The natural and manufactured compounds of carbon number over 200,000. These compounds are so numerous they are treated by themselves in a branch of chemistry called **Organic Chemistry**. Carbon is the fundamental element of plant and animal life. Compounds composed of carbon, hydrogen, and oxygen, and in some

cases also of nitrogen, form such common substances as sugar, starch, fat, cotton, paper, flour, rubber, soap, wool, and meat. With hydrogen it forms a large class of compounds called hydrocarbons, which are found in illuminating and fuel gases, petroleum, kerosene, gasolene, lubricating oils, paraffin wax, and turpentine. The manufactured compounds of carbon include dyes, medicines, perfumes, and a vast number of other substances.

The commonest inorganic compounds — those usually considered in the branch of chemistry we are studying — are the carbonates and the oxides. The carbonates are compounds of carbon, oxygen, and a metal such as calcium, magnesium, or sodium. Thus, calcium carbonate (CaCO_3) is the natural substance called limestone, marble, or chalk. Sodium carbonate (Na_2CO_3) is the common substance washing soda. There are two carbon oxides — carbon dioxide (CO_2) and carbon monoxide (CO).

In later chapters we shall consider more fully carbon and some of its important compounds. In this chapter we shall limit our study to carbon and its two oxides.

33. Formation of carbon dioxide. — We have already seen that carbon dioxide is formed when carbon burns in oxygen and also when a candle burns in air (20, 1). These are examples of a common chemical change, viz. the formation of the compound carbon dioxide when the element carbon, or a combustible compound of carbon, burns in oxygen or in air.

We have also found that the process called burning or combustion consists usually in the union of carbon (and also, of course, hydrogen, if present) with oxygen (25, 26). This means that carbon dioxide is being constantly formed by the burning of such common fuels as wood, paper, coke, coal, charcoal, oil, and gas. In fact, carbon dioxide is

always one of the products of combustion, as they are often called, yielded by burning any substance which contains carbon, *e.g.* sugar, starch, wax, meat, milk, camphor, alcohol, oil, dyes, fat, and drugs. The presence of carbon dioxide can be shown by bubbling the products of combustion, *e.g.* smoke, through limewater (1).

Reference was made in 27 to the digestion of food. One of the products of this complex process is carbon dioxide. This means in simple language that the element carbon, which is one of the constituents of our food, is oxidized to carbon dioxide. Heat is liberated when carbon is oxidized, and this chemical change is one part of the continuous and complicated process by which our bodies keep uniformly warm. The two main products of digestion are exhaled from the lungs. The presence of carbon dioxide in exhaled breath may be readily shown by blowing through a glass tube into a bottle containing limewater (Fig. 12). The liquid becomes milky, owing to the reaction between the carbon dioxide and the limewater. Limewater contains cal-

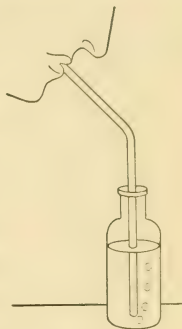
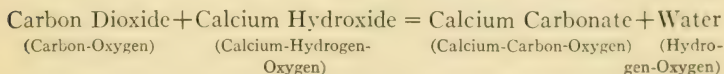


Fig. 12. — Blowing through limewater to show the presence of carbon dioxide in the breath

cium hydroxide, which reacts with the carbon dioxide and forms the white insoluble compound calcium carbonate. This chemical change is a **test for carbon dioxide** (from any source). We express the chemical change thus: —



Carbon dioxide is also formed by other chemical changes, such as the decay of many kinds of animal and vegetable

matter and fermentation of organic substances like sugar. The latter process is illustrated by the liberation of carbon dioxide during the raising of bread.

34. Preparation of carbon dioxide. — We can prepare carbon dioxide by burning carbon, or a combustible compound of carbon, in oxygen or air, but the gas could not be conveniently separated from the smoke or the other gases, such as the unused oxygen or the nitrogen (in the air). On a large scale, however, the gas is prepared by passing air over hot coke, purifying the gaseous product, and finally extracting the carbon dioxide by a special cooling process.

In the laboratory carbon dioxide is most conveniently prepared by the interaction of an acid and a carbonate. Dilute hydrochloric acid and calcium carbonate (in the form of marble chips)

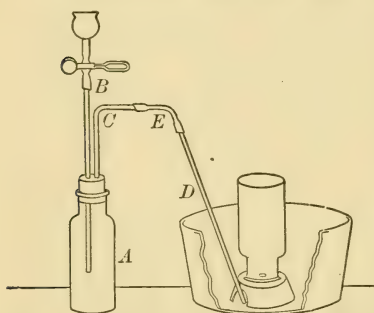


Fig. 13. — Apparatus for preparing carbon dioxide from acid and marble in the laboratory

usually used. When the acid is poured on the calcium carbonate, the gas is rapidly liberated. The apparatus shown in Fig. 13 can be used for this experiment. Calcium carbonate is put in the bottle *A* and the dilute hydrochloric acid is introduced through the dropping tube *B* by pressing the clamp. The carbon dioxide passes out through the delivery tube *D* into the pneumatic trough, bub-

bles up into the bottles (previously filled with water), and displaces the water. The bottles when full of gas are immediately removed and covered with filter paper or a glass plate.

35. Some experiments with carbon dioxide. — If several bottles of carbon dioxide are collected, we can perform experiments which will give us information about the properties of this gas.

(1) A blazing joss stick or splinter of wood, if plunged into a bottle of carbon dioxide, is immediately extinguished. (2) If we lower a short, lighted candle into a bottle of air and quickly invert a bottle of

carbon dioxide loosely over it, the gas falls down upon the candle, which is soon extinguished. (3) When we fill a bottle of carbon dioxide one third full of water, cover it tightly with the hand, shake vigorously a minute or two, then invert the bottle in a dish of water, and remove the hand, water rushes up into the bottle.

36. Some properties of carbon dioxide.

— Carbon dioxide is a colorless and odorless gas. It is heavier than air — about 1.5 times heavier. A liter of the pure gas weighs 1.98 grams (at 0° C. and 760 mm.). It dissolves in water. At ordinary temperature and pressure, water dissolves about its own volume of carbon dioxide. Under increased pressure the solubility increases, but the gas escapes when the pressure is lessened. Soda water is manufactured by dissolving carbon dioxide under pressure in water;

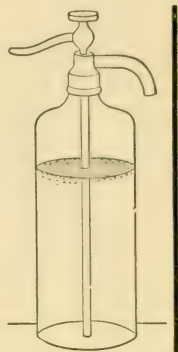


Fig. 14. — A siphon of soda water



Fig. 15. — Experiment to show that carbon dioxide escapes from a carbonated beverage

hence when soda water is drawn from a soda fountain or siphon (Fig. 14), the water bubbles and forms a froth, owing to the escape of the gas under diminished pressure. Many beverages, such as ginger ale, are "carbonated," *i.e.* they are manufactured by forcing carbon dioxide into the prepared liquid; the bottle is closed tightly with a cork or cap. When the bottle is opened, the gas which escapes (Fig. 15) will turn lime-water milky; hence the gas is carbon dioxide.

37. Liquid and solid carbon dioxide. — Unlike oxygen, carbon dioxide can be readily liquefied and solidified. If enough pressure is applied at ordinary temperatures, the gas becomes a liquid. Liquid carbon dioxide is stored and sold in strong steel tanks. If the tank is properly opened, part of the escaping liquid by evaporating quickly removes so much heat that the remainder becomes white, snowlike, solid carbon dioxide.

38. Chemical conduct of carbon dioxide. — In our experiments we noticed that carbon dioxide, unlike oxygen, did not assist combustion. Nor did it burn. This negative behavior, so to speak, is sometimes called inertness. We may say, then, that carbon dioxide is an inert gas. However, it does react with some substances. Thus, it combines with water to form a compound called carbonic acid; but this compound is not stable, *i.e.* it decomposes readily and re-forms the water and carbon dioxide.

We have called attention several times to the reaction in which carbon dioxide and limewater form calcium carbonate and water. This chemical change, we have also said, serves as a **test for carbon dioxide**. A similar reaction takes place between carbon dioxide and sodium hydroxide. The product, in this case, however, is sodium carbonate. Sodium carbonate is soluble in water and the solution feels slippery, like soap; in fact, sodium carbonate is sometimes called washing soda and is used in large quantities as a cleansing agent. Sodium bicarbonate is closely related to sodium carbonate. Sodium bicarbonate is cooking soda. Alone, or as an ingredient of baking powder, it is widely used in cooking because it gives off carbon dioxide which puffs up the dough.

39. Relation of carbon dioxide to life. — Carbon dioxide is not poisonous, though the presence of a small quantity in the air of a room is objectionable. As already stated, the carbon dioxide that is exhaled from our lungs

is one of the products formed by the oxidation of the tissues of the body, new tissue itself being formed from the food (27). The carbon needed for the rebuilding of tissue is supplied by starch and other substances we eat. Carbon dioxide is a waste product of animal life.

On the other hand, carbon dioxide is an essential food of plants. Through their leaves, especially, they absorb carbon dioxide from the atmosphere, decompose it, reject part of the oxygen, and store up the carbon in the form of complex compounds, such as starch. The sunlight and the green coloring matter (called chlorophyll) aid the plant in the formation of these compounds.

The relation of carbon dioxide to life is clear. Plants absorb carbon dioxide and transform it into starch, whereas animals eat starch as food, assimilate it, and oxidize the carbon to carbon dioxide, which is exhaled into the atmosphere ready for the plants again, and so on.

The fact that plants take up carbon dioxide and reject oxygen can be readily illustrated, as shown in Fig. 16. Fresh green leaves are put into the flask, which is then completely filled with water saturated with carbon dioxide. The stopper with its funnel is pushed in to exclude the air, the funnel is partly filled with the same liquid, and the test tube is filled and arranged as shown in the figure. On exposure to the sunlight for several hours, a gas collects in the test tube. The usual test shows that the gas is oxygen (21). No oxygen is produced if water free from carbon dioxide is used.

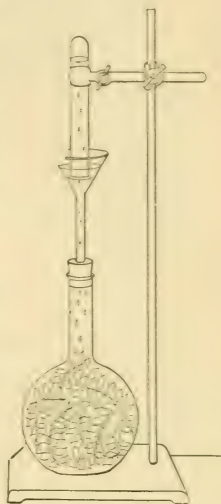


Fig. 16. — Experiment showing the absorption of carbon dioxide and liberation of oxygen by plants

The significant relation of carbon dioxide and oxygen to plants and animals, which is often spoken of as the cycle of carbon and oxygen, is shown in Fig. 17.

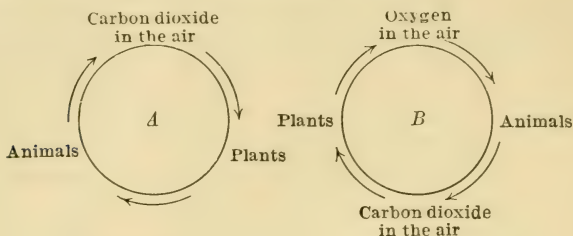


Fig. 17. — Cycle of carbon (A) and oxygen (B)

40. Carbon dioxide and fire extinguishers. — Carbon dioxide does not burn, but extinguishes burning substances. Instead of the gas itself, a saturated solution is frequently used to put out small fires. The solution is prepared, as

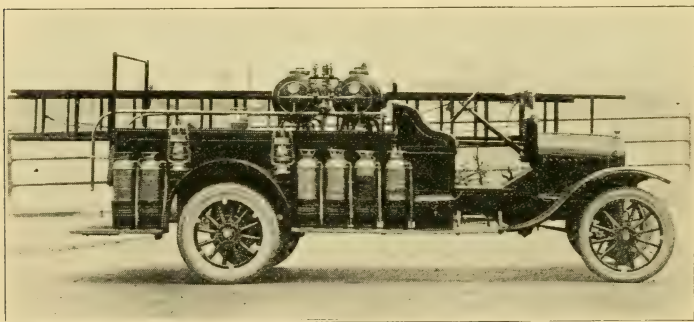


Fig. 18. — Special type of motor chemical engine for extinguishing forest fires and grass fires. Two large generating tanks are on top and portable extinguishers are on the running board

needed, in portable fire extinguishers and in chemical engines (Fig. 18) by the interaction of sulphuric acid and sodium bicarbonate. The ordinary fire extinguisher contains a solution of sodium bicarbonate and a loosely stop-

pered bottle of sulphuric acid; upon inverting the tank, the stopper of the acid bottle falls out, the two liquids mix, and the pressure of the generated gas forces the saturated solution of carbon dioxide out of the nozzle of the extinguisher; some of the carbon dioxide itself escapes (Fig. 19). The water solution of carbon dioxide together with the gas forces the oxygen of the air away from the fire and thereby reduces or entirely prevents combustion.

41. Carbon monoxide differs from carbon dioxide. — Carbon monoxide is a compound of carbon and oxygen, but the two compounds differ in properties and composition. They can be prepared from each other by chemical processes.

Carbon monoxide, like carbon dioxide, is a gas without color, odor, or taste. But in other properties the two gases differ. Thus, carbon monoxide is only slightly soluble in water, and does not form a compound with water. It is lighter than carbon dioxide; a liter weighs 1.25 gm.

42. Carbon monoxide is poisonous. — Carbon monoxide is a dangerous poison because the lack of odor prevents its detection. A small fraction of a per cent of this gas in the air produces a stupefying effect. Many deaths have been caused by breathing air containing it. Carbon monoxide impoverishes the blood by forming a compound with one of its constituents, and persons who have been poisoned by this gas cannot usually be revived by air, as in the case of suffocation by carbon dioxide. It is an ingredient of ordinary illuminating gas, and care should always be taken

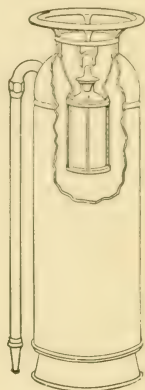
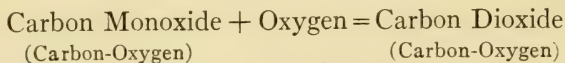


Fig. 19. — Portable fire extinguisher (partly open) showing stoppered acid bottle in original position

to prevent the escape of illuminating gas (as well as the gas from a coal stove or furnace) into rooms occupied by human beings. The exhaust gases from an automobile engine contain carbon monoxide, and special care should be taken to ventilate a small garage. The pulmotor is often used to revive persons who have been overcome by gases containing carbon monoxide (29).

43. Chemical conduct of carbon monoxide. — Carbon monoxide, unlike the dioxide, burns in air or oxygen. The flame is blue. The product is carbon dioxide. The equation for this chemical change is: —



The flickering bluish flame often seen on the top of a coal fire is caused by the burning carbon monoxide.

Not only does carbon monoxide unite readily with oxygen, but it withdraws oxygen from hot oxides; carbon itself acts in the same way. In chemical language carbon monoxide (and also carbon) is a **reducing agent**; *i.e.* it withdraws oxygen from compounds. This chemical removal of oxygen is called **reduction**. In the manufacture of iron from iron ores, the ore, which is an oxide (Fe_2O_3), is reduced by carbon monoxide in a blast furnace, the gas for this purpose being produced by the incomplete combustion of coke. The same kind of chemical change takes place easily with copper oxide and hydrogen (55).

44. The two carbon oxides are formed in a coal fire. — The oxygen of the air entering at the bottom of a coal fire combines with the hot carbon of the coal and forms carbon dioxide — the first change. But the carbon dioxide in passing up through the upper layer of hot coal is reduced by the carbon to carbon monoxide — the second

change. The carbon monoxide escapes through the top of the fire into the air, where much, or all, of it burns to carbon dioxide — the third change. Therefore we see that the two oxides are closely related chemically and pass into one another readily, especially in a coal fire (Fig. 20).

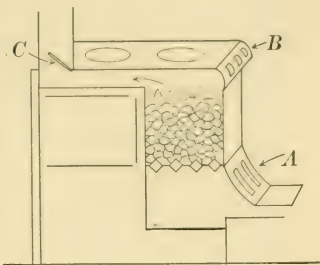


Fig. 20. — Carbon oxides are formed in a coal fire

45. Formation and preparation of carbon monoxide. — Carbon monoxide is always formed when carbon and certain carbon compounds (*e.g.* gasolene) burn in a limited supply

of air. It is also formed when steam is passed through a hot fire of hard coal or coke. The gaseous product is a mixture of carbon monoxide and hydrogen; this mixture if enriched by vapor from petroleum oil so that it burns with a yellow flame, is called **water gas** and is used, alone or with other gases, as illuminating gas. Recall that the carbon monoxide makes such a gas poisonous.

If steam and air are together passed through hot carbon, the gaseous product contains nitrogen and some carbon dioxide besides carbon monoxide and hydrogen; it is called fuel or **producer gas**. It is easily made and liberates considerable heat in burning, and is therefore used extensively as a fuel in industrial processes, *e.g.* in making open-hearth steel.

Carbon monoxide is usually prepared in the laboratory by heating a mixture of oxalic acid, or formic acid, and sulphuric acid, and collecting the gaseous product over water (294).

46. Carbon dioxide and monoxide are good examples of compounds. — In 9 we learned that compounds have three essential characteristics. These are briefly: (1) The elements in compounds are united chemically, (2) the properties of compounds differ from the elements in them, and, most important of all, (3) compounds have a definite composition.

The chemical conduct, formation, and preparation of both oxides show how well these two compounds exhibit the first and second characteristics. Both require specific chemical action — usually involving heat as an agent for their formation, preparation, and chemical conduct. And obviously both differ in properties from carbon and oxygen, the elements that compose them.

The third characteristic, viz. constant composition, is not apparent from any experiment thus far described. The **composition of a compound** is the proportion by weight of each element in it. This proportion can be found by simple experiments, though the work must be done accurately. One method is to weigh the carbon and oxygen that combine to form carbon dioxide and also carbon monoxide. Another method is to decompose a known weight of each compound and weigh the carbon and oxygen obtained. We know from many accurate experiments that the proportion of carbon to oxygen in carbon dioxide is 1 to 2.66, and in carbon monoxide it is 1 to 1.33. These results mean, to repeat, that these two substances are composed of the elements carbon and oxygen chemically combined in a definite, unvarying proportion by weight. That is, these substances are chemical compounds.

Let us consider these figures more carefully. First, in the case of each compound the proportion is definite and unvarying. If it were not, these substances would not be compounds but mixtures; in a mixture, you will remember, the proportion of the ingredients may vary (7). Second, if we compare the two proportions, we notice they are different. If they were not, we should not have the two different compounds. Third, if we compare the numbers expressing the oxygen (2.66 and 1.33), we notice a simple relation, *i.e.* one is exactly twice the other. This

means, in other words, that the weight of the oxygen combined with the carbon in carbon dioxide is twice the weight combined with the carbon in carbon monoxide.

47. Law of multiple proportions. — There are many other cases like carbon dioxide and carbon monoxide. That is, there are groups of compounds of the same elements, and in any one group there is a simple multiple relation ($1:2$, $2:3$, $1:3$, etc.) between the weights of the element that are combined with a fixed weight of the other element. (This is fully worked out in **99**.) The general fact of multiple relations is sometimes summarized in a brief form called the **law of multiple proportions**, which may be stated thus: —

In a group of compounds of the same elements, small whole numbers will express the different weights of one element that combine with a fixed weight of the other element.

This law and the law of definite composition (**9** and this section above) are important laws in chemistry. Later we shall study them more fully. (See especially Chapter VII.)

EXERCISES

1. Prepare a brief summary of this Chapter (*a*) in the form of short topics, and (*b*) as a connected narrative.
2. Prepare a summary of Chapters I, II, III showing (*a*) the relations of elements and compounds, (*b*) the properties of compounds, and (*c*) the laws (**4**, **9**, **47**).
3. In what form does free carbon occur in nature? Name ten familiar solids, three liquids, and two gases which contain carbon.
4. Name several ways in which carbon dioxide is formed.
5. How is carbon dioxide prepared in the laboratory? State the properties of carbon dioxide. Describe its chemical conduct.
6. How is carbon dioxide related to plant and animal life?
7. Describe a fire extinguisher.
8. Compare carbon dioxide and carbon monoxide.
9. How are the two carbon oxides related to a coal fire?

10. Describe fully the action of carbon dioxide on calcium hydroxide. State the reaction by an equation.

11. What is the test for (a) carbon, (b) carbon monoxide, (c) carbon dioxide, (d) a carbonate?

12. State the equation for (a) the oxidation of carbon to carbon monoxide and (b) the reduction of carbon dioxide to carbon monoxide.

13. Illuminating gas, water gas, and the gas that escapes from a coal fire are poisonous. Why? What is a pulmotor and for what is it used?

14. State and illustrate the law of (a) constant (or definite) composition and (b) multiple proportions.

15. Define and illustrate reduction. Name two reducing agents studied in this chapter.

16. Make a list of the new chemical words in this chapter and define each.

17. Make a list of the compounds mentioned in this chapter and state as fully as possible the elements in each.

PROBLEMS

1. What is the weight of 10 liters of carbon dioxide gas? Of 10,000 cc.? Of 3 l.?

2. A pupil prepared 5 bottles of carbon dioxide gas each holding 250 cc. How many gm. of carbon dioxide were prepared?

3. Marble, if treated with acid, yields about 44 per cent of its weight as carbon dioxide. If 0.5 kg. of marble was used, how many (a) gm. and (b) l. of carbon dioxide were formed?

4. What weight of marble corresponds to 150 l. of carbon dioxide?

CHAPTER IV

HYDROGEN

48. Occurrence of hydrogen. — Hydrogen, like oxygen, is a gaseous element. But it does not occur free to any great extent in nature; natural gas — a mixture of combustible gases which issues from the earth in certain localities — contains about 2 per cent. Mixtures of gases for lighting and heating, *e.g.* water gas and producer gas (**45**), contain from 35 to 50 per cent of hydrogen. Combined hydrogen is a constituent of many important compounds. Water is 11.18 per cent of hydrogen. The human body is about 10 per cent of hydrogen. Hydrogen is a constituent of all acids and bases — important classes of compounds to be studied later. (See Chapter XII.)

All plants and animals contain compounds of hydrogen with carbon and oxygen, and in some cases with nitrogen also.

Compounds of hydrogen and carbon form a large and important class of compounds called hydrocarbons, which are ingredients of petroleum (and its products, such as kerosene, gasolene, paraffin, and lubricating oils), illuminating gas, and producer gas.

49. Hydrogen is prepared from acids or water. — Hydrogen is readily and conveniently prepared by the interaction of certain metals and acids. The metals are usually zinc, iron, or magnesium, and the acids are dilute water solutions of sulphuric acid (H_2SO_4) or hydrochloric acid (HCl). The hydrogen is liberated from the acid, and the metal com-

bines with the rest of the acid to form a compound which usually remains dissolved in the liquid. On a large scale a Kipp apparatus (Fig. 21) is sometimes used.

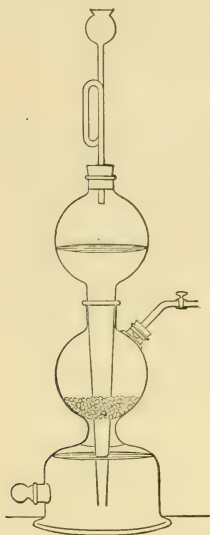


Fig. 21. — Kipp apparatus for generating hydrogen

In the laboratory hydrogen is usually prepared in a small generator, and collected over water in a pneumatic trough (Fig. 22). Zinc is put in the bottle *A* and acid is introduced through the dropping tube *B* by pressing the clamp. The hydrogen passes out through the delivery tube *D* into the pneumatic trough, bubbles up into the bottles, and displaces the water. No flame should be near during the preparation of hydrogen, because mixtures of air and hydrogen explode violently when ignited.

Hydrogen can also be prepared by allowing certain metals and water to interact. Sodium interacts less rapidly than potassium. Calcium interacts slowly with water. But potassium

interacts so rapidly that the heat ignites the liberated hydrogen (Fig. 23). If a small piece of sodium is dropped upon cold water, the sodium melts into a shining globule, which spins about rapidly on the water with a hissing sound and finally disappears with a slight explosion. If the

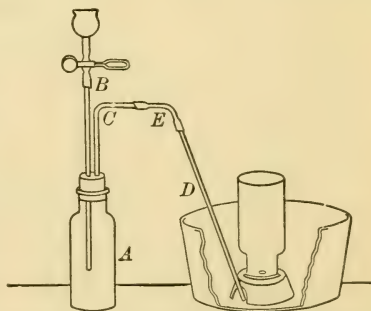


Fig. 22. — Apparatus for preparing hydrogen in the laboratory

sodium is wrapped in a piece of fine wire gauze, or of tea lead pierced with small holes, and dropped into a dish of water, the hydrogen gas can be collected in an inverted test tube full of water (Fig. 24).

Hydrogen, together with oxygen, is liberated from water by passing a current of electricity through water containing sulphuric acid or sodium hydroxide (16, 88).

Hydrogen can also be prepared by passing steam—the gaseous form of water—over heated metals (Fig. 25). This experiment was first performed by Lavoisier, in 1783, while he was studying the composition of water. He passed steam through a red-hot gun barrel containing bits of iron. The oxygen of the steam combined with the iron, and the

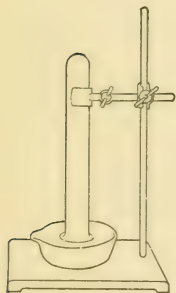


Fig. 24. — Apparatus for collecting hydrogen liberated by the interaction of water and sodium.

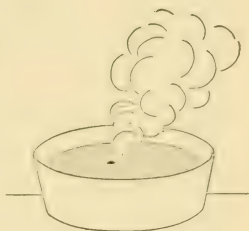


Fig. 23. — The interaction of water and potassium produces enough heat to ignite the liberated hydrogen.

hydrogen escaped from the tube. Since Lavoisier was then studying the composition of water and not especially the properties of hydrogen, he naturally thought of the gas as essential for forming water. So he named the gas hydrogen, which means literally “water former.”

50. Hydrogen can be prepared from alkalis. — Hydrogen can also be prepared by boiling solutions of certain alkalies with some elements. Thus, if sodium hydroxide (NaOH) is boiled with aluminium or silicon, hydrogen is liberated.

51. A new kind of chemical change illustrated by the preparation of hydrogen. — The preparation of hydrogen by

the interaction of a metal and an acid, water, or an alkali illustrates a third kind of chemical change, viz. **substitution**, or, as it is sometimes called, displacement or replace-

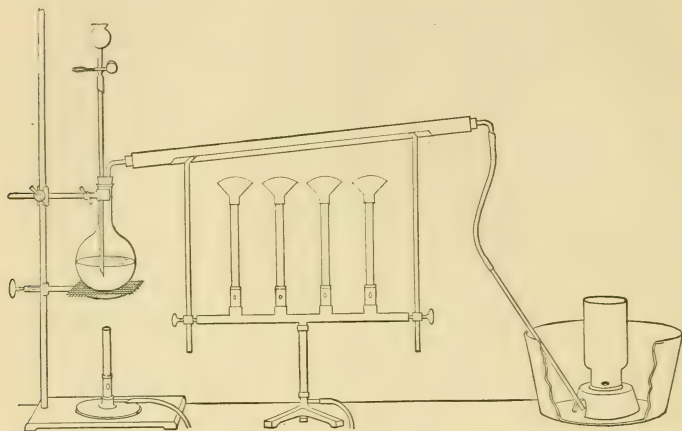
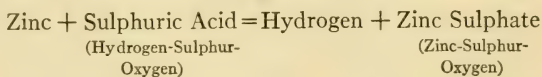
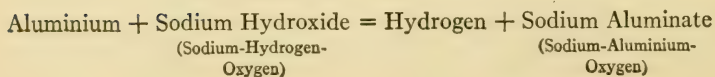
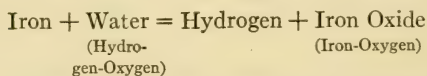
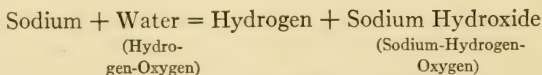


Fig. 25. — Modern form of Lavoisier's apparatus for showing the formation of hydrogen by the interaction of steam and heated iron

ment. In the case of zinc and sulphuric acid, zinc is substituted chemically for hydrogen, *i.e.* the hydrogen is displaced from the acid by the zinc. This chemical change can be expressed by the following equation : —



Similarly we have :—



We define **substitution** as a chemical change in which one element displaces another in a compound.

52. Some properties of hydrogen. — Hydrogen has no taste or color. The pure gas has no odor, though hydrogen as ordinarily prepared has a disagreeable odor, due mainly to impurities in the metals used. Hydrogen is very slightly soluble in water, less so than oxygen.

Hydrogen is the lightest known substance. Volume for volume hydrogen is about one fourteenth as heavy as air and one sixteenth as heavy as oxygen. One liter at 0° C. and 760 mm. weighs only 0.09 gm. (exactly 0.0898 gm.). Hydrogen, being so light, diffuses rapidly, *i.e.* it quickly passes through porous substances (*e.g.* unglazed porcelain, rubber, and thin sheets of metal), mixes rapidly with other gases, and freely escapes into space in all directions.

The extreme lightness as well as the rapid diffusion of hydrogen can be shown by simple experiments. If a bottle of hydrogen is exposed to the air a minute or two, and a lighted match then dropped in, the match merely burns; if hydrogen were present, a loud explosion would have occurred. Or, if a bottle of hydrogen is held just beneath a bottle of air, the gases quickly change places more or less completely, the hydrogen rising into the upper bottle and forcing out some of the air; if the experiment is well done, the gas in the upper bottle burns or explodes gently, but usually the loud explosion shows that only a part of the hydrogen flowed into the upper bottle.

53. Chemical conduct of hydrogen. — At ordinary temperatures and under ordinary conditions, hydrogen, like oxygen, is not an active element. A mixture of hydrogen and oxygen can be kept indefinitely at the temperature of the laboratory. But if the mixture is heated to about 800° C. or if a flame is brought very near it, the gases unite with a violent explosion.

Under special conditions hydrogen unites with oxygen quietly, *i.e.* hydrogen can be made to burn quietly in oxygen

or air. Hydrogen is generated in the apparatus shown in Fig. 26; the gas passes through the drying tube and escapes in a fine stream through the small opening in the platinum tip. After *all* the air has been driven out of the whole

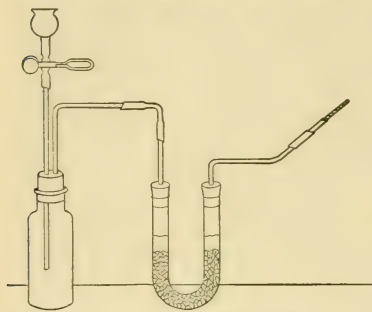
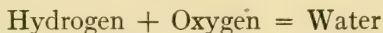


Fig. 26. — Apparatus for burning hydrogen

apparatus by the hydrogen, the gas is lighted by holding a lighted match at the end of the tip. The hydrogen burns in the air with an almost invisible but very hot flame. If a small, dry, cold bottle is held over the flame, water vapor is deposited inside the bottle. Water

is the product of the combustion of hydrogen. That is, hydrogen in burning unites with oxygen, just as other burning substances do. Thus :



This chemical change is an example of combination and also of oxidation (22). The two elements, hydrogen and oxygen, unite to form the compound water; hydrogen is oxidized, and the product might be called hydrogen oxide, though it is called by its more familiar name water.

The film of water that may be seen on the bottom of a vessel placed over a lighted gas range or a Bunsen burner is the condensed vapor formed by the burning hydrogen, and hydrogen compounds, of the illuminating gas. Organic substances containing hydrogen, such as wood and paper, when burned, yield water as one of their products.

Although a small jet of hydrogen burns quietly in air or in oxygen, a mixture of hydrogen and air burns so rapidly that the combustion is practically an explosion. Therefore, the air should be fully expelled from the apparatus

in which hydrogen is being generated and all leaky joints should be tightened before the gas is collected; no flames, large or small, should be near. Neglect of these precautions has caused serious accidents.

The chemical conduct of hydrogen with the element chlorine is similar to that with oxygen. If the two gases are mixed in the dark, they do not react. But if a mixture of hydrogen and chlorine is heated or exposed to the sunlight, the two gases combine with explosive violence. However, a hydrogen flame, if lowered into a bottle of chlorine, continues to burn quietly. In this case, as with oxygen, the two elements, hydrogen and chlorine, unite; the product is the compound hydrogen chloride. The burning of hydrogen in chlorine illustrates an extension of the term *combustion*. No oxygen is involved, but it is a case of chemical combination accompanied by light and heat. (See 25.)

Certain metals under special conditions hasten the rate at which hydrogen combines with elements. Thus, if a mixture of hydrogen and oxygen is passed over finely divided platinum, the gases, which ordinarily would scarcely combine at all, now begin to react to form water. Similarly, hydrogen and nitrogen can be made to unite into the compound ammonia, if the mixture is passed under proper conditions over certain metals. The platinum and the other metals, as far as we know now, do not undergo a chemical change in these reactions. They hasten a very slow chemical reaction. A metal which acts thus is called a **catalyst** or a catalytic agent. Its function is sometimes compared to that of lubricating oil on a machine.

54. Hydrogen does not support combustion. — Hydrogen burns, but does not support combustion. These facts are illustrated by putting a lighted taper into an inverted bottle of hydrogen (Fig. 27). The taper ignites the hydrogen, which burns at the mouth of the bottle. The taper does not burn inside the bottle, whereas when it

is slowly withdrawn through the burning hydrogen it is relighted.

55. Hydrogen is a reducing agent. — Hydrogen not only combines energetically with free oxygen, but it also withdraws oxygen from compounds. This chemical removal of oxygen is called **reduction**, and the substances that remove the oxygen are called **reducing agents**.

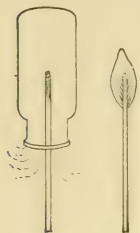
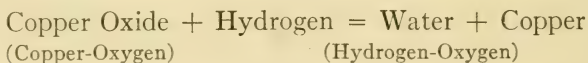


Fig. 27. — Hydrogen burns but does not support combustion

(Compare 43.) Hydrogen is a vigorous reducing agent, just as oxygen is an energetic oxidizing agent. When oxides of certain metals are heated in a current of hydrogen, the oxygen of the oxide is chemically removed and combines with the hydrogen to form water; the metal is left uncombined. Thus, by heating copper oxide in hydrogen, water and metallic copper are produced. Chemically speaking, the copper oxide is reduced by the hydrogen. The chemical change is substitution (the hydrogen being substituted chemically for the metal), and it can be expressed thus:—



This chemical change can be interpreted from the standpoint of oxidation, because the hydrogen is oxidized to water at the same time the copper oxide is reduced. In fact, the processes of reduction and oxidation are closely related and either one may be emphasized in interpreting the chemical change. In its simplest form, reduction is the opposite of oxidation. Later we shall see that the terms *oxidation* and *reduction* are both used in a broader sense.

56. Test for hydrogen. — A simple test for hydrogen is that it extinguishes a small flame, such as a blazing taper or joss stick, but

is lighted at the same time, often with an explosion, and continues to burn until the gas is exhausted. A conclusive test is that it burns with a hot flame and forms water as the sole product.

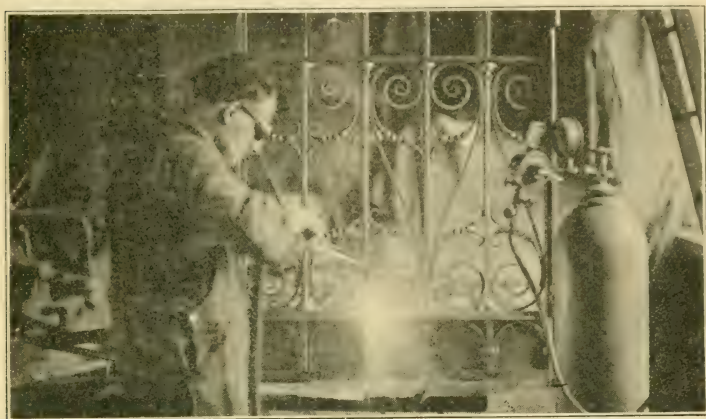


Fig. 28. — Welding an iron grill with an oxy-acetylene flame

57. Uses of hydrogen. — On account of its extreme lightness, hydrogen is used to fill balloons and dirigible airships; small balloons are usually filled with coal gas and larger dirigible craft will, it is predicted, be filled with the incombustible gas helium (127).

The intense heat of the hydrogen flame is utilized in the oxy-hydrogen blowpipe. The essential part of the burner is two pointed metal tubes. The inner and smaller one is for oxygen, and the outer and larger one for hydrogen; the gases are forced out of these small openings by the pressure maintained in the storage tanks. The temperature of the oxy-hydrogen flame is about 2000°C . The flame is used to melt platinum. When the flame strikes against a piece of lime, the latter becomes intensely bright. Thus used, it is called the lime or calcium light, and is utilized in the stereopticon. The oxy-hydrogen flame has been largely replaced by the electric furnace and the oxy-acety-

lene flame (Fig. 28) as sources of intense heat. (Acetylene is a compound of carbon and hydrogen — C_2H_2 .)

A substitute for the oxy-hydrogen flame is used in the laboratory. It is called a blast lamp (Fig. 29). Illuminating gas (which contains hydrogen and hydrocarbons) and air are used instead of hydrogen and oxygen.

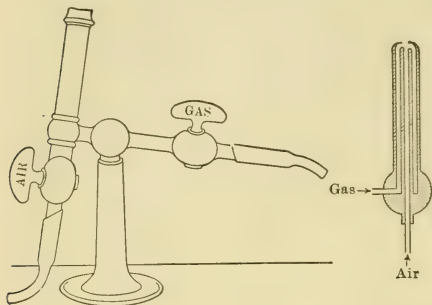


Fig. 29. — A blast lamp

The most extensive use of hydrogen is in transforming certain oils, *e.g.* cotton-seed oil, into solid edible fats. This process is called hydrogenation (363).

The hydrogen needed for these uses is prepared by the electrolysis of water (16).

EXERCISES

1. Prepare a summary of this chapter.
2. Compare oxygen and hydrogen in tabular form.
3. How can hydrogen be distinguished from (a) oxygen, (b) carbon monoxide, (c) carbon dioxide, (d) air?
4. Summarize the conspicuous properties of hydrogen. Describe its chemical conduct.
5. Why is there danger of an explosion in generating hydrogen? How can the danger be avoided?
6. Define and illustrate (a) reduction and (b) reducing agent. Compare with (a) oxidation and (b) oxidizing agent.
7. Make a list of the new chemical words in this chapter and define each.
8. In using hydrogen for balloons, what property of the gas might cause disaster?
9. Topics for home study. (a) Burning of hydrogen. (b) Relation of hydrogen to water. (c) Lavoisier's experiment. (d) Review of chemical change. (e) Uses of hydrogen.

PROBLEMS

1. Sulphuric acid contains 2.04 per cent of hydrogen. (a) How many grams must be decomposed to yield 85 gm. of hydrogen (at 0° C. and 760 mm.)? (b) 85 cc.?

2. Hydrochloric acid contains 2.74 per cent of hydrogen. How many tons must be decomposed to yield a ton of hydrogen?

3. Water contains 11.18 per cent of hydrogen. How many grams of hydrogen can be prepared from 230 gm. of water? How many liters (at 0° C. and 760 mm.)?

4. (a) How many liters (at 0° C. and 760 mm.) will 45 gm. of hydrogen occupy? (b) How many grams will 45 l. weigh?

5. A student prepared enough hydrogen (at 0° C. and 760 mm.) to fill six bottles, each holding 250 cc. (a) How many grams were prepared? (b) How much sulphuric acid was used up?

6. A cylindrical tank 1 m. long and 25 cm. in diameter is filled with hydrogen (at 0° C. and 760 mm.). How many grams does the gas weigh?

7. A hydrogen manufactory produces daily 19,000 cubic meters of gas. (a) Express this volume in liters and in cc. (b) What would this volume weigh, if measured at 0° C. and 760 mm.?

8. A Zeppelin balloon had a capacity of 351,150 cubic feet. What weight of hydrogen was needed to fill it? (Assume 1 cu. m. = 35.32 cu. ft.; also that the volume of hydrogen was measured at 0° C. and 760 mm.)

CHAPTER V

THE MEASUREMENT OF GASES

58. Introduction. — So far we have studied four gases: the two elements, oxygen and hydrogen, and the two compounds, carbon dioxide and carbon monoxide. We shall study many other gases in the succeeding chapters.

59. What is our problem? — In chemistry we often need to know the weight of a given volume of gas, or to compare the weights of the same volume. But we cannot determine the weight of a gas nor compare weights until we agree on the conditions under which we are to measure the volume. Thus, when we say one liter of oxygen weighs 1.43 gm., we really mean that the liter has this weight *if the volume is measured at a certain temperature and pressure* (0° C. and 760 mm.).

All gases change in volume with changes in temperature and pressure. In this chapter we shall study: (1) the effect of changes of temperature and pressure on the volume of a gas, (2) how the required volume of a gas is found at the standard temperature and pressure, and (3) how the weight of a given volume of a gas is found.

60. Change in the volume of a gas with changes in temperature. — Gases expand when heated and contract when cooled. This change in volume is uniform for all gases, provided of course there is no change in pressure. Thus, if the pressure is kept constant, 273 cc. of a gas at 0° C. becomes 274 cc. at 1° C., 280 cc. at 7° C., 272 cc. at -1° C., 266 cc. at -7° C., and so on. That is, for each degree of

change in temperature the volume at 0° C. changes $\frac{1}{273}$. This general fact is stated as the **law of Charles**, thus:—

Gases under constant pressure change in volume uniformly with the same change in temperature.

At this rate of contraction a gas would have no volume at -273° C.! But this rather startling result does not actually happen, because gases become liquids above this temperature. Nevertheless this point (-273°) on the centigrade thermometer is useful, for it serves as the starting point of a temperature scale called absolute temperature. The temperature -273° C. is called **absolute zero**, and temperatures reckoned from this point as zero are called **absolute temperatures**. If an "absolute thermometer" were constructed, and compared with a centigrade thermometer, the scales would be seen to be simply related (Fig. 30). If we designate absolute temperatures by A. and centigrade by C., then we see that 273° A. is 0° C., 373° A. is 100° C., and 0° A. is -273° C. That is, absolute degrees are obtained by adding 273 to centigrade degrees.

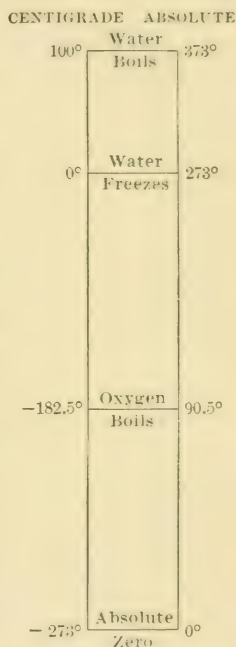


Fig. 30. — Centigrade and absolute scales

How is absolute temperature used?

Suppose, as above, we have 273 cc. of gas at 0° C. This volume becomes 274 cc. at 1° C. and 280 cc. at 7° C. Now 0° C., 1° C., and 7° C. are 273° A., 274° A., and 280° A. That is, stated in general terms, the volumes of a given weight of gas at different temperatures are in the same ratio as the absolute temperatures.

61. How we apply the law of Charles. — Suppose we have 100 cc. of oxygen at 25° C. and we wish to know what the volume would be at 0° C. It is not necessary to cool the gas to 0° C. and measure the volume. We know: (1) that a gas contracts uniformly for each degree of decrease in temperature, and (2) that the volumes are in the same ratio as the absolute temperatures. Hence we can compute the volume to which the 100 cc. would contract if it were cooled from 25° to 0° C. The steps in the process are these: (a) change the centigrade temperatures to absolute temperatures by adding 273 to each; (b) make 273 (*i.e.* $0 + 273$) the numerator of a fraction and the other sum the denominator; (c) multiply the volume by this fraction. Thus: (a) $0 + 273 = 273$, and $25 + 273 = 298$; (b) $\frac{273}{298}$; (c) $100 \times \frac{273}{298} = 91.61$. That is, 91.61 cc. is the volume 100 cc. would become if cooled from 25° C. to 0° C.

In solving problems involving change in temperature, care should be taken to notice the conditions. For example, 273 is the numerator *only* when the final temperature is 0° C.; if the final temperature is another number, the numerator is this number + 273. In checking results, it should be remembered that decrease in temperature means decrease in volume.

62. Change in the volume of a gas with changes in pressure. — Many gases are collected in bottles or tubes over water or mercury in a pneumatic trough or tall jar. In measuring the volume of the gas, the levels of the liquid are made the same inside and outside the bottle or tube by raising or lowering it. The gas thus becomes under atmospheric pressure, *i.e.* the pressure of the atmosphere exerted on the exposed surface of the liquid in the trough or jar is transmitted through the water to the gas. Hence the pressure which the gas is under is the same as the pressure of the atmosphere when the gas volume is read.

The pressure of the atmosphere is found merely by reading the barometer. A common form of barometer is shown in Fig. 31. It consists of a small-bore, strong glass tube, about one meter long, and closed at the upper end. The tube is nearly full of mercury and the open, lower end dips into a small reservoir of mercury. The space above the mercury at the upper end of the tube is a vacuum. As the pressure of the atmosphere changes, the column rises or falls. Near the top of the supporting board back of the tube is a scale by which we can tell the height of the mercury column above the surface of the mercury in the reservoir. That is, by reading on the scale the height of the mercury — “reading the barometer” — we are measuring the pressure of the atmosphere at the time of the observation. The normal, or average, height of the barometer is 760 millimeters (mm.).



Fig. 31. — A barometer

As stated in 59 the volume of a gas changes with change in pressure. The volume contracts if the pressure is increased and expands if the pressure is decreased. The effect of pressure on the volume of a gas was first studied by Boyle (Fig. 32). He found that 100 cc. of air, for example, contracts to 50 cc. if the pressure is doubled, and also that 100 cc. expands to 200 cc. if the pressure is halved. This relation of volume to pressure, which applies to all gases, is sometimes stated as the **law of Boyle**, thus: —

The volume of a gas at constant temperature changes inversely with changes in pressure.

63. How we apply Boyle's law. — In most of the experi-

ments in chemistry we actually read a gas volume at the prevailing pressure, although we need to know what the volume would be if the pressure were 760 mm. As in the

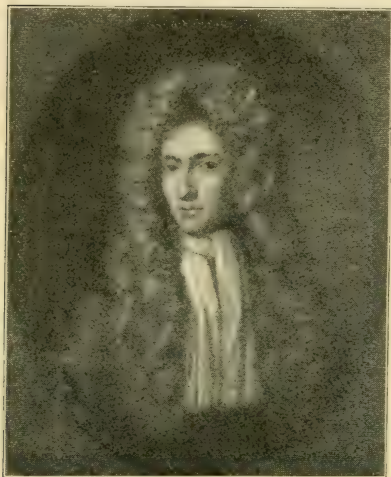


Fig. 32. — Boyle (1626–1691)

case of temperature and volume, it is not necessary (and certainly not convenient!) to wait until the barometer becomes 760 mm. We know that volumes are inversely related to their corresponding pressures (62). Hence we can compute the volume which 100 cc. of gas, for example, would have if the pressure were changed from 775 mm. to 760 mm. The steps in the

process are these: (a) Make 760 the denominator of a fraction and 775 its numerator; (b) multiply the volume by this fraction. Thus: (a) $\frac{775}{760}$; (b) $100 \times \frac{775}{760} = 101.97$.

In solving problems involving change in pressure, care should be taken to notice the conditions. (Compare end of 61.) For example, 760 is the denominator of the fraction *only* when the final pressure is the normal pressure (760 mm.); if the final (or desired) pressure is another number, the denominator is this number. It is advisable also to check the result by comparison with the original volume, remembering that decrease in pressure means increase in volume.

64. How we reduce a gas volume to standard conditions. — Measuring gases usually involves reading both temperature and pressure. The **normal or standard temperature** selected in chemistry for measuring gases is 0°C. , and the

normal or standard pressure is 760 mm. These conditions (0° C. and 760 mm.) are called **normal or standard conditions**. It is inconvenient, often impossible, to measure gas volumes at exactly 0° C. and 760 mm. So it is customary to measure the volume at the prevailing temperature and pressure, and then compute the volume the gas would have if it were at 0° C. and 760 mm. This mathematical calculation is called **reducing to standard conditions** or **correcting the volume for temperature and pressure**. The final volume is called the **corrected volume**. Let us take an example. Suppose a gas volume measures 100 cc. at 25° C. and 775 mm., and we wish to reduce this observed volume to standard conditions. We apply the laws of Charles and Boyle, and merely combine the two mathematical processes already described (61, 63). Thus:—

$$100 \times \frac{273}{298} \times \frac{775}{760} = 93.41.$$

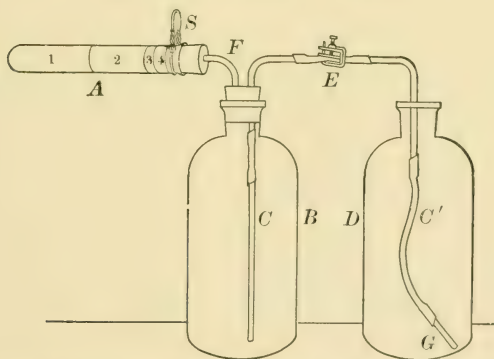


Fig. 33. — Apparatus for finding the weight of a liter of oxygen

65. How we find the weight of a given volume of a gas. —

In preceding sections the weight of one liter of different gases is given. Thus, oxygen is 1.43, carbon dioxide is 1.98, carbon monoxide is 1.25, and hydrogen is 0.09 gm.

Let us see how the weight of one liter of oxygen is found. (a) The apparatus is shown in Fig. 33. A mixture of potassium chlorate and manganese dioxide is put in the test tube *A*. The part *AF* is weighed. The bottle *B* is filled with water. The empty bottle *D* is weighed. The mixture is heated and oxygen forces water from *B* into *D*. When sufficient gas has been liberated, the heating is stopped and the apparatus is allowed to cool. (b) The temperature and pressure are read — say 20° C. and 755 mm. The levels in *B* and *D* are made the same (by raising one bottle). The water in *D* is measured; its volume is the same as the *volume of the oxygen* — say 1.75 liters. *AF* is weighed; its loss is the weight of the oxygen — say 2.322 gm. (c) The observed volume is reduced to standard conditions; thus: $1.75 \times \frac{273}{293} \times \frac{760}{755} = 1.625$. (d) The weight of one liter of oxygen at 0° C. and 760 mm. is found by dividing the weight of the oxygen by its corrected volume; thus, $2.322 \div 1.625 = 1.429$.

We shall see later that a slight modification must be made in the value of the pressure when the oxygen is collected over water (74).

66. The nature of gases. — We have seen in this chapter that gases change uniformly in volume with changes in temperature and pressure. They behave alike in many other ways, *e.g.* they diffuse readily. The similarity in properties suggested long ago that gases are fundamentally alike. We believe that gases are made up of minute particles, too small to be seen with a microscope. These particles are called **molecules**. The molecules of a gas are far apart, *i.e.* the distances between molecules are large compared with the molecules. They are exceedingly small particles in a large space. Furthermore, we believe that the molecules are in constant motion, *i.e.* flying about

rapidly in all directions, striking each other and the walls of the containing vessel, rebounding, and so on ceaselessly. Moreover, the movements, so it is believed, increase in velocity as temperature rises, and decrease as it falls.

These suppositions are part of the **kinetic-molecular theory** of gases. We cannot see the moving (kinetic) molecules, but many facts lead us to believe in their existence. We state our belief as a theory, *i.e.* a supposition or mental picture which enables us to interpret related facts.

The law of Boyle seems much clearer if we interpret it by the kinetic-molecular theory. Thus, when a gas is compressed, the molecules are pressed more closely together. And when a gas is compressed to half its volume, the pressure produced by the blows of the moving molecules is doubled because the number of blows per second against the walls is doubled.

Similarly, the law of Charles is more readily understood if we think of the molecules of a gas as moving more rapidly, and consequently requiring more space when the temperature is raised.

Again, the constant motion of the molecules helps us understand the rapid movement of gases called diffusion, *e.g.* the rising of illuminating gas throughout a building from a small leak in the cellar.

More will be said later about the nature of gases; the nature of liquids, too, will be considered. (See **86** and **101**.)

EXERCISES

1. Prepare a summary of this chapter.
2. (a) State Boyle's law. Illustrate it. (b) State Charles's law. Illustrate it.
3. Give examples from everyday life of (a) expansion and of (b) contraction of gases caused by change of temperature.
4. Apply Exercise 3 to change of pressure.

5. (a) Change these centigrade readings to absolute: 100, 0, 15, -15, 250, 273, -273. (b) Change these absolute readings to centigrade: 273, 0, 200, 100, 473, 180, 373.

6. (a) When a given volume of gas is reduced to standard conditions, is the weight of the gas changed? (b) Is the gas itself actually reduced to 0° C. and 760 mm.?

7. From the data given in 65, calculate the weight of a liter of oxygen without making the correction for temperature and pressure. Compare the result with the correct weight.

8. Topics for home study. (a) Boyle's contributions to science. (b) Thermometers. (c) Barometers. (d) Atmospheric pressure.

PROBLEMS

1. Reduce the following to the volume occupied at 760 mm.: (a) 20 cc. at 745 mm.; (b) 45 cc. at 765 mm.; (c) 450 cc. at 755 mm.; (d) 1.5 l. at 763 mm.; (e) 2.5 l. at 745 mm.; (f) 500 cc. at 75 cm.; (g) 76 cc. at 76 cm.; (h) 900 l. at 749 mm.

2. Reduce the following to the volume occupied at 0° C.: (a) 170 cc. at 80° C.; (b) 450 cc. at 15° C.; (c) 70.6 cc. at 17° C.; (d) 49 cc. at 19° C.; (e) 356 cc. at 34° C.; (f) 48 cc. at 27° C.

3. Reduce the following to the volume at standard conditions: (a) 250 cc. at 780 mm. and 20° C.; (b) 140 cc. at 745 mm. and 21° C.

4. Reduce the following to the volume at standard conditions: (a) 247 cc. at 720 mm. and 14° C.; (b) 1000 cc. at 750 mm. and 18° C.; (c) 1480 cc. at 765 mm. and 81° C.

5. A volume of oxygen measured 375 cc. when the barometer was 740 mm., and the thermometer was 27° C. What would be the volume at the standard pressure and temperature? *Ans.* 332.3 cc.

6. Find the weight of 29 cc. of oxygen at 23° C. and 776 mm. *Ans.* 0.039 gm.

7. Calculate the weight of hydrogen in a vessel of 10 liters capacity, filled when the barometer reads 756 mm. and the thermometer 18° C.

8. If a volume of hydrogen measures 100 cc. at 14° C. and 755 mm., what will be its volume when measured at -8° C. and 780 mm.?

9. A gas measures 637 cc. at 755 mm. and 17° C. Find its volume at 730 mm. and 30° C.

10. Correct 250 cc. of oxygen at 18° C. and 745 mm. for temperature and pressure. *Ans.* 229.9 cc.

11. (a) What is the volume of 200 gm. of hydrogen at 0° C. and 760 mm.? (b) What would be its volume at 15° C. and 750 mm.?

CHAPTER VI

WATER

67. Importance and occurrence of water.—Water is one of the most familiar of natural substances. Its varied properties and common uses make it an indispensable substance. It is a compound of hydrogen and oxygen.

Water is always present in the air as a vapor, which is continually condensing into rain, clouds, mist, fog, dew, hail, frost, and snow. Water occurs in vast quantities on and beneath the surface of the earth as a liquid; and also as a solid (snow and ice). The soil and plants contain considerable water. Many common foods, especially vegetables, contain from 40 to 90 per cent of water. The human body is nearly 70 per cent water.

68. Natural waters are not pure.—Water is never found pure in nature. Even rain water, which is usually regarded as the purest natural water, contains dust and gases washed from the air. Water which flows along the surface of the earth or underground dissolves substances from the rocks and soil. Hence river water contains earthy impurities brought by the underground and surface water; it is also often contaminated with compounds formed by the decomposition of animal and vegetable matter, the so-called “organic matter,” or with refuse from manufactories.

Ocean water contains a large proportion of impurities, especially mineral substances like common salt and similar compounds of calcium and magnesium. The peculiar taste of ocean water is due chiefly to the presence of these substances.

69. Purification of water.—Since natural waters are not pure, it is often necessary to remove certain impurities to

make the water suitable for the desired use. Besides dissolved mineral matter and organic matter, water may contain suspended matter such as fine particles of clay or other earthy substances and partly disintegrated organic substances. Water, too, often contains sewage or organic matter and bacteria more or less associated with sewage.

Water used for drinking and cooking should be as pure as possible, and it is desirable as well as economical that water be purified sufficiently for all practical purposes. The water of some towns and cities is purified by **filtering** it slowly on a large scale through layers of sand and gravel. Such a filter removes suspended matter almost completely, though it must be frequently cleaned. In some localities the water is **stored** in a large settling basin or reservoir; here the suspended solid matter slowly settles, the process sometimes being hastened or aided by adding alum, which forms a sticky substance to which particles cling. Sometimes the water is freed from organic matter by **spraying** it into the air (Fig. 34). This is an oxidation process.

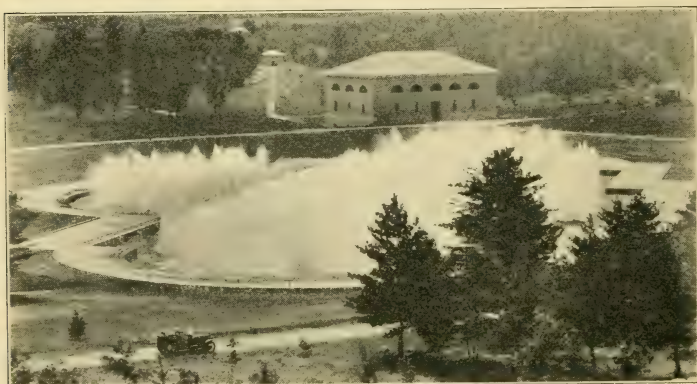


Fig. 34. — Purification of water by spraying it into the air. An aëerator of the New York City water system by which 376 million gallons are purified daily

The most effective method of destroying organic matter, especially bacteria, is by **chemical treatment**. Ozone, a gas like oxygen but much more active, is sometimes used (30). In recent years chlorine, or one of its compounds, has come into general use because of its simplicity and certainty. A small amount of liquid chlorine is allowed to flow into the entering supply (Fig. 35). During the war,

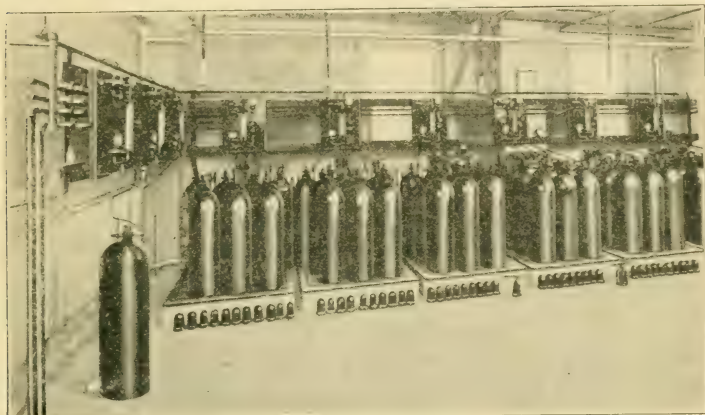


Fig. 35. — Plant for the purification of water by chlorine. A chlorinator of the New York City water system by which 400 million gallons are purified daily.

water contaminated through accident or intent was often rendered fit for drinking by means of chlorine compounds.

Water containing bacteria can be purified on a small scale or in an emergency, *e.g.* for household use during an epidemic, by **boiling** ten or fifteen minutes, and then putting it in a bottle or jar stoppered with cotton. The bottle or jar for keeping the water should also be boiled in water before use.

If the purity of a drinking water is doubtful, a sample should be subjected to a chemical and microscopic examination, supplemented by a rigid sanitary inspection of the surroundings and the source of supply.

70. Distillation. — Water can be purified on a small or local scale by **distillation**. This operation is often performed in the laboratory in a condenser, which is shown in Fig. 36 arranged for use.

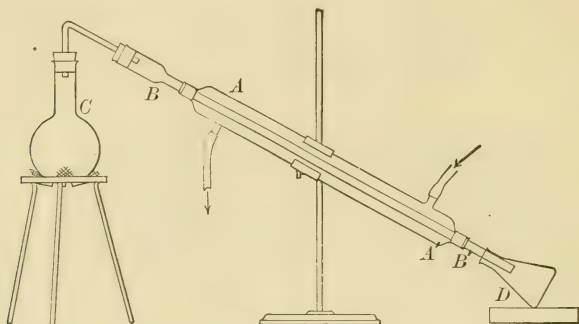


Fig. 36. — Condenser arranged for distillation of water.

The condenser consists of an outer tube AA' , provided with an inlet and an outlet for a current of cold water which surrounds the inner tube BB' . The vapor from the water boiling in the flask C condenses in the inner tube, owing to the decrease in temperature, and drops off the lower end of this tube, as the distillate, into the receiver D , while the non-volatile impurities remain behind in the flask. Other forms of condensers are used, especially for continuous work (Fig. 37). Cold water enters the condenser at the lower inlet and is kept level in the chamber by the upper outlet. The chamber is heated, and the steam in passing down through the condenser drops off the lower end as distilled water.

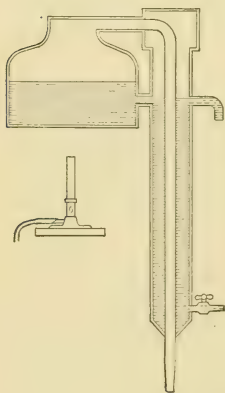


Fig. 37. — Apparatus for distilling water

Distilled water is prepared on a large scale by boiling the water in a metal vessel and condensing the vapor in a block tin pipe coiled around the inside of a vessel through which a current of cold water is flowing (Fig. 38).

Distilled water has a flat taste. If it is to be used as a beverage, air is bubbled through the water, which soon acquires the accustomed flavor. Much distilled water is used in the chemical laboratory to prepare solutions and in experiments requiring water free from organic and mineral matter.

71. Some properties of water. — At ordinary temperatures pure water is a tasteless and odorless liquid. It is usually colorless, but thick layers are blue. When water is cooled sufficiently, the liquid becomes the familiar solid, ice. The temperature at which water solidifies or freezes is 0° C. (or 32° F. — Fahrenheit). When water freezes, it expands about one tenth of its volume. That is, a given volume of water produces a larger volume of ice. If we weigh the same volume of water and ice, we find the ice weighs less. In other words, the specific gravity of ice is less than 1, which is the standard. Since the specific gravity of ice is about 0.92, ice floats in water.

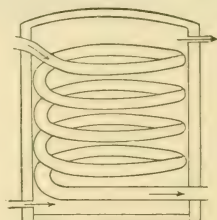


Fig. 38. — Coiled pipe condenser

The pressure exerted by water when it freezes is powerful. Vessels or pipes completely filled with water often burst when the water freezes. It is a popular idea that "thawing out" a pipe bursts it. This is not true, because ice contracts when it melts. As a matter of fact, pipes crack as soon as the water freezes, and when the ice melts, the water flows out of the crack.

Ice melts at 0° C. (32° F.), which is also the freezing point of water. Ice often crystallizes in forming, but individual crystals are seldom visible except during the first stages of the process. Snow crystals are common (Fig. 39). They are always six-sided or six-pointed, and are formed in the atmosphere by the freezing of water vapor.

When water is heated sufficiently in an open vessel, the liquid becomes a vapor, and the vapor escapes rapidly until the temperature reaches 100°C. (or 212°F.). At this point water boils, *i.e.* it changes rapidly into vapor without rise of temperature. This vapor is invisible, but as it leaves the vessel



Fig. 39. — Snow crystals. (From a photograph by permission of Wilson A. Bentley)

it cools and condenses quickly into a cloud of minute drops of liquid water. This cloud is called **steam**.

The relation of water vapor to steam can be shown by a simple experiment. Water is put in a flask (Fig. 40) and boiled vigorously. The flask is now full of invisible water vapor and steam is seen escaping from the bent exit tube. When the steam itself is heated, the cloud disappears from the end of the exit tube, *i.e.* the vapor no longer condenses into droplets but escapes unchanged as an invisible gas.

Water exists in three states — liquid, solid, and gaseous. That is, water, ice, and vapor are three common states of the same compound. And, furthermore, the transformation from one state to another is a matter of temperature. Hence the temperatures at which these transformations take place

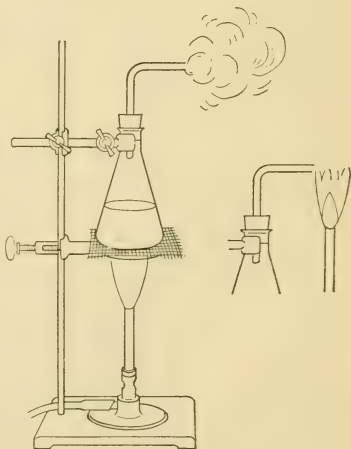


Fig. 40. — Experiment to show the relation of water vapor to steam

are important; they should be learned. Change of state does not lead to the formation of a new compound. Such a change is called a **physical change**.

72. Evaporation. — Liquid water is always changing into vapor, whatever the temperature. This process is called **evaporation**. Water vapor is escaping constantly on an enormous scale from the surface of the ocean, lakes, and rivers. This vapor is transported by air currents to great heights and to regions remote from the water surface. When the vapor reaches places where the temperature is low, a part condenses to the liquid or solid state and produces clouds, rain, snow, or other forms of water. By evaporation heat is absorbed. By condensation heat is liberated. These two processes produce a fundamental effect on climate, not only in regulating temperature but in distributing water through the air and upon the land.

On a small scale water vapor is escaping from puddles of water, moist soil, and wet objects. We speak of this process as drying. The rate at which drying takes place depends largely on the amount of water vapor in the air, the rate being in general low on wet days and high on dry days. This subject will be treated in Chapter IX.

73. What is vapor pressure? — Evaporation produces pressure. This fact is not apparent in the mere escape of water vapor into the air from a surface of water or from a wet object. Nevertheless the pressure is produced and it is called the vapor pressure of water, or **vapor pressure**.

A simple experiment will illustrate the fact of vapor pressure. The apparatus is shown in Fig. 41. The dry bottle (left) is fitted with an open U-shaped tube partly filled with a colored liquid (e.g. ink) to serve as an indicator of pressure. When the stopper is removed, a little water poured into the bottle, and the stopper quickly replaced, the water begins to evaporate. As the water evaporates, the colored liquid shows an increase in pressure (right).

The pressure exerted by water vapor depends solely on the temperature. This is readily seen by comparing the

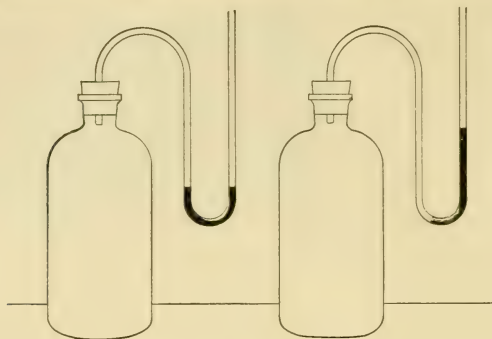


Fig. 41. — Experiment to illustrate vapor pressure

heights of the mercury in the fine-bore tubes shown in Fig. 42. Each tube was first filled with mercury and inverted in the dish of mercury.

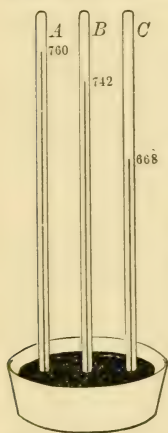


Fig. 42. — Experiment to show the relation between vapor pressure and temperature

In each tube the mercury sank to the same point (760). In tube *A* there is no water vapor in the space above the mercury, and the height of the mercury column is 760 mm. A small drop of water is forced up into the tubes *B* and *C* by means of a medicine dropper. In *B* the space above the mercury is filled with water vapor at 20° C.; the vapor exerts a pressure and forces the mercury down to nearly 742 mm. That is, water vapor at 20° C. exerts a pressure equal to 18 mm. of mercury. Similarly, in *C* the space is filled with water vapor at 50° C., and the mercury is forced down to 668 mm., the water vapor at this temperature exerting a pressure of 92 mm.

If the water vapor in a tube were at 100°

C., the vapor pressure would be 760 mm. The latter value is instructive, for it means that at the boiling point of water (100° C.) the vapor pressure equals numerically the normal atmospheric pressure. This means in other words that the vapor escaping from water boiling in an open vessel overcomes the pressure of the atmosphere upon the surface of the water. Since the normal pressure of the atmosphere is 760 mm., the normal boiling point, so to speak, is 100° C.

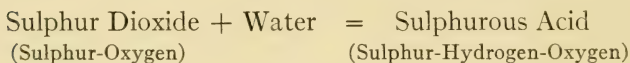
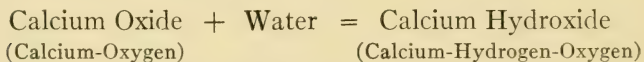
The boiling point becomes lower as the pressure is decreased and higher as the pressure is increased. Warm water will boil under the receiver of an air pump and on the top of a high mountain. In a pressure cooker the temperature of the water is above 100° C. In a vacuum vessel, such as is used to evaporate sugar solutions, the boiling point is often as low as 70° C.

The pressure exerted by water vapor depends solely, as shown above, on the temperature of the evaporating water, and has a maximum value for each temperature. These values have been carefully determined by experiment, and can be found in the Table of Vapor Pressure given in the Appendix, § 4.

74. A practical application of vapor pressure is made in finding accurately the weight of a liter of oxygen and in similar experiments where gases are measured over water. The oxygen is collected in a bottle or graduated tube inverted in a vessel of water. The gas should be allowed to stand confined over the water long enough to become saturated with water vapor, *i.e.* the tube finally contains a mixture of oxygen and the maximum amount of water vapor at the given temperature. In such a mixture, each gas shares the total atmospheric pressure. Hence the actual pressure exerted by the oxygen is found by subtracting the pressure of the water vapor (found in the table) from the total pressure (indicated by the barometer). The corrected pressure is used in the formula for reducing the volume of a gas to its volume at 0° C. and 760 mm. (65).

75. Chemical conduct of water. — We have already seen that water at ordinary temperatures interacts with certain metals, especially calcium, sodium, and potassium, and at higher temperatures with iron (49). Water is decomposed to some extent into its component elements (oxygen and hydrogen) by intense heat; at about 2000° C. the decomposition is less than 2 per cent. As the temperature falls, the elements recombine to form water. In other words, water is a stable substance towards heat.

Water combines directly with many oxides. Thus, lime, which is calcium oxide, combines directly with water and forms calcium hydroxide; this chemical change is often attended by considerable heat, as may be seen when mortar is being prepared. Similarly, sulphur dioxide forms the compound sulphurous acid. These chemical changes may be represented thus: —



Such oxides are called **anhydrides**.

Water combines with certain solids when they separate from a solution by crystallization. Thus, from a solution of copper sulphate blue crystals are obtained, which when heated give off water and crumble to a gray white powder. (See Water of Crystallization, 83.)

76. Solvent power of water. — Water dissolves a great many substances, *i.e.* they disappear when put into water. The liquid which results from this process of dissolving is called a **solution**. The dissolved substance is distributed uniformly throughout the whole liquid and will not settle out. The liquid in which the substance dissolves is called

the **solvent**. The dissolved substance is called the **solute**. A water solution of a substance is sometimes called an aqueous solution — the kind we are considering in this chapter. Substances differ widely in their solubility. A solution which contains a small proportion of solute is called a **dilute solution**; one containing a large proportion of solute is called a **concentrated solution**.

77. Solution of gases. — Water dissolves many gases. Some like ammonia, are very soluble, while others, such as oxygen and nitrogen, are only slightly soluble. Air dissolves slightly in water. Thus, if faucet water, or water that has been shaken in a bottle, is heated, bubbles gather and escape as the heat is increased. As a rule, the solubility of a gas decreases with rise of temperature. Pressure, too, influences the solubility of gases. Thus, as we have already seen (**36**), carbon dioxide is forced into cylinders of water in preparing soda water. When the pressure is decreased by opening the valve, the gas escapes rapidly and causes the soda water to froth or foam. Bubbles caused by escaping carbon dioxide may also be seen when the stopper is removed from a bottle containing a charged beverage (Figs. 14, 15).

This rapid escape of a gas is called **effervescence**. Underground waters often contain considerable carbon dioxide, owing to the great pressure to which subterranean gases are subjected. Hence, many natural mineral waters effervesce when they come to the surface.

78. Solutions of liquids. — Some liquids, such as alcohol and glycerin, dissolve in water in all proportions; others, *e.g.* gasoline and kerosene, are very slightly soluble, as is shown by the fact that after agitation with water they separate almost entirely as distinct layers of oil and water.

Some liquids dissolve to a limited extent in water. Ether

is an example. If ether is shaken with water and the liquid is allowed to stand a short time, two layers form. The upper layer consists of ether and a little water; the lower layer is the opposite.

On the other hand alcohol and water form no such layers, not simply because each is soluble in the other, but because each is soluble without limit in the other; that is, alcohol-water is a case of perfect mutual solubility, whereas ether-water is a case of limited solubility.

79. Solutions of solids. — Water dissolves many solids, and such solutions are very useful. The solubility of solids in water is a matter of the utmost practical importance, not only in its far-reaching effect in nature but also in its indispensable use to man.

The solubility of solids in water depends on the substance. Some, like sand, dissolve scarcely at all and are often described as insoluble. Others, like salt, are moderately soluble, while still others, like magnesium chloride or sodium hydroxide, are highly soluble.

The degree of solubility depends on temperature. In most cases solubility increases with rise of temperature; hence the common practice of heating to hasten solution. A few solids (*e.g.* calcium hydroxide) are less soluble in hot water than in cold, and a few others (*e.g.* sodium chloride) dissolve to about the same degree in hot and cold water.

There is a limit to the solubility of most substances. As a general rule, a given weight of water at a fixed temperature will dissolve only a definite weight of solid; and this is the case, even though more undissolved solid is available for solution. A solution conforming to the conditions just stated is said to be **saturated**. For general purposes, solubility may be expressed by such terms as *insoluble*,

TABLE OF THE SOLUBILITY OF SOLIDS IN WATER

SOLIDS	NUMBER OF GRAMS IN SOLUTION IN 100 GRAMS OF WATER	
	20° C.	100° C.
Calcium chloride	74.5	159.0
Calcium hydroxide	0.165	0.077
Magnesium sulphate	36.2	73.8
Potassium dichromate	13.0	102.0
Potassium nitrate	31.6	246.0
Sodium chloride	36.0	39.8

slightly soluble, or *very soluble*. It is more accurate to represent the amount of solvent by 100 gm.; on this basis the solubility of a solid is the number of grams of solid dissolved by 100 gm. of water.

80. Solubility tables and curves. — The accompanying table of solubility shows the solubility of some solids. But this table is limited, only two temperatures being given.

A better way of representing the solubility of a substance is by a **solubility curve**. The curves of several substances are shown in Fig. 43. The temperature is read along the vertical lines and the number of grams of solute in 100 gm. of water along the horizontal lines. Many facts can be read from solubility curves. For example, if we wish to know the temperature at which 40 gm. of potassium chlorate are held in solution by 100 gm. of water, it is only necessary to find where the horizontal line numbered 40 cuts the potassium chlorate curve, and then follow the vertical line down to the temperature number, where 80° C. is found.

81. Solution and crystallization. — If hot solutions are cooled or if enough of the solvent is removed by evaporation, the solute separates from the solvent in crystals. The process of separating a dissolved solid from its solution by

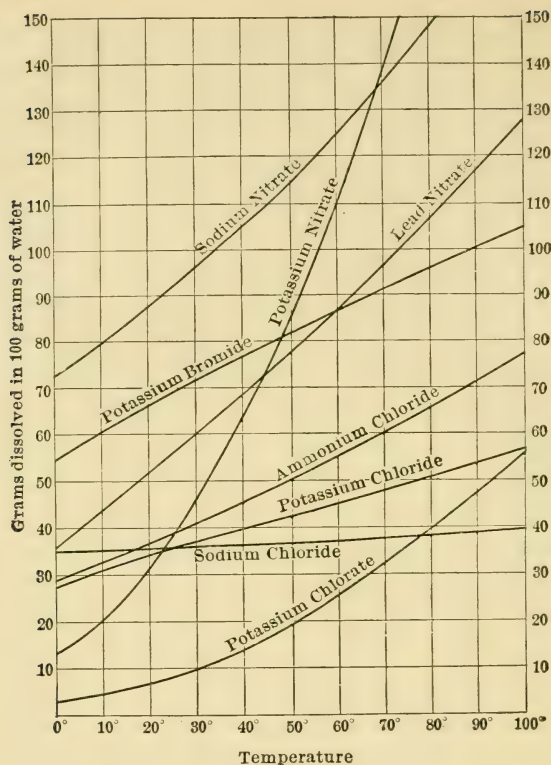


Fig. 43. — Solubility curves

either of these ways is called **crystallization**. The shape and color of the crystals are characteristic of the particular substance and serve to identify it. Thus, common salt crystallizes in white cubes. (See also 83.)

82. Supersaturated solutions. — Crystals are not always deposited from a cooled or a concentrated solution, as just stated. Thus, a hot, very concentrated solution of some solids, such as sodium sulphate or sodium thiosulphate, deposits no crystals when the *clear* solution cools, although the solution actually contains more solute than the solvent

could ordinarily dissolve at the lower temperature! Solutions which contain more solute than is needed for normal saturation are called **supersaturated**. Supersaturation occurs only under special conditions. For example, if a supersaturated solution is stirred or violently shaken, crystals begin to form. Moreover, if a fragment of the solid is dropped into the supersaturated solution, crystals very quickly form upon the fragment and soon accumulate in a conspicuously large quantity (Fig 44).

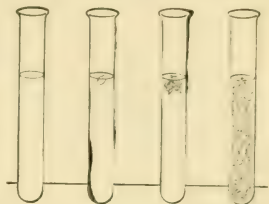


Fig. 44.— Experiment illustrating supersaturation

Supersaturation can be shown by a simple experiment. A test tube containing two or three cubic centimeters of water and considerable crystallized sodium thiosulphate is heated until a solution is produced. The clear solution is then poured into a warm test tube, a cork or wad of cotton is inserted, and the solution is allowed to cool. It remains clear. Now if a fragment of a crystal of the solid is dropped in, the crystals soon form and may become a solid mass. In Fig. 44 the successive stages are shown.

83. Solution and water of crystallization. — Crystals of some solids contain water, which is an essential part of the compound. The combined water must not be confused with water which adheres to a crystal or is inclosed in it. Crystals containing combined water are dry even after the crystals are powdered. The combined water can be removed by heat or sometimes merely by exposure to air. Loss of water is usually attended by loss of color and always by loss of crystalline appearance. Thus, crystallized copper sulphate loses its blue color slowly at ordinary temperatures and very rapidly when heated, finally becoming a gray powder.

The proportion of combined water in crystals is constant in the same compound, but in different substances the proportion varies between wide limits. Water chemically combined in a crystal and readily removed in a definite proportion by heating is called **water of crystallization**.

Compounds containing water of crystallization are sometimes called **hydrates** or hydrated compounds. Conversely, compounds which have been deprived of water of crystallization are said to be **anhydrous** or dehydrated. For example, blue crystallized copper sulphate is a hydrate of the compound copper sulphate; but after the blue compound has been heated, it is anhydrous or dehydrated copper sulphate, which is a gray powder. Anhydrous compounds often readily become hydrated again. Thus, when the gray anhydrous copper sulphate is added to water, a blue solution is produced from which blue crystals of hydrated copper sulphate are readily obtained.

84. Efflorescence. — Some crystallized substances lose water of crystallization merely by exposure to air and become powders. This property is called **efflorescence**, and such substances are said to be efflorescent or to effloresce. Crystals of washing soda, alum, and borax effloresce readily.

An explanation of efflorescence is found in the principle of vapor pressure. Solids containing water of crystallization exert a slight vapor pressure. If this vapor pressure is greater than the pressure of the water vapor in the atmosphere, the substance loses water until the vapor pressures are equal or until all the water has escaped from the substance. On the other hand, some substances containing water of crystallization do not effloresce because their tendency to lose water is counteracted by the water vapor in the air. Crystallized barium chloride and gypsum belong to the latter class.

85. Deliquescence. — Many substances when exposed to air become moist, and sometimes even dissolve in the absorbed water. Calcium chloride, potassium carbonate, zinc chloride, sodium hydroxide, and potassium hydroxide belong to this class. This property is called **deliquescence** and the substances are said to deliquesce, or to be deliquescent. Deliquescence is a property of very soluble substances. Common salt often deliquesces, especially in damp weather, owing to small quantities of magnesium and calcium chlorides which are present as impurities. The property of deliquescence is utilized in the laboratory to dry substances, calcium chloride being often employed for this purpose. One form of apparatus used is called a desiccator (Fig. 45).

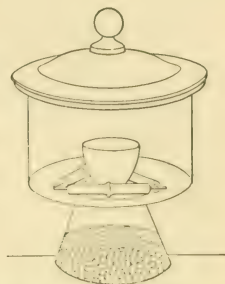


Fig. 45. — A desiccator containing calcium chloride (in the bottom)

Deliquescence is readily explained. Water vapor from the air condenses on the surface of the solid and produces a very concentrated solution, which has a vapor pressure much lower than the average pressure of the water vapor in the air; the solution, therefore, continues to take up water until its vapor pressure equals the pressure of the water vapor in the air.

86. What is a solution? — Let us try three experiments: (1) If we shake a little salt with water, the salt dissolves. We have a solution, *i.e.* a mixture in which the salt is uniformly distributed and from which the salt will not settle out. (2) If we shake a little powdered starch with cold water, the starch is distributed more or less uniformly throughout the liquid. But on standing, the starch begins to settle out, and finally the mixture separates into water and starch. The starch was not dissolved, but merely

suspended in the water. Such a mixture of a solid and water is called a **suspension**. (3) If we shake kerosene oil vigorously with water, the oil breaks up into fine drops which are distributed throughout the liquid. After a time, however, the oil separates from the water. Such a mixture of a liquid and water is called an **emulsion**.

Suspensions and emulsions have a common property, viz. sooner or later the substance separates from the water. On the other hand, the substance does not separate from a solution. This distinctive property of a solution, viz. absence of settling, is doubtless due to the fact that in a solution the dissolved particles are exceedingly minute — too minute to be seen through a microscope or detected by a beam of light. It was found many years ago that if a beam of light is passed into a dark room, the path is revealed by the dust particles that reflect the light; this effect may be seen when a sunbeam comes through an opening in a blind or a hole in a curtain. But when a strong beam of light is passed through a solution, no bright path is revealed, because the dissolved particles are much too small to reflect light.

Certain substances, however, form clear mixtures with water from which the substance does not settle nor can it be removed by filtering. These liquids look homogeneous, *i.e.* all parts appear to be just alike. And yet, if we pass a beam of light through them, the path is bright, thereby proving that these mixtures contain particles in suspension. Such mixtures are not true solutions, but **colloidal solutions**, *i.e.* mixtures in which the particles in suspension are very fine — only a little coarser, in fact, than the particles in a true solution. Colloidal solutions should really be called **colloidal suspensions**, but the term *solution* is often used. Many substances can be reduced to the colloidal state.

They are called **colloids**. Typical examples are starch (349), silicic acid (339), clay, and metals like gold. (See especially 101.)

In true solutions, then, the particles of the solute are in an exceedingly fine state of division. Whereas in suspensions and emulsions the particles are much larger — large enough to be seen through a microscope and often with the eye. Between these two classes come colloidal solutions; in them the particles are too fine to settle out, though large enough to reflect light, ranging in size from those in true solutions to those in typical suspensions (101). In passing from true solutions through colloidal solutions to suspensions (and emulsions), the change is gradual, not abrupt, since the distinction seems to be based fundamentally on the size of the particles.

87. Composition of water. — Water is a compound of hydrogen and oxygen. That is, its constituents are the elements hydrogen and oxygen, and they are chemically combined in a constant ratio.

We have already learned in several ways that hydrogen and oxygen are constituents of water. (1) Metals, such as calcium, sodium, and iron, liberate hydrogen from water and form simultaneously compounds containing oxygen (49). (2) If an electric current is passed through an acid (or alkaline) solution of water, hydrogen and oxygen are liberated (16). (3) When hydrogen is burned in air or in oxygen, water is produced (53).

We can show by a simple experiment that oxygen is a chemical constituent of water. A tube about a meter long and closed at one end is completely filled with chlorine water (prepared by saturating water with chlorine — an element to be studied in Chapter XI). The open end is immersed in a vessel containing some of the same solution, and the whole apparatus is placed in the direct sunlight.

The chlorine and water interact, forming hydrochloric acid and oxygen. Bubbles of gas soon appear in the liquid, and after a few hours a small volume of gas collects at the top of the tube (Fig. 46). The gas can be shown to be oxygen by the usual test, viz. relighting a glowing joss stick or splint of wood.

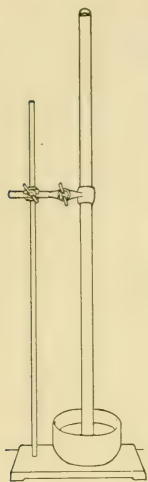


Fig. 46. — Preparing oxygen from water by chlorine

88. Electrolysis of water. — The decomposition of water by electricity, or, as it is called traditionally, the electrolysis of water, shows by a single experiment that water consists of the elements hydrogen and oxygen.

It is done in the laboratory in a special form of apparatus (Fig. 47).

Pure water does not conduct electricity, so a mixture of water (10 vols.) and concentrated sulphuric acid (1 vol.) is poured into the apparatus until the reservoir is half full (after the stopcocks have been closed).

As soon as an electric battery of three or more cells (or a reduced street current) is connected with the piece of platinum near the bottom of each tube, bubbles of gas appear on the platinum, rise, collect in the upper part of the tubes, and slowly force liquid from each tube into the reservoir.

The volume of gas is greater in one tube than in the other, when the electrolysis is stopped. Assuming that the tubes have the same diameter, the gas volumes are in the same ratio as their heights, which will be found by measurement to be approximately two to one. Tests applied to each gas (by letting a little out through the stopcock) show that the gas having the larger volume is hydrogen and that the other gas is oxygen.

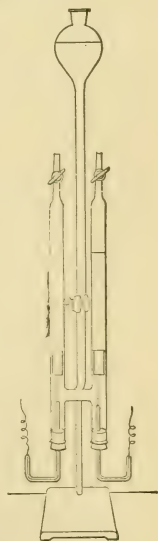


Fig. 47. — Electrolysis of water

89. How the exact composition of water is found. — The experiments just cited and described show the **qualitative composition** of water. That is, they show that water is a compound of the two elements hydrogen and oxygen. But they give us no information about the proportion of the elements in the compound. To find the **quantitative composition** of water, we must study the results of experiments performed for the purpose of determining the exact proportions — “the quantity” — in which the two elements combine to form the compound.

Since the constituents of water are gases, we can find the composition by volume, *i.e.* volumetrically, as well as by weight, *i.e.* gravimetrically. Moreover, we can determine the quantitative composition

by **analysis**, *i.e.* taking the compound apart chemically, or by **synthesis**, *i.e.* putting its parts together chemically.

90. Morley's determination of the gravimetric composition of water by synthesis. — The most accurate determination of the gravimetric composition of water ever made was completed by the American chemist Morley in 1895 (Fig. 48). In his experiments he not only weighed the hydrogen and oxygen that combined but also the water formed by their synthesis.

The apparatus (Fig. 49) was weighed *vacuous* (*i.e.* free

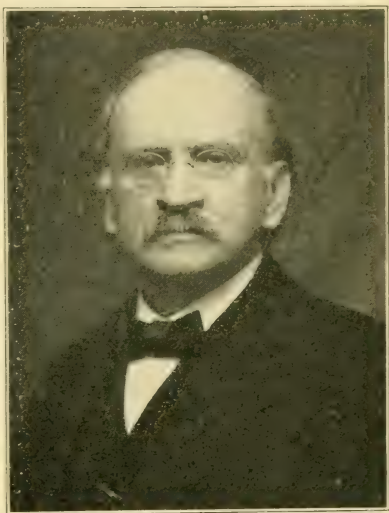


Fig. 48. — Morley (1838- —)

from air or other gases). The tubes *aa* were connected with the weighed reservoirs of pure oxygen and hydrogen, and the oxygen was introduced. Sparks were next passed between the platinum wires *cc*, and the heat ignited the hydrogen, which was slowly admitted, the combination of gases taking place at *bb*. The water vapor condensed in the tube *dd*, the lower portion of which was immersed in cold water. The combustion of the hydrogen was continued until a suitable weight of water was formed. The introduction of the gases was then stopped. The water and its vapor were then converted into ice by putting the apparatus into a freezing mixture. The gases left over when the combustion was stopped were drawn off, passing in their exit through tubes of phosphorus pentoxide in *ee* which retained all traces of water. This mixture was analyzed and allowance made for the hydrogen and oxygen in it. The whole apparatus, freed from hydrogen and oxygen, was finally weighed; the increase was the weight of water formed by the combination of known weights of hydrogen and oxygen. As the result of exceptionally accurate experiments Morley found that 1 part

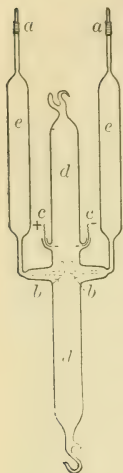


Fig. 49. — Morley's apparatus for determining the gravimetric composition of water

by weight of hydrogen combines with 7.9395 parts by weight of oxygen.

91. Dumas' determination. — Another method was used by the famous French chemist Dumas in 1843. It consisted in passing dry hydrogen over heated copper oxide. We have seen (55) that in this chemical change hydrogen reduces copper oxide and thereby forms copper and water. If the copper oxide and copper are weighed, the loss is the weight of the oxygen used. If the water is collected and weighed, the difference between the weights of the water formed and

the oxygen used is the weight of the hydrogen. The result obtained by Dumas has long ceased to be regarded as accurate, but the determination has historical interest.

92. The volumetric composition of water. — The electrolysis of water is good evidence that the volumetric composition of water is 2 of hydrogen to 1 of oxygen. An accurate determination is made by synthesis, *i.e.* by measuring accurately the volumes of hydrogen and oxygen that combine to form water. A sketch of one form of apparatus is shown in Fig. 50. The essential part is the eudiometer *A*. It is a graduated glass tube closed at the upper end. Near this end two platinum wires are fused into the glass; the outer ends are looped and the inner ends are near together so that an electric spark will leap across the gap and produce enough heat to cause the two gases to unite.

The experiment is readily performed. The eudiometer is filled with mercury and inverted in the jar of the same liquid. Hydrogen is introduced until the eudiometer is about one fourth full. The mercury levels inside and outside are made the same, and the volume of hydrogen is read accurately. The temperature and pressure are also read. Approximately an equal volume of oxygen is introduced, the levels are adjusted, and the total volume read accurately. Each volume is corrected for temperature and pressure. The difference between the two corrected volumes is the volume of oxygen. An excess of oxygen is needed to lessen the violence of the explosion; this excess takes no part in the chemical change.

The combination of the two gases is caused by connecting the looped ends of the platinum wires with an induction coil and battery, and passing a spark across the gap. A slight explosion indicates combination. The mercury, after the shock from the explosion, rises and nearly fills the eudiometer. The volume of water is too



Fig. 50. — Apparatus for determining the volumetric composition of water

minute to measure in this apparatus. After the mercury and residual gas (oxygen) are cool, the levels are adjusted, and the volume of gas is read (as well as the temperature and pressure). The corrected volume of this gas is subtracted from the volume of oxygen originally introduced, thus giving the actual volume of oxygen that combined with all the hydrogen to form water.

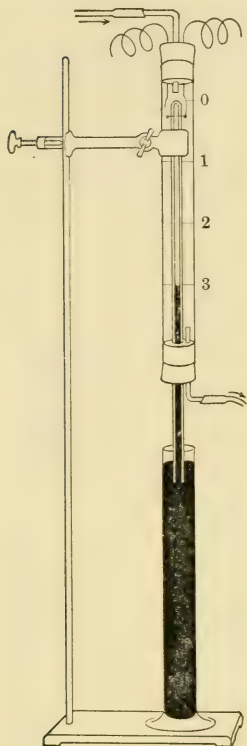


Fig. 51. — Apparatus for showing that 2 volumes of water vapor are formed by exploding 2 volumes of hydrogen and 1 volume of oxygen

of gas is read (as well as the temperature and pressure). The corrected volume of this gas is subtracted from the volume of oxygen originally introduced, thus giving the actual volume of oxygen that combined with all the hydrogen to form water.

An example will make this experiment clear. Suppose the corrected volumes were : —

Volume of hydrogen added . . .	22.3 cc.
Volume of hydrogen and oxygen added	41.5 cc.
Volume of oxygen added . . .	19.2 cc.
Volume of oxygen left . . .	8.0 cc.

This means that $19.2 - 8$, *i.e.* 11.2 cc. of oxygen were actually used. In other words the two gases combined in the ratio of 22.3 to 11.2, or very nearly 2 volumes of hydrogen to 1 volume of oxygen.

Very exact experiments show that the volumetric ratio of hydrogen to oxygen in water is 2.00268 to 1.

93. Gay-Lussac's law of gas volumes. — A modification of the experiment described in 92 shows that 2 volumes of water vapor are formed when 2 volumes of hydrogen and 1 volume of oxygen unite. In the

apparatus (Fig. 51) the eudiometer is surrounded by a large tube through which steam is passed, thereby preventing the condensation of the water vapor. If 2 volumes of hy-

drogen and 1 volume of oxygen are exploded, 2 volumes of water vapor are formed — provided all the gases are measured at the same pressure and the same temperature (about 100° C.). This result means that the volumes of hydrogen, oxygen, and steam are expressed by 2, 1, and 2, *i.e.* by small whole numbers.

When other chemical changes involving gases are studied, similar simple relations are found. This general fact, which was discovered by the French chemist Gay-Lussac (Fig. 52), in 1808, may be stated as a **law**, thus: —

In a chemical change the volumes of the gases can be expressed by small whole numbers.

This law will be used in a later chapter (XV; see also 157, 176).

94. Summary of the composition of water. —

Experiments show that water consists of the two elements hydrogen and oxygen combined in a fixed ratio by weight, viz. 1 to 7.9395; they are also combined in the ratio of 2.00268 to 1 by volume. Usually these ratios are stated approximately as 2 to 16 by weight and 2 to 1 by volume. Often the gravimetric composition of water is stated in per cent, viz. 11.18 per cent of hydrogen and 88.82 per cent of oxygen. Sometimes, we say, briefly, water is $\frac{1}{9}$ hydrogen and $\frac{8}{9}$ oxygen.

95. Hydrogen peroxide. — Hydrogen peroxide is a com-



Fig. 52. — Gay-Lussac (1778–1850)

pound of hydrogen and oxygen. But the proportion of the constituents is not the same as in water. Water consists of 11.18 per cent of hydrogen and 88.82 per cent of oxygen, whereas hydrogen peroxide consists of 5.88 per cent of hydrogen and 94.11 per cent of oxygen. Stated differently, water consists of 2 parts of hydrogen and 16 parts of oxygen, and hydrogen peroxide of 2 parts of hydrogen and 32 parts of oxygen — all parts by weight. If we compare the composition of water and hydrogen peroxide, we see that in hydrogen peroxide there is twice as much oxygen as in water. This fact is brought out in the old name **hydrogen dioxide**, which is sometimes used now.

The two compounds, water and hydrogen peroxide, are a good example of the law of multiple proportions (47).

Hydrogen peroxide is a colorless liquid which dissolves readily in water. It is sold usually as a 3 per cent solution, which has a rather sharp odor and a metallic taste. The hydrogen peroxide decomposes slowly into oxygen and water. Hence it is an oxidizing agent. It is used to bleach (*i.e.* whiten) hair, feathers, fur, silk, ivory, and bone. It destroys bacteria and is used as an antiseptic, *e.g.* in cleansing wounds, though its effectiveness is often overestimated.

EXERCISES

1. Prepare a summary of (a) the properties of water and (b) the composition of water.

2. Topics for home study. (a) Purification of drinking water. (b) Distillation. (c) Water as an erosive agent. (d) Crystals. (e) Vapor pressure. (f) Chemical conduct of water.

3. Define and illustrate (a) water of crystallization, (b) efflorescence, (c) deliquescence, (d) anhydrous, (e) dehydrated.

4. Define and illustrate (a) solution, (b) solvent, (c) solute, (d) dilute, (e) concentrated, (f) unsaturated solution, (g) saturated solution, (h) supersaturated solution, (i) solubility, (j) solubility curve.

5. Practical topics. (1) How would you prove that a given liquid is pure water? (2) What conditions are favorable for (a) evaporation, (b) efflorescence, (c) deliquescence? (3) Suggest experiments (a) to find the solubility of a solid in water at 40°C ., (b) to show that water from a crystal is not water of crystallization, (c) to find the per cent of water in a potato. (4) Why is sea water salt? How might sea water be rendered suitable for drinking?

6. State (a) the volumetric and (b) the gravimetric composition of water. How is each found?

7. What do these show about the composition of water: (a) Lavoisier's experiment (49)? (b) Burning of hydrogen? (c) Electrolysis of water?

8. Describe Morley's experiment on the composition of water.

9. State and illustrate Gay-Lussac's law.

PROBLEMS

1. Find the volume of the dry gas at 0°C . and 760 mm. in: (a) 80 cc. at 760 mm. and 17°C .; (b) 80 cc. at 745 mm. and 19°C .; (c) 100 cc. at 765 mm. and 17.5°C .; (d) 97 cc. at 757 mm. and 20.5°C .

2. Plot the following data on cross section paper and draw the solubility curve of the substance: Temperature — 0, 10, 20, 30, 40, 50, 55; corresponding solubility (*i.e.* number of gm. soluble in 100 gm. of water) — 13, 21, 31, 45, 64, 86, 100.

3. If the density of ice is 0.92, what volume will a liter of water at 4°C . occupy when frozen? *Ans.* 1.087 l.

4. By the use of the solubility curves in Fig. 43 answer the following: (a) How many gm. of sodium chloride are in solution at 20° , 30° , 55° , 65° , 0° , 100° ? (b) At what temperatures are 60 gm. and 95 gm. of potassium bromide in solution? (c) Compare the solubility of sodium nitrate and sodium chloride. How much of each is in solution at 20° , 25° , 30° ?

5. Calculate the per cent of water of crystallization in each crystallized substance from the following: (a) 5 gm. of aluminium sulphate lose 2.43 gm. on heating; (b) 7 gm. of calcium sulphate lose 1.464 gm.; (c) 3 gm. of cadmium nitrate lose 0.7 gm.; (d) 3 gm. of cobalt nitrate lose 1.113 gm.

6. Suppose 15 gm. of water are decomposed. What weight of (a) oxygen and (b) hydrogen is produced? What volume (at 0°C . and 760 mm.) of (c) oxygen and (d) hydrogen?

7. What volume of oxygen (at 0°C . and 760 mm.) must be used to unite with 175 gm. of hydrogen to form water?

8. What volume of hydrogen (at 0° C. and 760 mm.) must be used to convert 175 gm. of oxygen into water?

9. A mixture of 500 cc. of oxygen and 1250 cc. of hydrogen (both at 0° C. and 760 mm.) is exploded. What weight of water is formed?
Ans. 0.805 gm.

10. 50 cc. of oxygen are mixed with 500 cc. of hydrogen, both measured at the normal temperature and pressure. An electric spark is passed through the mixture. What volume, if any, of gas will remain, and how would you ascertain whether it is hydrogen or oxygen?

CHAPTER VII

LAW AND THEORY — LAWS OF DEFINITE AND MULTIPLE PROPORTIONS — ATOMIC THEORY — ATOMS AND MOLECULES — ATOMIC WEIGHTS

96. Facts, laws, and theories. — The facts we study in chemistry were discovered by observation and experiment. Facts which always occur under the same conditions soon become well established. Many related facts are often summarized in a brief general statement called a **law**. The explanation we give of facts, especially groups of related facts, is called a **theory**.

Laws and theories are of great service in chemistry, since they help us gather into intelligible statements our knowledge of a vast number of related facts. They also help us discover new facts and interpret phenomena.

In this chapter we shall review three laws already studied, and interpret them by a theory called the atomic theory.

97. Law of the conservation of matter. — We have seen (5) that in a chemical change the total weight of the matter involved is not altered. That is, the sum of the weights of the substances entering into a chemical change always equals the sum of the weights of the substances resulting from the chemical change. This general fact about chemical change is summed up by the **law of the conservation of matter**, thus: —

No weight is lost or gained in a chemical change.

Sometimes this law is stated in another form, viz. *matter is indestructible*.

98. Law of constant composition. — We learned in **9** that constant composition is an essential characteristic of a compound, *e.g.* water contains 88.82 per cent oxygen and 11.18 per cent hydrogen. Experiments show that in all chemical compounds the different constituents are present in a definite and constant proportion by weight. This general fact, stated in the form of a law, becomes the **law of constant composition** or the **law of definite proportions**, thus: —

A given chemical compound always contains the same elements in the same proportion by weight.

99. Law of multiple proportions. — We saw in **47** that if the composition of different compounds of the same elements is expressed in a special way, multiple relations exist between the weights of one constituent. Composition is usually expressed in per cent. But if a fixed weight of one constituent is adopted as a basis, and the composition of the compounds is expressed in terms of this weight, then the simple multiple relation which exists between the weights of the other constituent (or constituents) may be clearly seen.

Consider this case. No multiple relation appears in the statement that the two compounds of carbon and oxygen consist respectively of 27.27 and 42.85 per cent of carbon and 72.72 and 57.14 per cent of oxygen. However, if we state these proportions in a different way, multiple relations will be clearly seen. We first reduce each proportion of carbon to 1 thus: $27.27 \div 27.27 = 1$, and $42.85 \div 27.27 = 1.57$. But in order to maintain the correct relation of carbon to oxygen (found by analysis and expressed above as per cent) we must divide each proportion of oxygen by the corresponding number, *i.e.* $72.72 \div 27.27 = 2.67$, and $57.14 \div 42.85 = 1.33$. These two operations give us: —

Ratio of carbon 1 to 1
 Ratio of oxygen 2.6 to 1.3

Now 2.6 and 1.3 are in the ratio of 2 to 1. Obviously the weights of oxygen in the carbon oxides are in a simple multiple relation.

The general fact of multiple proportions is expressed as the **law of multiple proportions**, thus: —

When elements unite to form a series of compounds, a fixed weight of one element always combines with such weights of the other element (or elements) that the ratio between these different weights can be expressed by small whole numbers.

100. The atomic theory. — The theory that explains the facts summarized in the three fundamental laws just reviewed is called the **atomic theory**. It was proposed about 1805 by the English chemist Dalton (Fig. 53). According to this theory: (1) an



Fig. 53. — Dalton (1766–1844)

element is made up of a vast number of very small particles called atoms; (2) atoms of the same element have the same weight; (3) atoms of different elements differ from one another in weight; (4) chemical change is the union, separation, or exchange of whole atoms. The atomic theory means in a few words that matter is composed of atoms, which remain undivided in chemical changes.

With the help of the atomic theory, many facts about elements, compounds, and chemical change can be made very much clearer.

101. Atoms and molecules. — An **atom** is the smallest, indivisible particle of an element. In a chemical change the atom is the vehicle. It is the smallest part of an element which participates in a chemical change. If two or more atoms are held together by chemical attraction, the product of this combination of atoms is called a **molecule**. If the atoms are alike, the molecule is a molecule of an element, *e.g.* a molecule of oxygen consists of two atoms of the element oxygen (O_2). If the atoms are not alike, the molecule is a molecule of a compound, *e.g.* a molecule of water consists of two atoms of hydrogen and one of oxygen (H_2O). A molecule of a compound always contains one or more atoms of different elements; hence, we may think of such molecules as the smallest particles of the compound. Thus, a molecule of water is the smallest particle of the compound water because if we try to produce a smaller particle, we obtain atoms of the elements hydrogen and oxygen.

Although atoms and molecules are exceedingly small, too small to be seen by direct observation, nevertheless certain experiments give conclusive evidence of their existence. Atoms will be considered later; we can consider molecules now.

We found in **66** that certain properties of gases can be readily and adequately explained by the kinetic-molecular theory, *i.e.* the supposition that gases consist of exceedingly minute, rapidly moving particles called molecules.

Are there molecules in a liquid? When a colloidal solution (**86**) is examined with an ordinary microscope under favorable conditions, tiny moving points of light are seen.

If an ultra-microscope is used, the result is startling. The tiny points of light seen in the liquid dart about with a zig-zag motion. An ultra-microscope is one arranged so we can look down against a dark background into the liquid through which a beam of strong light is sent horizontally. These moving points are colloidal particles, which, although invisible, reveal their presence by reflected light.

The path traversed by one of these points seen in a colloidal solution is complicated (Fig. 54). This motion, which is called the **Brownian movement**, is seen in all colloidal solutions regardless of the nature of the particles (though seen best with finest particles) or the age of the solution. The erratic movement of the colloidal particles is due to the ceaseless, irregular bombardment of the particles by the molecules of water. The movements and the size of the colloidal particles have been carefully investigated, and the results furnish conclusive evidence of the existence of molecules in solutions.



Fig. 54. — Path of a colloidal particle

102. Interpretation of chemical change by the atomic theory. — Let us picture a chemical change in terms of the atomic theory, *e.g.* the combination of copper and oxygen. A piece of the element copper consists of many millions of atoms of copper; a mass of oxygen likewise consists of a very large number of atoms of oxygen. When the chemical change occurs between copper and oxygen, atoms of copper combine with atoms of oxygen and form molecules of the compound copper oxide. And this combining of atoms into molecules continues until all the atoms of cop-

per or all the atoms of oxygen (or under certain conditions all the atoms of both substances) have been used up. Similarly, the decomposition of mercury oxide is the separation of numberless molecules of the compound mercury oxide into atoms of the elements mercury and oxygen. So also, the liberation of hydrogen from sulphuric acid is the exchange of atoms of zinc for the atoms of hydrogen in the compound sulphuric acid.

103. How the atomic theory assists us in explaining the three fundamental laws of chemical change. — These laws, we have already found, are the law of the conservation of matter, the law of constant composition, and the law of multiple proportions.

Let us take first the **law of the conservation of matter**, viz. unvarying weight in a chemical change. According to the atomic theory the weight of an atom is never changed. In the case of copper and oxygen and all other chemical changes, no atoms are created or destroyed; they are merely redistributed on another plan. Nor are atoms changed in weight; the weight of the copper oxide formed equals the sum of the weights of the copper and oxygen used up. Inasmuch as all chemical changes have this characteristic, viz. unvarying total weight, it is obvious that the atomic theory, which assumes unchanging weights of atoms, is in accord with the law of the conservation of matter.

Second, we consider the **law of constant composition**, viz. a given compound always consists of the same elements in a fixed proportion. According to the atomic theory, molecules are formed by the union of some whole number of atoms of an element with some whole number of atoms of another element or elements. Each molecule of the compound copper oxide, for example, would therefore consist of one or more atoms of copper united with one or more

atoms of oxygen, and the composition of each molecule of copper oxide would be constant, *i.e.* each molecule would consist of the same elements united in a constant ratio by weight. This means that the composition of copper oxide would always be a certain per cent of copper and a certain per cent of oxygen. Since all other chemical compounds have been found to have a constant composition, the atomic theory is in harmony with the law of constant composition.

Finally, we interpret the **law of multiple proportions**, *viz.* simple multiple relations exist between the weights of one of the constituents of a series of compounds. According to the atomic theory atoms are transferred as wholes; this means there are no fractions of atoms. Consider the two oxides of carbon. Each contains carbon and oxygen in a definite ratio, but the ratios are different. In one the ratio of carbon to oxygen is 1 to 1.33, and in the other 1 to 2.66 (99). That is, there is twice as much oxygen combined with carbon in one case as in the other. In other words, if a molecule of one compound consists of one atom of carbon and one of oxygen, a molecule of the other consists of one of carbon and two of oxygen. Since other series of compounds exhibit a simple multiple relation, the atomic theory agrees with the law of multiple proportions.

104. Atomic weights. — According to the atomic theory atoms of the same element always have the same weight but atoms of different elements have different weights. This means (1) that an atom of oxygen, for example, throughout all its varied changes retains its weight, and (2) that this weight differs from the weight of other kinds of atoms. The weights of different kinds of atoms are called the atomic weights of the elements or briefly **atomic weights**. These weights have been determined by very accurate

experiment. A table giving the exact, as well as the approximate, values can be found on the inside of the back cover of this book.

Atoms are exceedingly small, so small, in fact, that no attempt is made to weigh a single atom. If, however, the proportions in which elements combine are reduced to a special standard, we obtain the relative weights of atoms. **The standard atomic weight is oxygen = 16.** The atomic weight of carbon is 12, of hydrogen 1, of copper 63.57. Other weights can be found in the table.

The approximate atomic weights are accurate enough for general use, and the common ones should be learned.

It must be remembered that the atomic weights are relative weights. That is, the atomic weight of copper is 63.57, not 63.57 gm. or any other actual weight, but 63.57 as long as 16 is accepted as the standard atomic weight of oxygen.

The exact determination of atomic weights is a difficult task. Several principles must be considered in making the final selection. Until this subject is discussed (see Chapter XVI), it will be well enough to regard atomic weights as the numerical values of the elements in chemical changes and to select the approximate weights from the table as needed.

EXERCISES

1. Define law and theory as used in science.
2. State the law of conservation of matter. Illustrate it by the decomposition of mercury oxide.
3. State the law of constant composition. Illustrate it by the gravimetric composition of water.
4. State the law of multiple proportions. Illustrate it by the two carbon oxides.
5. State the four points in the atomic theory.
6. (a) What is an atom? A molecule? (b) Discuss the relation of atoms to molecules.
7. Describe a chemical change in terms of the atomic theory.

8. Interpret by the atomic theory the three laws: (*a*) conservation of matter, (*b*) constant composition, (*c*) multiple proportions.

9. What are atomic weights?

10. Learn the approximate atomic weight of these elements: Hydrogen, oxygen, nitrogen, carbon, copper, iron, sulphur, chlorine.

11. As in Exercise 10: Potassium, sodium, calcium, lead, magnesium, mercury, silver, zinc.

CHAPTER VIII

SYMBOLS AND FORMULAS

105. What do symbols mean?— We learned in **12** that each element is designated by a symbol. Thus, O is the symbol of oxygen, C of carbon, H of hydrogen, Cu of copper.



Fig. 55. — Berzelius (1779–1848)

The symbols of the elements are given in the table on the back inside cover. These symbols were introduced and first used extensively by the Swedish chemist Berzelius (Fig. 55). He analyzed many substances and used the symbols to express the explicit relations of elements and compounds in chemical changes.

Symbols are not merely abbreviations of the names of the elements. **Each symbol stands for one atom** of an element. Thus, H represents one atom of hydrogen. If more than one free atom is to be designated, the proper numeral is placed before the symbol. Thus, 2H means 2 free atoms of hydrogen. If we wish to represent atoms in chemical combination, either with themselves or with

other atoms, a subscript is used instead of a coefficient. Thus, H_2 means 2 combined atoms of hydrogen, as in H_2 or H_2O .

Symbols not only represent atoms, but **they also express atomic weights**. Thus O represents an atom of oxygen which has the atomic weight 16.

To sum up, a symbol has these meanings: (1) an element, (2) one atom of the element, (3) the atomic weight of the element.

106. What are chemical formulas? We learned in 13 that a **formula** is a group of symbols which **expresses the composition of a compound**. In writing a formula, the symbols of the atoms making up a molecule of the compound are placed side by side. Thus, CO is the formula of carbon monoxide, because one molecule of this compound consists of one atom each of carbon and oxygen. Whereas CO_2 is the formula of carbon dioxide, because one molecule is composed of 1 atom of carbon and 2 atoms of oxygen. The symbols making up a formula might be written in different orders, but usage has determined the order in most cases.

A formula **represents one molecule**. If we wish to designate several molecules, we place the proper numeral before the formula. Thus, $KClO_3$ means 1 molecule and $2KClO_3$ means 2 molecules of potassium chlorate. Similarly, $2O_2$ means 2 molecules of oxygen each containing 2 atoms.

In certain compounds some of the atoms in a molecule act chemically like a single atom. This fact is expressed by inclosing the group in a parenthesis, *e.g.* calcium hydroxide has the formula $Ca(OH)_2$ because the group OH often acts like an atom. Sometimes the parenthesis is replaced by a period, *e.g.* $C_2H_5.OH$ (ethyl hydroxide) and

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (copper sulphate pentahydrate (83)). The period and parenthesis are omitted if the composition of the compound is well understood, *e.g.* ammonium hydroxide, NH_4OH .

If a group of atoms is to be multiplied, it is placed within a parenthesis. Thus, the formula of lead nitrate is $\text{Pb}(\text{NO}_3)_2$. This means that the group NO_3 is to be multiplied by 2. The expression $2\text{Pb}(\text{NO}_3)_2$ means that the *whole* formula must be multiplied by 2. That is, in two molecules of lead nitrate there are 2 atoms of lead, 4 of nitrogen, and 12 of oxygen.

Formulas are the outcome of experiments. We shall learn more about formulas.

107. What do we mean by molecular weights? — Since a symbol stands for the atomic weight of an element, a formula stands for the sum of the atomic weights represented by the group of symbols. This sum is called a **molecular weight**. In a few words, a symbol stands for an atomic weight and a formula stands for a molecular weight. Thus, the symbols H and Cl stand for the atomic weights 1 and 35.5 respectively, and the formula HCl stands for their sum $1 + 35.5$, or 36.5. If we know the formula of a compound, a simple way of finding the molecular weights is to add the atomic weights corresponding to the atoms in the formula. Using approximate values, the molecular weight of water (H_2O) is $2 + 16 = 18$. Similarly, the molecular weight of lead nitrate ($\text{Pb}(\text{NO}_3)_2$) is $207 + 2(14 + 48) = 331$.

108. How a formula expresses composition. — We have seen by several examples that the composition of a compound can be expressed in per cent and also by a formula. Thus, we can express the composition of water by the formula H_2O , and also by hydrogen = 11.18 per cent and

oxygen = 88.82 per cent. How are these chemical and mathematical expressions related? The answer is simple. The symbols stand for numbers, and the mathematical expression is the equivalent of the chemical formula.

Suppose we have the formula of potassium chlorate, KClO_3 , and we wish to express the composition in per cent. The process consists in transposing the chemical formula KClO_3 into the equivalent mathematical expression. This is done by: (1) dividing the weight of each element by the molecular weight and (2) multiplying the quotient by 100. Let us take an example. The formula KClO_3 stands for $\text{K} = 39$, $\text{Cl} = 35.5$, and $3\text{O} = 48$ (*i.e.* 3×16), or the molecular weight is 122.5. Then:—

$$\frac{39}{122.5} = 0.3184, \text{ or } 31.84 \text{ per cent of potassium}$$

$$\frac{35.5}{122.5} = 0.2898, \text{ or } 28.98 \text{ per cent of chlorine}$$

$$\frac{48}{122.5} = 0.3918, \text{ or } 39.18 \text{ per cent of oxygen}$$

Total	100.00
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The process of finding the composition in per cent from the formula is often called calculating the **percentage composition** of a compound.

109. The simplest formula of a compound can be calculated from its percentage composition. — The calculation of a formula from the percentage composition is simply the process of finding the small whole numbers by which each atomic weight, as represented by its symbol, must be multiplied in order to express the composition. The process is as follows: (1) divide each per cent by the corresponding atomic weight; (2) reduce the quotients to whole numbers; (3) write the formula. Let us take an example. The composition of sulphuric acid is hydrogen = 2.04 per cent,

sulphur = 32.65 per cent, oxygen = 65.31 per cent. If the percentage of each element is divided by the corresponding atomic weight, the quotients are 2.04, 1.02, and 4.08. Reducing these quotients to whole numbers (by dividing by 1.02 in this case), the final quotients are 2, 1, 4. These quotients represent the ratio of the atomic weights in a molecule of this compound. And since atoms are represented by symbols, a molecule of sulphuric acid contains 2 atoms of hydrogen, 1 of sulphur, and 4 of oxygen. This means that the formula of sulphuric acid must be H_2SO_4 . Formulas calculated by this method are called **simplest formulas**. (See Determination of Molecular Formulas of Compounds, Chapter XV.)

EXERCISES

1. Prepare a summary of this chapter (a) in the form of short topics and (b) as a connected narrative.

2. What three meanings do symbols have?

3. Learn the symbols of these elements: (a) Aluminium, argon, barium, bromine, calcium, carbon, chlorine, copper, fluorine, gold. (b) Helium, hydrogen, iodine, iron, lead, magnesium, manganese, mercury, nitrogen, oxygen. (c) Phosphorus, potassium, silicon, silver, sodium, sulphur, tin, zinc.

4. What elements correspond to C, Cl, Ca, Cu, S, Si, Sn, Mg, Mn, Hg, H, He, A, Al?

5. What do these mean? (a) H, H_2 , 2H, 2O, O_2 , 2 O_2 , Cl, Cl_2 , 3Cl, 3 Cl_2 ; (b) N_2 , K, 2Ca, 3Fe, S_2 , Cu, Al₂.

6. What is a formula? Illustrate. What does a single formula represent?

7. State all that these mean. (a) H_2O , 2 H_2O , KNO_3 , 4 H_2SO_4 , NaOH, NH_4OH , CH_3OH , 3Ca(OH)₂, $\text{Al}_2(\text{SO}_4)_3$, HNO_3 ; (b) $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, 2FeS, 3CaCl₂, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, 2ZnCl₂, 3Al(OH)₃, 4Ba(NO₃)₂.

8. Give from memory the formulas of the following compounds: water, potassium chlorate, sulphuric acid, magnesium oxide, copper oxide, sodium hydroxide.

9. How many atoms of the different elements are in each formula in Exercise 7?

10. Define and illustrate molecular weight. How is it related to (a) a formula and (b) symbols?
11. What is the molecular weight of each substance in Exercise 7?
12. How does a formula express composition? Illustrate by KNO_3 .
13. State the steps in calculating the simplest formula of a compound.
14. As in Exercise 13, in calculating percentage composition.

PROBLEMS

1. Calculate the molecular weight (or multimolecular weight) of the following compounds by finding the sum of the atomic weights: (a) magnesium oxide (MgO), (b) hydrogen peroxide, (c) zinc chloride (ZnCl_2), (d) $2\text{Cu}(\text{NO}_3)_2$, (e) $3\text{Al}_2(\text{SO}_4)_3$, (f) potassium ferrocyanide ($\text{K}_4\text{Fe}(\text{CN})_6$), (g) $2\text{Na}_2\text{B}_4\text{O}_7$, (h) crystallized ferrous sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$).

2. Calculate the simplest formula of the compounds which have the following percentage composition: (a) $\text{Cl} = 60.68$, $\text{Na} = 39.31$; (b) $\text{S} = 23.52$, $\text{Ca} = 29.41$, $\text{O} = 47.05$; (c) $\text{C} = 40$, $\text{H} = 6.67$, $\text{O} = 53.33$.

3. As in Problem 2: (a) $\text{N} = 26.17$, $\text{H} = 7.48$, $\text{Cl} = 66.35$; (b) $\text{As} = 75.8$, $\text{O} = 24.2$; (c) $\text{N} = 82.35$, $\text{H} = 17.65$.

4. As in Problem 2: (a) $\text{Si} = 19.5$, $\text{C} = 66.62$, $\text{H} = 13.88$; (b) $\text{Ca} = 38.71$, $\text{P} = 20$, $\text{O} = 41.29$; (c) $\text{H} = 1$, $\text{K} = 39.06$, $\text{C} = 11.99$, $\text{O} = 47.95$.

5. Calculate the formula of a compound 18 gm. of which contain 8.4 gm. of iron and 9.6 gm. of sulphur.

6. As in Problem 5: 0.84 gm. contain 0.587 gm. of iron and 0.253 gm. of oxygen.

7. Calculate the percentage composition of (a) hydrochloric acid, (b) hydrogen sulphide (H_2S), (c) ammonia (NH_3), (d) hydrogen peroxide.

8. As in Problem 7: (a) calcium oxide (CaO), (b) calcium carbonate (CaCO_3), (c) calcium sulphate (CaSO_4), (d) calcium fluoride (CaF_2).

9. As in Problem 7: (a) cane sugar ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) and (b) grape sugar ($\text{C}_6\text{H}_{12}\text{O}_6$).

10. As in Problem 7: (a) sodium phosphate (Na_3PO_4), (b) disodium phosphate (HNa_2PO_4), (c) monosodium phosphate (H_2NaPO_4), (d) phosphoric acid (H_3PO_4).

11. Calculate the per cent of (a) copper and (b) water in crystallized copper sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$).

12. Calculate the per cent of (a) F in SiF_4 , (b) Al in AlPO_4 , (c) O in MnO_2 , (d) Pb in PbCO_3 .

CHAPTER IX

NITROGEN — THE AIR — ARGON AND HELIUM — LIQUID AIR

110. Introduction. — Reference has already been made to the element nitrogen and its presence in the air. We have also learned a little about the atmosphere — the great mass of gas that envelops the earth and extends several miles into space. The terms *atmosphere*, *the air*, and *air* are often used interchangeably; though by *the air* or *air* we usually mean a limited portion of the atmosphere, *e.g.* the air over a city, the air of a room, or a bottle of air.

In Chapter II we studied oxygen, and learned among other things that this very active gas makes up about one fifth of the air. Since most of the remainder is nitrogen, we shall study this element before considering the air.

111. Occurrence of nitrogen. — The elementary gas nitrogen constitutes about four fifths (or exactly 78.122 per cent) of the air. Nitrogen is a constituent of nitric acid (HNO_3) and ammonia (NH_3), and of important compounds related to them. Nitrogen is also found in many animal and vegetable substances essential to life, *e.g.* the compounds called proteins, which are indispensable ingredients of our food and also of the muscles and nerves of our bodies. (See Chapter XXIV.)

112. Preparation of nitrogen. — Nitrogen is prepared on a large scale from liquid air (129). It can also be ob-

tained from air by removing the oxygen from air by phosphorus (Fig. 56).

Phosphorus is put in a small dish or a crucible cover supported on a cork floating in a vessel of water. Upon igniting the phosphorus with a hot wire and placing a bell jar quickly over the cork, the phosphorus and oxygen unite, forming clouds of white phosphorus pentoxide (P_2O_5). This solid soon dissolves in the water, which rises inside the jar owing to the removal of the oxygen, and the nitrogen is finally left.



Fig. 56. — Preparation of nitrogen by burning phosphorus in confined air

Nitrogen is prepared in the laboratory by heating a solution of sodium nitrite ($NaNO_2$) and ammonium chloride (NH_4Cl). These two compounds form the unstable compound ammonium nitrite (NH_4NO_2) which decomposes into nitrogen (N_2) and water (H_2O); the gas is collected in bottles over water, just as in the case of oxygen and hydrogen. Small quantities of nitrogen may be readily obtained by heating ammonium dichromate ($(NH_4)_2Cr_2O_7$) in a test tube.

113. Properties of nitrogen. — Nitrogen is a colorless gas, and has no taste or odor. It is a little lighter than oxygen and air. A liter at standard conditions weighs 1.25 gm. (A liter of oxygen weighs 1.43 gm. and one of air 1.29 gm.) It is only slightly soluble in water. Subjected to a low temperature and increased pressure, nitrogen becomes a colorless liquid and ultimately a white solid.

114. Chemical conduct of nitrogen. — Nitrogen does not support combustion nor sustain life. Flames are extinguished by nitrogen and animals die in it, because the supply of oxygen is cut off. The fact that nitrogen quickly extinguishes a candle flame and kills a mouse was first ob-

served by Rutherford, a Scottish physician, who discovered the gas in 1772. Soon after, Lavoisier showed the true relation of nitrogen to the atmosphere; and because the gas would not support life, he called the gas *azote* — a name now used by some French chemists. The name nitrogen was given to it because it is a constituent of the important compound niter (*i.e.* saltpeter, potassium nitrate, KNO_3).

Nitrogen is very much less active chemically than oxygen. Indeed, if we test it, as we did oxygen and hydrogen, we find that it responds to none of the common tests. It is sometimes called an **inert element**, because it does not combine with elements at ordinary temperatures. At high temperatures and under special conditions, however, nitrogen forms many compounds. It combines with magnesium and a few other metals at red heat, forming nitrides, *e.g.* magnesium nitride (Mg_3N_2). Electric sparks cause nitrogen to combine with oxygen and with hydrogen, forming nitrogen oxides and ammonia (NH_3). Both these reactions, if hastened by a catalyst, proceed rapidly enough to enable us to convert nitrogen from the air into compounds needed as fertilizers and explosives (196, 197).

115. Uses of nitrogen. — Nitrogen on account of its inertness is used to fill some kinds of electric light bulbs, and the stem of high-boiling thermometers. It is also used in making ammonia, nitric acid, and a nitrogen fertilizer called calcium cyanamide (CaCN_2).

116. Nitrogen and life. — Nitrogen, as well as oxygen, is vitally connected with life, though in a different way. All animals need nitrogen for their growth. But although we live in an atmosphere containing such a large proportion of this gas, we cannot assimilate it directly. The nitrogen we inhale (along with the oxygen) is exhaled again unused. The nitrogen needed by animals must be eaten in the

form of nitrogenous food, such as lean meat, fish, wheat, and other grains. (See Protein, Chapter XXIV.)

Nor have plants, with few exceptions, power to assimilate free nitrogen from the atmosphere. Most plants take up combined nitrogen from the soil in the form of nitrates or of ammonia. Hence combined nitrogen is being constantly removed from the soil. In order to restore it, some nitrogen compound must be added, *e.g.* sodium nitrate (NaNO_3), calcium nitrate ($\text{Ca}(\text{NO}_3)_2$), ammonium chloride (NH_4Cl), ammonium sulphate ($(\text{NH}_4)_2\text{SO}_4$), or calcium cyanamide (CaCN_2); organic materials are often used, *e.g.* manure, dried blood, and meat or fish scraps. A substance or mixture which restores nitrogen (or some other chemical element like phosphorus or potassium) to the soil is called a **fertilizer**.

Many experiments have shown, however, that leguminous plants, such as peas, beans, and clover, take up nitrogen from the air by means of bacteria, which are in nodules on their roots (Fig. 57). Sometimes soil is treated with a preparation which contains nitrogen-forming bacteria.



Fig. 57. — A plant with nodules on the roots

117. Air is a mixture and not a compound. — Air is a mixture of several gases. Oxygen, nitrogen, and argon are the three ingredients that are always present in nearly constant proportions. Variable proportions of water vapor and carbon dioxide gas are always found, and also small quantities of compounds related to ammonia and

nitric acid. Near cities the air may contain considerable dust, sulphur compounds, and acids; at the ocean some salt is often found.

Hitherto we have dealt almost exclusively with compounds, and we have found that compounds have a constant composition, *i.e.* the constituents are united in a proportion which is always the same in the case of a given compound. Furthermore, we have seen that if we wish to make a compound, we must cause the elements to unite chemically, and conversely if we wish to decompose a compound we must tear the compound apart chemically. In a few words, chemical action is always concerned where compounds are formed or decomposed. Moreover, this action is usually accompanied by heat changes. The following facts show that **air is not a compound but a mixture** of gases: —

(1) The proportion of oxygen and of nitrogen is not fixed, but varies between small limits. Therefore air does not have a constant composition and cannot be represented by a formula.

(2) When nitrogen and oxygen are mixed in approximately the proportions that form air, the product is identical with air, but the act of mixing gives no evidence of chemical action.

(3) When air is dissolved in water, a larger proportion of oxygen than nitrogen dissolves. If the oxygen and nitrogen were combined, the dissolved air would contain the same proportions of oxygen and nitrogen as air itself.

(4) When air is liquefied and allowed to boil, the nitrogen boils off first (129). If air were a compound, liquid air would have a fixed boiling point.

118. Proportions of the constant ingredients of air. — For many years it was believed that pure air consisted solely of oxygen and nitrogen. But in 1894 it was found

that nearly 1.2 per cent (by volume) of the gas hitherto called nitrogen is argon (124). The normal proportions (by volume) of the constant ingredients of air are nitrogen 78.122 per cent, oxygen 20.941 per cent, and argon 0.937 per cent. These numbers are often stated approximately as oxygen 21, nitrogen 78, and argon 0.94.

119. "Composition" of air. — Although air is a mixture, we usually speak of its "composition." Samples of air from various parts of the globe show such a remarkable uniformity in the proportions of the constant ingredients that chemists have fallen into the habit of applying the term *composition* to air.

The proportion of oxygen in the air can be found by several methods. In one, a known volume of air is shaken in a closed bottle with a mixture of pyrogallic acid and sodium hydroxide; this solution absorbs the oxygen and leaves the nitrogen and argon unchanged. In another, a graduated glass tube, containing a known volume of air, is inverted in a jar of water, and a piece of phosphorus attached to a wire is introduced into the tube (Fig. 58). The oxygen combines with the phosphorus. In a few hours the phosphorus is removed, and the volume of residual gas is read. The difference between the first and last volumes is oxygen. There is no simple way of separating the nitrogen and argon.

120. Water vapor in the air. — Water vapor is always present in air, owing to constant evaporation from the ocean and other bodies of water. When the temperature of the air falls sufficiently, the water vapor condenses and is deposited in the form of dew, rain, fog, mist, frost, snow, sleet, or hail (67). The clouds are masses of minute drops of liquid water formed by condensation of the water vapor

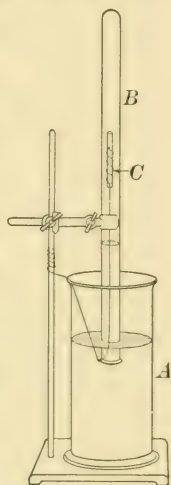


Fig. 58. — Finding the per cent of oxygen in air by phosphorus

in the cold upper air. The condensation of considerable moisture forms large drops, which fall to the earth as rain.

The total amount of water vapor in the lower regions of the atmosphere is very large. However, the proportion in the air of different regions varies between wide limits. In rainy regions, such as tropical countries, it is large, while in desert countries it is small.

A given volume of air absorbs a definite volume of water vapor and no more. Warm air holds more than cool air. Air containing its maximum amount of water vapor is said to be saturated at that temperature, or to contain 100 per cent of water vapor. The saturation point is also called the **dew point**, *i.e.* the temperature at which it begins to deposit dew. On a pleasant day in a temperate climate the **relative humidity**, *i.e.* the relative amount of water vapor present, may vary from 30 to 90 per cent, the average being about 65 per cent.

121. Test for moisture in the air. — The presence of water vapor in the air is shown by the moisture which collects on the outside of a vessel containing cold water, such as a pitcher of iced water. The moisture comes from the air around the vessel. For a similar reason, water pipes in a cellar and the cellar walls themselves are moist in summer.

In the laboratory the presence of water vapor may be shown by exposing to the air a deliquescent substance, such as calcium chloride (85). If a known volume of air is drawn slowly through a weighed tube containing calcium chloride, the increase in weight gives the weight of water in the volume of air.

The **relative humidity** may be calculated by first ascertaining the dew point and then comparing the final (dew point) pressure and the original (observed) pressure. For example, if air at 20° C. must be cooled to 12° C. before it deposits dew, its moisture content would be expressed as 10.48 mm. (73). If it were saturated at 20° C., its moisture content would have been equivalent to 17.41 mm. That is, its relative humidity was $10.48 \div 17.41$, or 60.19 per cent.

122. Physical comfort depends on water vapor in the air. — The proportion of water vapor in the air has a marked effect on our bodily comfort. When the relative humidity is near the average, we feel comfortable. But if the air is moist or dry we are very uncomfortable.

The relation of water vapor to bodily comfort is simple. Our bodies have a normal and nearly constant temperature of 98.6° F. This temperature is maintained by the heat produced by the chemical changes in our bodies, especially the oxidation of waste tissue by the oxygen carried by the blood to all parts of the body (27). But this temperature is regulated partly by radiation of heat and partly by evaporation of water from the surface of the body. Now if the air is moist, evaporation proceeds with difficulty; whereas if the air is dry, it proceeds too fast. In either case, we are uncomfortable, and try by various devices to increase our comfort. Thus, we use fans and wear thin clothing to promote evaporation, or we moisten the air by exposing pans of water.

Our comfort and efficiency depend on maintaining constant, moderate evaporation from the surface of the body. This desirable condition may be accomplished, or at least favored, by living in the open air as much as possible, maintaining the average humidity in our houses, wearing clothing adapted to climatic conditions, and ventilating the rooms in which we live.

123. Carbon dioxide in the air. — Carbon dioxide is one product of the breathing of animals, the combustion of fuels, and the decay of organic substances (33). By these processes vast quantities of carbon dioxide are being constantly introduced into the air. The proportion in ordinary air is 3 to 4 parts in 10,000 parts of air, *i.e.* 0.03 to 0.04 per cent. In crowded rooms it is often as high as 33 parts

in 10,000. The proportion of carbon dioxide in the atmosphere as a whole is practically constant, owing to winds and air currents, and largely, also, to the fact that this gas is absorbed by all green plants (39).

The presence of carbon dioxide in air is detected by calcium hydroxide. If calcium hydroxide solution is exposed to air, the carbon dioxide interacts with the calcium hydroxide, forming a thin, white crust of insoluble calcium carbonate on the surface of the liquid. If considerable air is drawn through the calcium hydroxide solution, the liquid becomes milky, because the particles of calcium carbonate are suspended in the liquid (33 and Fig. 12).

124. Argon in the air. — Argon, as stated above (118), is an essential and constant ingredient of the air, the proportion being 0.937 per cent by volume.

Argon is a colorless, odorless gas which is a little heavier than oxygen. It dissolves in water to the extent of about 4 volumes in 100. It can be liquefied and solidified.

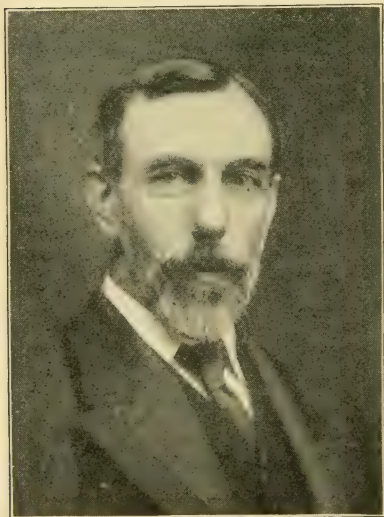


Fig. 59. — Ramsay (1852-1916)

A conspicuous property of argon is its lack of chemical activity. No compounds of this element have as yet been prepared or discovered. The name *argon* is happily chosen, being derived from Greek words signifying inert.

125. Discovery of argon. — Argon was detected and first studied in 1894 by Rayleigh and

Ramsay (Fig. 59). Rayleigh found that nitrogen extracted from air had a greater weight than an equal volume of nitrogen obtained from compounds of nitrogen. Consequently, they believed that the nitrogen from air contained another gas hitherto overlooked. Experiments (by Ramsay) showed that after the oxygen and nitrogen were removed from purified air, there still remained a small quantity of a new gas. It was named **argon** and given the symbol A.

Argon was first obtained by Ramsay by passing pure air over heated copper to remove the oxygen, and then the remaining gas over heated magnesium or calcium to remove the nitrogen. He also passed electric sparks through a mixture of air and oxygen, and absorbed the nitrogen oxides in potassium hydroxide solution. The latter method is a repetition of the one used by Cavendish in 1785 when he determined the composition of air; he observed and recorded the fact that a small bubble of gas always remained, which was doubtless argon. To Cavendish belongs the honor of first observing this element.

A recent method of obtaining argon consists in liquefying air, and allowing the nitrogen and then the argon to boil off from the oxygen. This method is based on the fact that liquid argon boils at a higher temperature (-186°C.) than nitrogen (-195.7°C.).

126. Other gases in the atmosphere. — Helium, neon, krypton, and xenon are inert gases discovered by Ramsay subsequently to argon. With the exception of neon, they constitute an exceedingly minute proportion of the atmosphere. Like argon they do not form compounds. Ramsay estimated that in 1,000,000 parts of the atmosphere there are 3 to 4 parts of helium, 10 to 20 of neon, 0.05 of krypton, and 0.006 of xenon.

127. Helium was detected in the atmosphere of the sun by Lockyer in 1868. It was found by Ramsay, soon after he discovered argon, in the gases expelled from certain rare minerals and in the gas and water of some mineral springs. Helium is now obtained from natural gas which issues from the ground in certain parts of the United

States. By liquefying the gas, the helium can be separated from the other ingredients, owing to its low boiling point (-269° C.). It is a light, non-inflammable gas. Both of these properties make helium an excellent gas for filling balloons and lighter-than-air airships, and successful experiments have been made along this line.

Helium is one of the disintegration products of radium (620).

128. What is liquid air? — Liquid air is a mixture of liquid oxygen and liquid nitrogen. It sometimes looks cloudy, owing to the presence of solid carbon dioxide and ice. When these solids are removed by filtering, the filtrate has a pale blue tint.

129. Properties of liquid air. — If a beaker is filled with liquid air, the latter boils vigorously, the surrounding air becomes intensely cold, frost gathers on the beaker, and in a short time the liquid air will disappear into the air of the room. If, however, liquid air is put into a Dewar flask, evaporation takes place so slowly that some liquid air will remain in the flask several days.

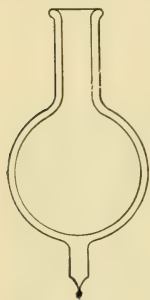


Fig. 60. — A
Dewar flask

A Dewar flask (Fig. 60) consists of two flasks, one within the other sealed together air-tight at the top; the space between the flasks is a vacuum. The surfaces of the flasks are coated with silver, which reflects heat and helps retard the evaporation of the liquid air. Liquid air is stored and transported in Dewar flasks.

Liquid air boils at about -190° C. If it is allowed to boil in a proper apparatus, the nitrogen (boiling point -195.7° C.) escapes first, leaving more or less pure oxygen (boiling point -182.9° C.). (See also 125.) The industrial separation is accomplished this way, the two gases being collected in separate tanks.

130. Some experiments with liquid air. — A tin or iron vessel which has been cooled by liquid air is so brittle that it may often be crushed with the fingers; while a piece of rubber tubing becomes as brittle as glass. Mercury freezes so hard in liquid air that it can be used as a hammer to drive a nail.

When liquid air is poured into a kettle standing on a block of ice, the liquid air boils vigorously because the ice is so much "hotter." If a kettle of liquid air is placed over a lighted Bunsen burner, frost and ice collect on the bottom of the kettle, because the intense cold produced by the evaporation of the liquid air in the kettle solidifies the water vapor and carbon dioxide, which are the two main products of burning illuminating gas. If water is now poured into the kettle, the liquid air boils over and the water is instantly frozen; the water is so much "hotter" than the liquid air that the latter boils more violently, and since its rapid evaporation causes the absorption of heat, the water loses heat and becomes ice.

Ordinary liquid air is from one half to one fifth liquid oxygen, and will support combustion. A glowing stick or a red-hot rod of steel burns brilliantly in this cold liquid.

131. Manufacture of liquid air. — Liquid air is manufactured by forcing air cooled by water through a pipe to a valve. As it escapes through the valve, it expands and its temperature falls, because expansion is a cooling process. After expansion, the cold air is led back over the outer surface of the same pipe by which it came, whereupon it rapidly regains its former temperature. But in so doing it cools the pipe itself and the air within it. This latter air in turn expands and falls in temperature, but as it was colder than the first portion before expansion, so it is colder after expansion. Since the pressure within the pipe is maintained by a continuous supply of air under pressure, the pipe becomes continually colder, until finally the expanding air at the valve liquefies in part.

EXERCISES

1. How is nitrogen prepared? Summarize its properties. Compare the chemical conduct of nitrogen and oxygen. For what is nitrogen used?

2. What is the relation of nitrogen to the life of (a) animals and (b) plants?

3. What are the two chief ingredients of the atmosphere? The constant ingredients? The variable ingredients? The ingredients found in traces? What special substances are sometimes found in the air of cities?

4. State the volumetric composition of air. How is it found?

5. Has air a chemical formula? If so, what is it? If not, why?

6. Describe the action of air upon (a) calcium hydroxide and (b) calcium chloride.

7. What is the meaning of the term *dew point*? *Relative humidity*?

8. Discuss the relation of physical comfort to water vapor in air.

9. Give several proofs that air is a mixture.

10. What is argon? Give a brief account of (a) its discovery, (b) its properties, (c) its method of preparation. What proportion of air is argon? What is the significance of the name argon?

11. What is liquid air? What are its chief properties? Describe a Dewar flask.

12. Topics for home study: (a) Helium. (b) Uses of nitrogen. (c) Function of oxygen in the air. (d) Atmospheric pressure. (e) Ventilation. (f) Carbon dioxide in the air. (g) Lavoisier and combustion. (h) Cavendish and air.

13. Practical topics: (a) How would you distinguish nitrogen from carbon dioxide? (b) Why are mines and cellars damp? (c) Why does the composition of the atmosphere vary so slightly? (d) How can the relative humidity of a room be increased in a heated house? (e) Of what advantage is helium in a balloon?

PROBLEMS

1. What is the weight of air in a room $6 \times 8 \times 5$ m.? (A liter of air weighs 1.29 gm.)

2. How many kilograms of pure air are needed to yield (a) 100 kg. and (b) 100 l. of oxygen (at standard conditions)?

3. Express in inches the following barometer readings: (a) 760 mm., (b) 745 mm., (c) 70 cm., (d) 0.769 m., (e) 7.49 dm., (f) 780 mm., (g) 5 mm.

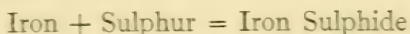
4. What is the weight at 0° C. and 760 mm. of (a) 1000 cc. of dry air? Of (b) 95 l., (c) 95 cc., (d) 95 cu. m.?

CHAPTER X

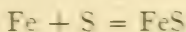
CHEMICAL REACTIONS — EQUATIONS — CALCULATIONS

132. Chemical reactions. — The substances that participate in a chemical change are said to undergo chemical action, to interact, or to react. A single chemical change is called a chemical reaction, an interaction, or simply a reaction.

133. What is a chemical equation? — We learned in 14 that a reaction can be represented in a condensed form called an equation. Thus: —



In the preceding chapters certain chemical changes were represented by equations. In 105, 106 we found that elements and compounds are represented by symbols and formulas. Therefore, we can now remodel the preliminary equations into chemical equations by using symbols and formulas in place of words. The above equation then becomes: —



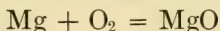
134. How to write an equation. — The mere change of words to symbols and formulas would not always give a correct equation. In order to write the equation that correctly expresses a chemical change, we must know certain facts and express them in the correct chemical way. Thus, we must know the symbols and formulas of the factors (the reacting substances) and of the products (the final substances). Next we must write a preliminary equation,

and then adjust it so that there is the same number of atoms of each element on both sides of the final equation.

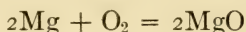
These are the steps in writing an equation: (1) Write on the left (of the equality sign) the symbol or formula of each factor. (2) Write on the right the symbol or formula of each product. (3) Balance the preliminary equation, if necessary.

To **balance an equation** we increase the number of atoms, or molecules, or both — as necessary — until the number of atoms of each element (free or combined) is the same on both sides of the equation. Let us take three examples.

First, when magnesium and oxygen form magnesium oxide, the preliminary equation is:—



Inspection shows that there are 2 atoms of oxygen (in O_2) on the left but only 1 (in MgO) on the right. Hence we must increase the number of oxygen atoms on the right. We do this by prefixing the coefficient 2 to the formula MgO (**not by altering the MgO**). This change necessitates multiplying Mg on the left by 2. The **final balanced equation** then becomes:—



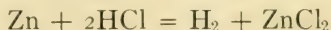
Final inspection shows that the same number of atoms of each element is on both sides of the equation, hence the equation is correct.

Second, when zinc and hydrochloric acid interact, hydrogen and zinc chloride are formed. The preliminary equation is:—



By inspection it is evident that 2 atoms of chlorine (in ZnCl_2) are on the right and only 1 is on the left. Hence we must

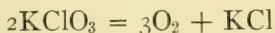
multiply HCl by 2, thereby providing 2 atoms of chlorine, and giving also the 2 atoms of hydrogen. The **final balanced equation** becomes : —



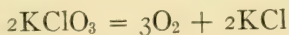
Third, when potassium chlorate is decomposed, oxygen and potassium chloride are produced. The preliminary equation is : —



By inspection we see that there are 3 atoms of oxygen (in KClO_3) on the left but only 2 (in O_2) on the right. To obtain the same number on each side, we must multiply KClO_3 by 2 and O_2 by 3. The second preliminary equation is : —

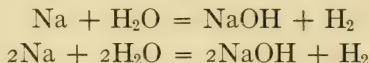


Inspecting again, it is clear that there are 2K and 2Cl on the left but only 1 each on the right. Therefore, we balance by multiplying KCl by 2, and obtain the **final correct equation** : —



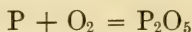
135. Some precautions to be observed in writing equations. — (a) Correct formulas must be used. If a formula is not remembered or is not given in the immediate text, it should be looked up in the book; this can be done by finding the name of the substance in the index and consulting the proper page where, as a rule, the formula is given. Thus, when sodium interacts with water, sodium hydroxide and hydrogen are formed. By referring to the page in the text under which sodium hydroxide is indexed,

we find its formula is NaOH. The preliminary and final equations are:—

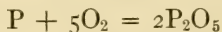


(b) It must not be overlooked that the correct formulas of many elementary *gases*, such as oxygen, hydrogen, nitrogen, and chlorine, are O_2 , H_2 , N_2 , Cl_2 respectively (not O, H, etc.).

(c) In balancing an equation these rules are helpful: (1) Start with the formula containing the most atoms of one element. (2) Find the other formula (or symbol) containing this element, and increase the number of atoms of this element by prefixing a coefficient, not by altering the formula (or symbol)—see middle of page 116. (3) Increase again, if necessary. (4) Balance in the same way for the other elements. (5) Check up, so that finally the total number of atoms of each element is the same on both sides. Let us take an example. When phosphorus burns in oxygen, phosphorus pentoxide is formed. The formula of phosphorus pentoxide is P_2O_5 . Hence the preliminary equation is:—



By inspection we see that P_2O_5 needs at least 5 atoms of oxygen. Clearly the only way to balance the equation for oxygen is to multiply O_2 by 5 and P_2O_5 by 2; this adjustment gives 10 atoms of oxygen on each side, thus:—



But multiplying P_2O_5 by 2 gives 4 atoms of P on the right, because a coefficient multiplies the whole formula. That is, $2\text{P}_2\text{O}_5$ means *two* molecules each containing 2P and 5O. Hence we balance for P by multiplying P on the left by 4. The final equation then becomes:—



(d) Only the substances that actually take part in the chemical change should be included in the equation. Thus, when magnesium is burned in air, the nitrogen of the air does not unite with the magnesium (to any extent). Hence nitrogen does not appear in the equation. Similarly in the equation for the preparation of hydrogen from zinc and hydrochloric acid, no water (H_2O) appears as a factor because the water (in the dilute sulphuric acid) does not participate in the reaction.

(e) The terms of an equation, *i.e.* symbols and formulas, cannot be transposed as in the case of an algebraic equation. A chemical equation is the expression of an actual chemical change; it is the outcome of an experiment. A chemical equation, although it contains the plus sign, has none of the properties of an algebraic equation except equality of the total weights on each side.

136. How to read an equation. — The plus (+) sign may be read *and* or *plus* and the equality (=) sign *form(s)*, *gives(s)*, or *equal(s)*. An arrow ($\longrightarrow$) is sometimes used instead of the equality sign (=); both signs are read in the same way. Since equations are really expressions of equality between two total weights, there is a good reason for using the sign of equality. (Compare **174**.)

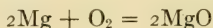
Consider the equation: —



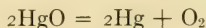
This equation may be read in several ways: (1) zinc and sulphuric acid form (or give) hydrogen and zinc sulphate; (2) zinc plus sulphuric acid equal hydrogen plus zinc sulphate; (3) one atom of zinc and one molecule of sulphuric acid form one molecule of hydrogen and one molecule of zinc sulphate. (A fourth way is given in **208**.)

137. Ordinary equations have a limited meaning. — The equations we are studying in this chapter might be called **ordinary equations** or **atomic equations**. They merely show the result of a reaction by the proper number of atoms and molecules. Other kinds of equations are used to tell other facts about chemical change, and these will be discussed in the proper places.

Ordinary equations show nothing about the physical conditions under which a reaction occurs. Thus, the equation

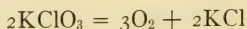


does not show that the reaction takes place quickly at a moderate temperature (*e.g.* heat from a burning match). Nor does the equation



show that the reaction takes place rather slowly and only by constant heating at a high temperature (*e.g.* heat from a Bunsen burner).

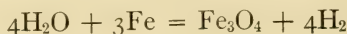
So also ordinary equations do not include the solvent, although many reactions occur only in solution. Moreover, ordinary equations tell nothing about the way in which a reaction occurs. Thus, in the equation



several chemical changes doubtless occur which do not appear in the equation. The main purpose of this equation is to express in the simplest way the transformation of potassium chlorate into the two products oxygen and potassium chloride.

138. Ordinary equations are gravimetric equations. — Ordinary equations, in spite of certain limitations, have a practical use which is very important.

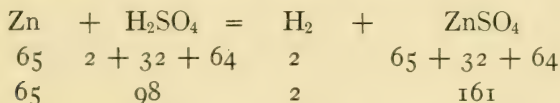
We have seen so far that equations show in a compact way the products formed by the reaction of certain substances and that they also show the number of molecules (and in some cases the atoms) of each substance involved in a reaction. Thus, the equation



not only shows that iron oxide and hydrogen are the products of the interaction of water (in the form of steam) and iron, but also that 4 molecules of water and 3 atoms of iron interact to form 1 molecule of iron oxide and 4 molecules of hydrogen.

Equations are quantitative expressions. They are based on the fact that a chemical change conforms to the law of the conservation of matter, viz., *No matter is lost or gained in a chemical change*. We start with a certain total weight and we have the same total weight at the end of the reaction. This is only another way of saying that we have the same number of atoms on each side of a balanced equation, because we have the same sum of atomic weights on each side of the equation. Indeed, there could be no "equation" unless both sides were equal in weight. Briefly, **ordinary equations are gravimetric**.

139. Calculations based on equations. — Each atom stands for a certain weight. Hence we can write the equation for the interaction of zinc and sulphuric acid thus: —



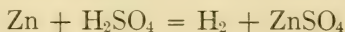
The equation in this form is read: 65 parts by weight of zinc plus 98 parts by weight of sulphuric acid equal 2 parts by weight of hydrogen and 161 parts by weight of zinc sulphate. That is, these numbers are the relative weights of the different substances involved in this reaction. Zinc and sulphuric acid always interact in the ratio of 65 to 98 and produce hydrogen and zinc sulphate in the ratio of 2 to 161.

In actual practice, of course, we do not have to start with exactly 65 gm. of zinc or with 98 gm. of sulphuric acid.

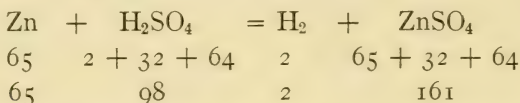
We can use any convenient weights; but whatever weights we use, these two substances interact in the ratio of 65 to 98 and the quantity of either substance greater than the amount for the required ratio will be left unchanged.

Suppose we start with 45 gm. of zinc, pour sulphuric acid upon it, and let the reaction continue until the zinc is used up. We can calculate readily the weight of the sulphuric acid used.

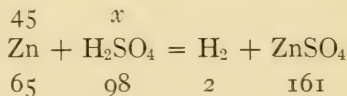
First, we write the equation. Thus:—



Second, we place under each term of the equation its correct relative weight, *i.e.* the weight for which the complete symbol or formula stands, using for this purpose the approximate atomic weights in the table on the back inside cover. Thus:—



Third, we place above the symbol for zinc the given weight, which is 45 in this example, and above the formula for sulphuric acid the letter *x* to denote the required weight. Thus:—



Fourth, we state in a proportion the four quantities involved. In this proportion the equation weights (below the equation) are the first and second terms, while the corresponding known and required weights (above the equation) are the other two terms. Thus:—

$$65 : 98 :: 45 : x$$

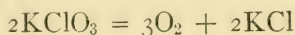
Fifth, we finally solve the proportion for x , remembering that the product of the means (the two inner terms) equals the product of the extremes (the two outer terms). Thus:—

$$98 \times 45 = 65 \times x \therefore x = \frac{98 \times 45}{65}, \text{ or } 67.8. \quad \text{Ans. } 67.8 \text{ gm.}$$

The quantity of each product can be found by a similar proportion.

Another example will make the process clearer. This time we start with 15 gm. of potassium chlorate and wish to know the weight of oxygen which can be obtained. Proceeding as above, we have these steps:—

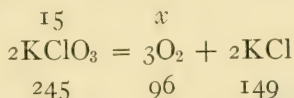
(1) Chemical equation:—



(2) Relative weight equation:—

$$\begin{array}{rcccl} 2\text{KClO}_3 & = & 3\text{O}_2 & + & 2\text{KCl} \\ 2(39 + 35.5 + 48) & & 3(32) & & 2(39 + 35.5) \\ 2(122.5) & & 96 & & 2(74.5) \\ 245 & & 96 & & 149 \end{array}$$

(3) Reacting weight equation:—



(4) Proportion:—

$$245 : 96 :: 15 : x$$

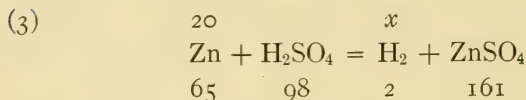
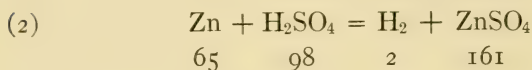
(5) Solution:—

$$96 \times 15 = 245 \times x \therefore x = \frac{96 \times 15}{245}, \text{ or } 5.87. \quad \text{Ans. } 5.87 \text{ gm.}$$

140. Calculations involving weight and volume.—Calculations like those in **139** are limited to weights—gravi-

metric calculations. But many reactions involve gases, and it is often necessary to know the volume of the gas as well as its weight. To calculate the volume, we calculate the weight in the usual way and then convert the weight into volume; or vice versa.

Let us take two examples. First, suppose we wish to know the volume of hydrogen liberated by the interaction of 20 gm. of zinc and sufficient dilute sulphuric acid. Proceeding as in **139**, we have:—



$$(4) \quad 65 : 2 :: 20 : x$$

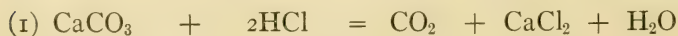
$$(5) \quad 2 \times 20 = 65 \times x \therefore x = \frac{2 \times 20}{65}, \text{ or } 0.615.$$

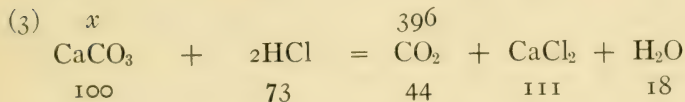
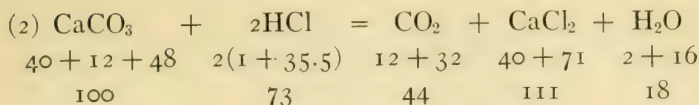
Then

(6) Since 1 liter of hydrogen weighs 0.09 gm. (**52**), the volume of hydrogen is:—

$$\frac{0.615}{0.09} = 6.83. \quad \text{Ans. } 6.83 \text{ l.}$$

As a second example, suppose we wish to know the weight of calcium carbonate needed to produce 200 liters of carbon dioxide. First, we find the weight of 200 liters of carbon dioxide. Since 1 liter weighs 1.98 gm. (**36** and Appendix, § **3**), the weight of 200 liters is 200×1.98 , or 396 grams. Proceeding as above we have:—



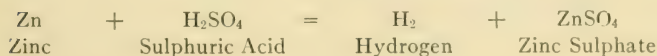
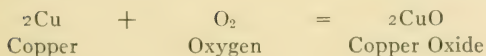
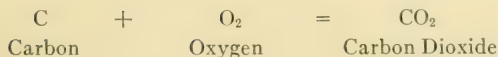
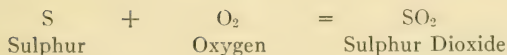
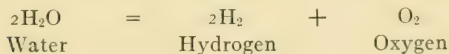
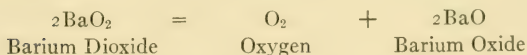
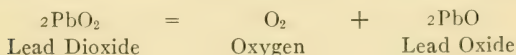
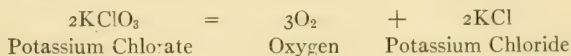


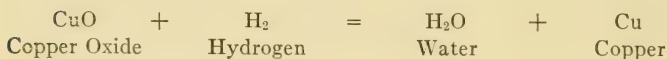
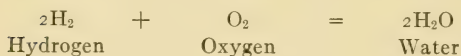
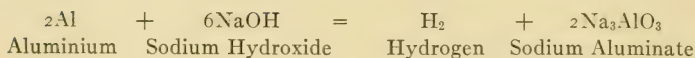
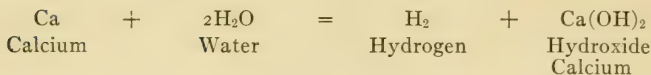
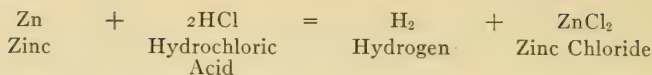
$$(4) \quad 100 : 44 :: x : 396$$

$$(5) \quad 44 \times x = 100 \times 396 \therefore x = \frac{100 \times 396}{44}, \text{ or } 900.$$

Ans. 900 grams.

141. Equations for preceding reactions. — The equations corresponding to many reactions already discussed may be collected here, partly for review and partly for use in solving problems.





EXERCISES

1. Prepare a summary of **132** to **138**.
2. Define and illustrate the terms *reaction* and *equation*.
3. State (a) the three steps in writing an equation, and (b) the rules for balancing an equation.
4. What precautions must be observed in writing equations?
5. Select an equation from **141** and read it in three different ways.
6. Interpret the equation $2\text{Cu} + \text{O}_2 = 2\text{CuO}$ by stating (a) what it means and (b) what it does not include or express.
7. Write equations for the following reactions: (a) Calcium and hydrochloric acid form calcium chloride and hydrogen. (b) Potassium sulphate and barium chloride form barium sulphate and potassium chloride. (c) Calcium carbonate and hydrochloric acid form calcium chloride, water, and carbon dioxide.
8. As in Exercise **7**: (a) Calcium oxide and carbon dioxide form calcium carbonate. (b) Chlorine and aluminium form aluminium trichloride. (c) Carbon and lead oxide (PbO) form lead and carbon monoxide.

9. What is a gravimetric equation? Illustrate.

10. Balance these equations: (a) $\text{BaCl}_2 + \text{H}_2\text{SO}_4 = \text{BaSO}_4 + \text{HCl}$; (b) $\text{Pb}(\text{NO}_3)_2 + \text{H}_2\text{S} = \text{PbS} + \text{HNO}_3$; (c) $\text{AlCl}_3 + \text{NH}_4\text{OH} = \text{Al}(\text{OH})_3 + \text{NH}_4\text{Cl}$; (d) $\text{NaOH} + \text{CO}_2 = \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$.

11. Balance these equations: (a) $\text{Zn} + \text{HNO}_3 = \text{H}_2 + \text{Zn}(\text{NO}_3)_2$; (b) $\text{HCl} + \text{ZnO} = \text{ZnCl}_2 + \text{H}_2\text{O}$; (c) $\text{H}_2\text{SO}_4 + \text{NaNO}_3 = \text{Na}_2\text{SO}_4 + \text{HNO}_3$; (d) $\text{SO}_2 + \text{O}_2 = \text{SO}_3$.

12. State in order the steps in calculating the weight of a substance when the weight of only one reacting substance is given (139).

PROBLEMS

1. How many grams of oxygen can be prepared from (a) 45 gm. of mercuric oxide, (b) 1 kg. of potassium chlorate, (c) 1000 gm. of water?

2. As in Problem 1, from (a) 750 gm. of lead oxide (PbO_2), (b) 2200 gm. of barium dioxide (BaO_2)?

3. Hydrogen is prepared from sulphuric acid and 40 gm. of zinc. Calculate the weights of the products of the reaction.

4. If a balloon holds 150 kg. of hydrogen, how much (a) zinc and (b) sulphuric acid are needed to generate the gas?

5. What volume of oxygen at standard conditions could be obtained from 10 gm. of potassium chlorate?

6. If 10 gm. of pure carbon are burned in air, what weights of other substances are involved?

7. One gram of copper is heated intensely in air, and the product is reduced by a gas. Calculate (a) the weights of the other substances involved in the two reactions, and (b) the volume of the gas in the second reaction.

8. How many grams of potassium chlorate are needed to prepare (a) 100 gm. of oxygen and (b) 100 l. (at standard conditions)?

9. Calculate the weights needed in the following reactions: (a) water and 100 milligrams of sodium, (b) calcium and 100 milligrams of water, (c) sodium hydroxide and 25 gm. of aluminium.

10. What weight of carbon dioxide is formed by burning a ton of coal which is 90 per cent carbon?

11. Suppose 85 gm. of water are decomposed. What (a) weights and (b) volumes of gases are produced?

12. Sixty grams of mercuric oxide are decomposed. What volume of oxygen at 91°C . and 380 mm. is produced?

13. How much water can be obtained from (a) 34 gm. of crystallized zinc sulphate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$), (b) 1000 kg. of selenite ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), (c) 1000 gm. of washing soda crystals ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$)?

14. Write the equation for the interaction of barium nitrate and sodium sulphate. If 170 gm. of barium nitrate are used, calculate the weights of the other compounds involved.

15. Ammonia and hydrogen chloride form solid ammonium chloride. Write the equation for this reaction. If 210 gm. of ammonia are used, calculate (a) the weights of the other compounds involved, and (b) the volumes of ammonia and hydrogen chloride needed.

16. The oxygen is liberated from 10 gm. of potassium chlorate, and 10 gm. of sulphur are burned in the gas. How much sulphur, if any, is left?

CHAPTER XI

CHLORINE -- HYDROGEN CHLORIDE— HYDROCHLORIC ACID

142. Introduction. — So far we have studied the elements oxygen, carbon, hydrogen, and nitrogen, the compounds carbon dioxide, carbon monoxide, and water, and the mixture air. In this chapter we shall study the **element chlorine** and its common **compound hydrogen chloride**.

143. Occurrence of chlorine. — Free chlorine is never found in nature, but its compounds, especially chlorides, are widely distributed, the most abundant being sodium chloride (NaCl) or common salt. Many compounds of chlorine with potassium, magnesium, and calcium are found in the deposits at Stassfurt in Germany. (See Potassium, Chapter XXIX.) Sea water contains sodium and magnesium chlorides.

144. Preparation of chlorine. — Chlorine is prepared on a large scale by the **electrolysis** of a solution of sodium chloride. When an electric current is passed through a solution of sodium chloride, chlorine gas is liberated in one compartment of the apparatus and sodium hydroxide is formed in the other. The chlorine is conducted off through pipes, and the dissolved sodium hydroxide is drawn off at intervals. This process is further described in **456**.

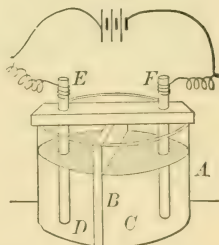


Fig. 61. — Apparatus to illustrate the preparation of chlorine by the electrolysis of a solution of sodium chloride.

This process can be readily demonstrated. The apparatus is shown in Fig. 61. A solution of sodium chloride is put in the battery jar *A*; a little litmus solution is added and then enough dilute hydrochloric acid to color the solution a distinct red. A block (*B*) divides the jar into two compartments (*C* and *D*), and the two pieces of electric light carbon serve as electrodes (*E* and *F*). Soon after the current (from four or more cells or from a reduced street current) is turned on, the solution is bleached by the liberated chlorine in one compartment and turned blue by the sodium hydroxide in the other. The chlorine can also be detected by its odor.

Chlorine is **prepared in the laboratory** by heating concentrated hydrochloric acid with manganese dioxide. The equation is:—

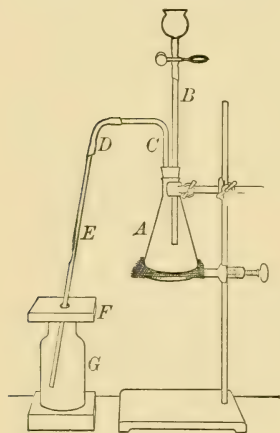
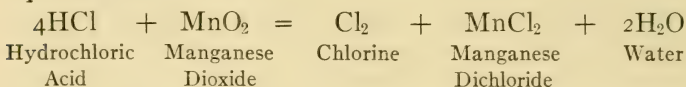


Fig. 62. — Apparatus for preparing chlorine in the laboratory

A simple form of laboratory apparatus is shown in Fig. 62. The manganese dioxide is put into the flask *A* and concentrated hydrochloric acid is introduced through the dropping tube *B*. By gently heating the flask, chlorine passes to the bottom of the bottle *G* and displaces the air.

145. Properties of chlorine. —

Chlorine is a greenish yellow gas. Its color suggested the name chlorine (from the Greek word *chloros*, meaning greenish yellow), which was given to it by Davy about 1810. It has a disagreeable odor, which is very penetrating. If breathed, it irritates the sensitive lining of the nose and throat; a large quantity produces lung trouble, and would ultimately cause death. Chlorine was the first

poison gas used in the World War. It is about 2.5 times as heavy as air. Hence it is easily collected by downward displacement, *i.e.* by conducting it downward to the bottom of a vessel and allowing it to displace the air. A liter of dry chlorine at 0° C. and 760 mm. weighs 3.22 gm.

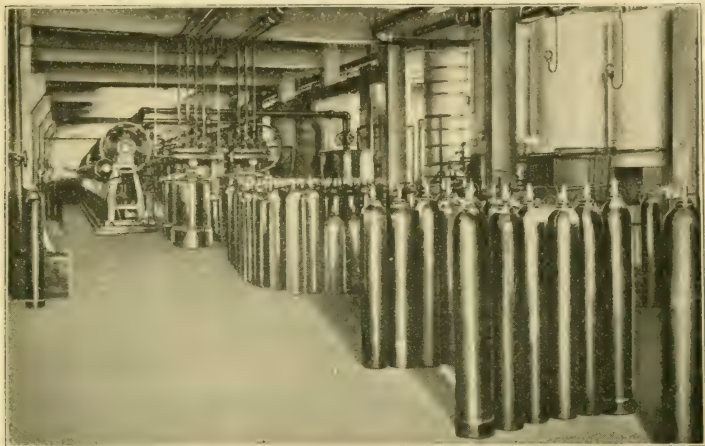
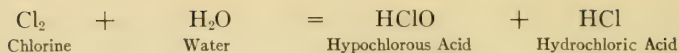


Fig. 63. — Interior of a plant for liquefying and storing chlorine. Cylinders full of chlorine are in the foreground

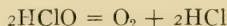
Chlorine can be readily liquefied and solidified. Liquid chlorine is sold in strong iron cylinders (Fig. 63 and also Fig. 35).

146. Chlorine dissolves in water. — The solution of chlorine is yellowish, and smells strongly of chlorine. **Chlorine water**, as the solution is called, is unstable. If the solution is placed in the sunlight, oxygen is slowly liberated and can be collected in a suitable apparatus, *e.g.* a long tube (87 and Fig. 46).

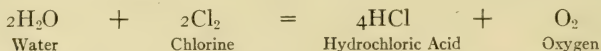
The oxygen does not come directly from the water but from a compound called hypochlorous acid (HClO), which is formed in small quantities in the solution; some hydrochloric acid is also formed. The reaction may be represented thus: —



The hypochlorous acid is unstable and decomposes, thus: —

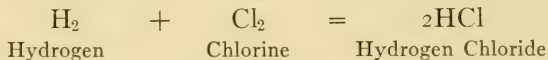


The reactions continue until all the chlorine is used up; the equation for the completed change is: —



147. Chemical conduct of chlorine. — Chlorine is a very active element. It unites vigorously with many elements at ordinary temperatures. Thus, if sodium, iron, copper, or other metals are merely warmed and then put into chlorine, they unite with the chlorine at once; the sodium produces a dazzling light, and the copper and iron glow and emit dense fumes. These chemical changes illustrate the broad use of the term *combustion*. (See 53.) The compound formed in each case is a **chloride**, *i.e.* a compound of chlorine and one other element, *e.g.* sodium chloride (NaCl) and iron chloride, (FeCl₃).

Chlorine combines readily with hydrogen (53). The equation for this reaction is: —



A jet of burning hydrogen when lowered into chlorine continues to burn, forming a colorless gas called hydrogen chloride; the latter becomes a white cloud when the breath is blown gently across the mouth of the vessel (155).

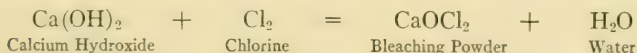
The tendency of chlorine to combine with hydrogen is so great that the hydrogen of many compounds is withdrawn chemically by chlorine. Thus, when cotton saturated with hot turpentine (C₁₀H₁₆) is put into chlorine, white fumes, due to the formation of hydrogen

chloride, appear almost at once; soon the chemical change is so vigorous that a flame is produced. Since carbon does not unite directly with chlorine, the white fumes of hydrogen chloride are finally obscured by a dense cloud of black smoke.

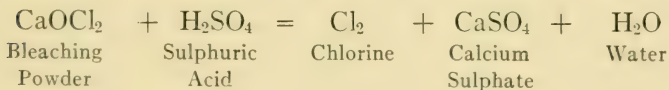
148. Chlorine bleaches. — Chlorine changes many colored substances into colorless ones. For example, colored cloth, whether dyed or naturally colored by impure substances, is whitened (*i.e.* bleached) by moist chlorine. Dry chlorine does not bleach.

149. Sources of chlorine for bleaching. — Chlorine water, prepared by bubbling chlorine through cold water, is sometimes used as a bleaching agent. The commonest source, however, is **bleaching powder** (CaOCl_2) or, as it is often called, **chloride of lime**. It is a yellowish white substance which smells like chlorine, but the smell is really due to hypochlorous acid.

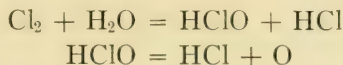
Bleaching powder is manufactured by treating slaked lime (Ca(OH)_2) with chlorine, the equation for the reaction being: —



If bleaching powder is treated with an acid, chlorine is liberated, thus: —



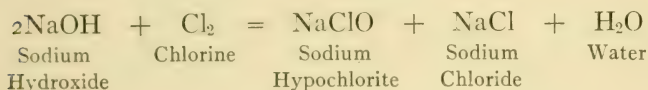
These reactions also take place: —



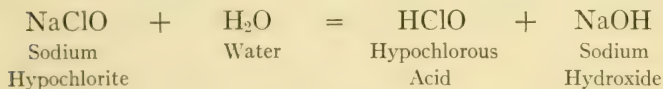
The bleaching action is really due to the liberated oxygen, which in this equation is represented by O, rather than O_2 . The formula O_2 represents oxygen gas — two atoms

united into one molecule. Whereas O represents an *uncombined* atom of oxygen; the free atom is in a more active chemical state, called the **nascent state**, because an atom of oxygen just liberated from a compound is ready, so to speak, to oxidize.

Another source of chlorine for bleaching is sodium hypochlorite (NaClO). This compound is prepared by passing a current of electricity through sodium chloride solution and allowing the products to react, thus:—



Sodium hypochlorite is unstable, and a cold dilute solution contains hypochlorous acid, owing to the interaction of the compound with water, thus:—



The hypochlorous acid furnishes nascent oxygen. Sodium hypochlorite solution is used by up-to-date laundries.

150. The process of bleaching.—Bleaching is an oxidizing process. Oxygen, as we have just seen, is liberated in the nascent state from hypochlorous acid and readily decomposes the colored substances and changes them into colorless compounds.

A conventional diagram of the process of bleaching cotton cloth is shown in Fig. 64. The pieces are sewed together end to end in long strips and drawn by machinery from the roll *A* successively through vats containing bleaching powder solution *B*, weak acid *C*, and water *D*. At some point toward the end of the process the cloth passes through a vat containing acid sodium sulphite solution (or

similar mixture) *E*, called the antichlor, to remove traces of hypochlorous acid. After thorough washing, the cloth is dried and ironed by passing over hot cylinders *FG*, and finally wound on the roll *H*.

The chemical process of bleaching can be shown in the laboratory by a simple experiment. Put a little bleaching powder in the beaker



Fig. 64. — Diagram of the process of bleaching cotton cloth

A (Fig. 65), fill the beaker about one third full of water, and mix well. Fill the beaker *B* one third full of dilute sulphuric acid; and the beaker *C* one third full of water. Press the lower half of the strip of colored cloth into the bleaching powder solution and then into the acid, passing it back and forth several times. Finally wash the cloth thoroughly in the water in *C*. The bleached cloth should have the general appearance shown in Fig. 65.

151. Uses of chlorine. —

Besides the use of chlorine in the manufacture of bleaching powder and bleaching mixtures, large quantities of the gas are made into useful compounds

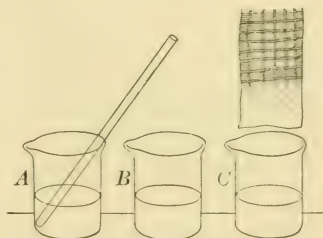


Fig. 65. — Bleaching colored cloth

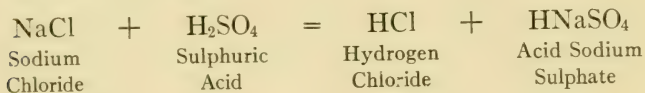


Fig. 66. — Fire extinguisher containing carbon tetrachloride

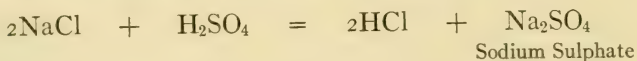
of chlorine. One is carbon tetrachloride (CCl_4), which is used in "pyrene" fire extinguishers (Fig. 66), and also as a solvent for extracting greases; the non-inflammable cleaning mixture called "carbona" contains carbon tetrachloride. Chlorine is also used in making disinfectants and in purifying water (69 and Fig. 35).

152. Hydrogen chloride and hydrochloric acid. — Hydrogen chloride is a gas, which is very soluble in water. **Hydrochloric acid** is the common name of a water solution of **hydrogen chloride**. This solution is known commercially as muriatic acid (from the Latin word *muria*, meaning brine), but it is more properly called hydrochloric acid. Hydrogen chloride is often called hydrochloric acid gas.

153. Preparation of hydrogen chloride. — This gas is prepared from sodium chloride by heating with sulphuric acid. If the mixture is gently heated, the chemical change is represented thus: —



But at a high temperature the equation is: —



The solution is prepared by passing the gas into water.

154. Hydrochloric acid is manufactured in enormous quantities by a method essentially like that used in the laboratory.

The mixture of salt and sulphuric acid is put into the cast iron retort *A* (Fig. 67) and heated by the furnace *B* to a moderate temper-

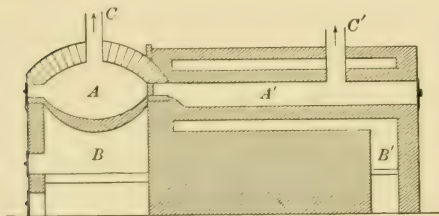


Fig. 67. — Sketch of the apparatus for the manufacture of hydrochloric acid

ature; as soon as the mass becomes pasty it is raked out upon the flat heater *A'* and heated to a high temperature by the furnace *B'*. The hydrogen chloride escapes through *C* and *C'* into an absorbing tower

filled with resistant material over which water trickles; as the gas passes up the tower, it is absorbed by the descending water, and the solution flows out at the bottom as concentrated acid.

Hydrochloric acid is also a by-product in the manufacture of sodium carbonate by the Leblanc process (450).

155. Properties of hydrogen chloride. — Hydrogen chloride is a colorless gas. It has a choking, sharp taste, and irritates the lining of the nose and throat. It is about 1.25 times as heavy as air. A liter at 0° C. and 760 mm. weighs 1.64 gm. The gas becomes a colorless liquid when subjected to pressure and a moderately low temperature. The marked solubility of hydrogen chloride in water is one of its most striking properties. Even when it escapes into moist air, it forms white fumes which are really minute drops of a solution of the gas in the moisture of the air (147). At ordinary temperatures about 500 l. of gas dissolve in 1 l. of water.

The solubility of hydrogen chloride in water can be shown by a simple experiment. The apparatus is arranged as in Fig. 68. The flask *A* is filled with hydrogen chloride. The medicine dropper *B* is partly filled with water, the stopper with its tubes is inserted, and the flask is then arranged as shown in the figure. By pinching the bulb of the dropper, a few drops of water are forced into the flask. This small quantity of water dissolves so much gas that a partial vacuum is formed in the flask; pressure within the flask is reduced so much that the atmospheric pressure forces water from the jar *C* up the tube *D* and through the small opening into the flask.

156. Chemical conduct of hydrogen chloride. — Hydrogen chloride does not burn nor support combustion. It is a very stable compound and can be heated to about 1800° C. before it begins to decompose. Perfectly dry hydrogen chloride has little or no chemical activity. Whereas the moist gas unites readily with certain substances, *e.g.* ammonia gas; in this case dense white clouds of

ammonium chloride (NH_4Cl) are formed. This reaction is sometimes used as a **test for hydrogen chloride (173)**.

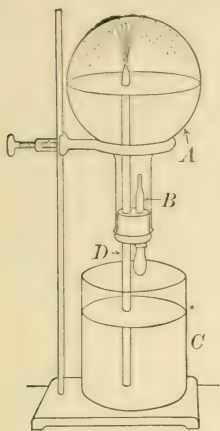
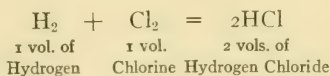


Fig. 68. — Hydrogen chloride fountain

157. Composition of hydrogen chloride. — Experiments show that hydrogen chloride is composed of hydrogen and chlorine in the ratio of 1 to 1 by volume. When a mixture of equal volumes of hydrogen and chlorine is exposed to the direct sunlight or to the action of an electric spark, the gases combine, hydrogen chloride is formed with no residue, and the volume of the resulting gas equals the sum of the volumes of hydrogen and chlorine used. We express the volumetric relations of hydrogen, chlorine, and hydrogen chloride by saying: 1 volume of hydrogen + 1 volume of chlorine = 2 volumes of hydrogen chloride. In the form of an equation, this fact becomes:—

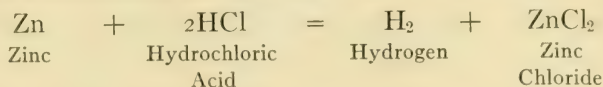


The simple volumetric relation of these three gases is a good illustration of Gay-Lussac's law (93, 176).

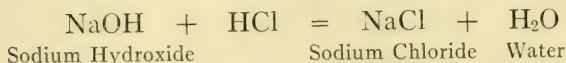
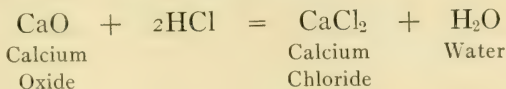
158. Hydrochloric acid. — The water solution of hydrogen chloride is the common substance **hydrochloric acid**. The ordinary kind contains from 30 to 40 per cent (by weight) of hydrogen chloride, and is called concentrated hydrochloric acid. Its specific gravity is about 1.2. In the laboratory we also use dilute hydrochloric acid, which is prepared from the concentrated acid by adding 4 to 5 times its volume of water.

Hydrochloric acid, like most members of the important class of compounds called acids, has a sour taste and reddens

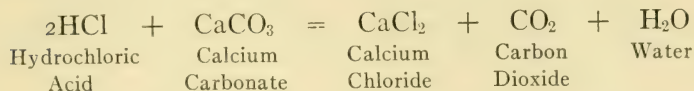
blue litmus. It reacts with many metals, liberating hydrogen and forming chlorides of the metals, thus:—



It also forms chlorides by interaction with oxides and hydroxides of metals, thus:—

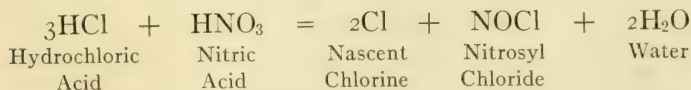


It interacts readily with carbonates. The equation in the case of calcium carbonate is:—



Hydrochloric acid is an indispensable compound, and is used in many industrial processes. Like other acids, it is sold in bottles holding 2.5 liters and in securely packed glass carboys containing 10 or more gallons (Fig. 69).

159. Aqua regia.— Hydrochloric acid and nitric acid interact and liberate chlorine, thus:—



A mixture of one volume of concentrated nitric acid and three volumes of concentrated hydrochloric acid is usually

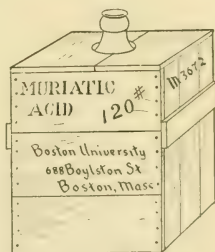
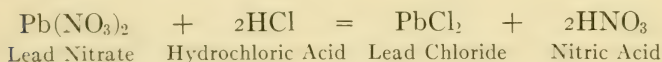


Fig. 69. — A carboy of hydrochloric acid packed for shipment

used. If such a mixture is added to a metal, the nascent chlorine (2Cl) forms a chloride of the metal. (Compare with nascent oxygen, end of **149**.) The alchemists named the mixtures **aqua regia**, meaning "royal water," to emphasize the fact that it dissolves the "noble" metal gold. Another name is nitro-hydrochloric acid.

160. Chlorides are compounds of chlorine with other elements. They are formed, as we have already seen, by the direct combination of chlorine and metals (**147**) and by the interaction of hydrochloric acid with metallic oxides or hydroxides (**158**). Most chlorides are soluble in water. But the chlorides of lead (PbCl_2), silver (AgCl), and one of the chlorides of mercury (HgCl) are not soluble; they are formed as insoluble solids, when hydrochloric acid or a soluble chloride is added to a solution of a lead compound, silver compound, or the proper mercury compound. Thus: —



The formation of insoluble solids by double decomposition (and certain other changes) is called **precipitation**, and the solid itself is called a **precipitate**. Precipitates often have properties which are readily determined. Thus, silver chloride is white and curdy, and soon turns purple in the light; moreover it dissolves in ammonium hydroxide owing to the formation of a complex soluble compound, which, however, is transformed by dilute nitric acid into silver chloride. Other chlorides have different properties. Hence, the precipitation of silver chloride serves as a **test for hydrochloric acid and soluble chlorides**.

A molecule of a chloride may contain one or more atoms of chlorine and occasionally the name of the compound indicates this fact, *e.g.*

manganese dichloride (MnCl_2), antimony trichloride (SbCl_3), carbon tetrachloride (CCl_4). If the same metal forms two chlorides, the two are distinguished by modifying the name of the metal; the one containing the smaller proportion of chlorine ends in *-ous*, that containing the larger in *-ic*. Thus, mercurous chloride is HgCl , and mercuric chloride is HgCl_2 .

EXERCISES

1. Prepare a summary of (a) chlorine and (b) hydrochloric acid.
2. Sketch from memory the apparatus used to prepare chlorine (a) on a large scale, and (b) in the laboratory.
3. How can chlorine be quickly distinguished from the gases previously studied?
4. Summarize the chemical conduct of chlorine.
5. Topics for home study. (a) Nascent state. (b) Chlorine water. (c) Liquid chlorine. (d) Chlorine is an oxidizing agent.
6. What is (a) muriatic acid, (b) chloride of lime, (c) bleaching powder?
7. State the equation for (a) preparation of chlorine, (b) interaction of chlorine and water, (c) decomposition of hypochlorous acid, (d) preparation of hydrogen chloride, (e) interaction of hydrogen chloride and ammonia, (f) interaction of sodium chloride and silver nitrate.
8. Write an essay on "bleaching with chlorine."
9. Complete and balance these equations: (a) $\text{NaCl} + \text{H}_2\text{SO}_4 = \text{---} + \text{Na}_2\text{SO}_4$; (b) $\text{H}_2 + \text{---} = \text{HCl}$; (c) $\text{HCl} + \text{Na}_2\text{CO}_3 = \text{---} + \text{CO}_2 + \text{---}$; (d) $\text{HgNO}_3 + \text{---} = \text{HgCl} + \text{HNO}_3$.

PROBLEMS

1. Calculate the weight of chlorine in (a) 2 kg. of sodium chloride. (b) 2 mg. of calcium chloride, (c) 1 gm. of aluminium chloride.
2. How many grams of each product are formed when hydrochloric acid interacts with 85 gm. of manganese dioxide?
3. (a) What is the weight of 15 l. of chlorine gas measured at 20°C . and 760 mm.? (b) How many grams of potassium chloride are needed to prepare the weight of chlorine found in (a)?
4. How many grams of hydrogen chloride can be obtained from 27 gm. of sodium chloride? How many liters (standard conditions)?
5. Calculate the percentage composition of (a) KCl , (b) CaCl_2 .
6. How much sodium chloride can be formed by burning sodium in 40 gm. of chlorine?
7. Calculate the simplest formula from (a) $\text{Hg} = 84.92$, $\text{Cl} = 15.07$; (b) $\text{Hg} = 73.8$, $\text{Cl} = 26.2$.

CHAPTER XII

ACIDS, SALTS, AND BASES

161. What are acids?—Hydrochloric acid is an example of an important class of compounds called **acids**. The general properties of hydrochloric acid are characteristic of the class.

Hydrogen is a constituent of all acids—an essential constituent. The hydrogen of acids can be replaced by certain metals; and the compound formed by this replacement is called a **salt**. Many compounds have hydrogen as a constituent, but they are not classed as acids unless they form salts by replacement of the hydrogen by a metal. Thus, water and sugar contain hydrogen, but the hydrogen in water does not form a salt by replacement of its hydrogen by a metal, nor can the hydrogen in sugar be replaced by a metal. Furthermore, most acids have a sour taste and change the color of a dye called litmus from blue to red. Substances which act thus on blue litmus are said to have an **acid reaction**.

The presence of acids is often conveniently detected by the litmus test. For example, vinegar, pickles, many fruits, and some wines have a sour taste and turn blue litmus red.

Other common acids are sulphuric (H_2SO_4), nitric (HNO_3), and acetic ($\text{HC}_2\text{H}_3\text{O}_2$).

162. What are salts?—These compounds are not sour, nor do they, as a rule, have any effect on either blue or red litmus. Substances which have no effect on litmus

are often described as having a **neutral reaction**. Many salts have the taste associated with a familiar member of this class, viz. common salt or sodium chloride; a few are sour and some are bitter. This class of compounds has many members and their properties are somewhat varied.

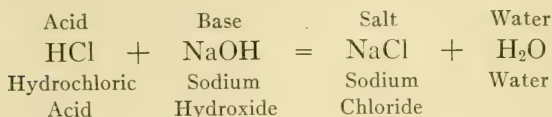
Salts invariably have a metal and a non-metal as constituents, and most salts also have oxygen. Chlorides are examples of salts which have only a metal and the non-metal chlorine as constituents, *e.g.* zinc chloride (ZnCl_2), sodium chloride (NaCl), calcium chloride (CaCl_2). Examples of salts composed of a metal, a non-metal, and also oxygen are potassium chlorate (KClO_3) and sodium sulphate (Na_2SO_4); these compounds are salts of chloric acid and sulphuric acid respectively.

163. What are bases? — Hydroxides are examples of the class of compounds called **bases**. Thus, sodium hydroxide (NaOH) is a typical base. Solutions of bases turn red litmus blue — just the opposite of acids, and are said to have a **basic** or an **alkaline reaction**. Solutions of strong bases (*e.g.* sodium hydroxide and potassium hydroxide) have a slippery feeling and a biting, caustic taste.

Bases are composed of a metal, oxygen, and hydrogen, *e.g.* sodium hydroxide (NaOH). The oxygen and hydrogen are the essential part of a base, just as hydrogen is of an acid. In fact, the oxygen and hydrogen of a base act as a unit in many chemical changes. This group of atoms (OH) is called **hydroxyl**. And since hydroxyl is the root or foundation of a class of compounds, it is called a **radical**.

164. Neutralization. — Acids, salts, and bases have fundamental chemical relations. When we mix solutions containing weights of an acid and a base proportional to

their molecular weights, the acid and base interact completely. The final solution has none of the characteristic properties of an acid or a base, but it does have the properties of a salt. That is, the acid and base destroy the marked properties of each other, and a salt is produced. The acid and base neutralize each other. For example, when hydrochloric acid and sodium hydroxide interact, sodium chloride and water are formed. The equation for the reaction may be written:—



A chemical change in which an acid and a base neutralize each other and form a salt and water is called **neutralization**.

Neutralization illustrates double decomposition. In the chemical change just cited both the hydrochloric acid and the sodium hydroxide are decomposed and their parts are recombined in a different way, *i.e.* sodium chloride and water are the new compounds resulting from the recombination.

Neutralization is usually done by means of burettes. These are graduated glass tubes, so marked that any desired portion of the contents can be drawn off by the stop-cock at the lower end (Fig. 70). In using burettes for neutralization, one is filled to the zero (upper) mark with a solution of an acid and the other with a solution of a base — one solution being of known concentration. A measured portion, say 15 cubic centimeters of the base, is drawn off into a beaker, several drops of litmus solution are added, and the acid is slowly dropped in with constant stirring until one drop more shows by the change in color (after thorough stirring) that the right

proportions of acid and base are present, *i.e.* that neutralization has occurred. If this solution is evaporated, nothing but a salt will be found in the residue.

If we wish to find the strength of the acid, the volume of acid is read accurately. Knowing the concentration (and volume) of the base solution and the volume of the acid solution, we can calculate the exact weight of the acid needed for the neutralization of the base, and from this weight we can find the strength of the acid solution.

165. Another definition of a salt. —

For the present, we may regard salts as compounds formed from acids and bases by neutralization. That is, the metal of the base unites with the non-metal or non-metallic group of the acid, *e.g.* Na of NaOH unites with NO_3 of HNO_3 to form the salt NaNO_3 . The nature and interrelation of acids, salts, and bases will be further discussed. (See Chapter XVIII.)

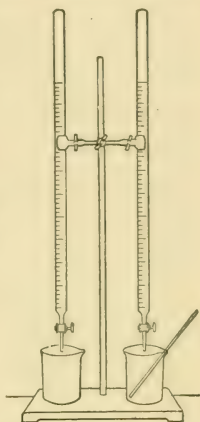


Fig. 70. — Burettes

166. Naming acids, salts, and bases. — There are three other non-oxygen acids besides hydrochloric acid, *viz.* hydrofluoric (HF), hydrobromic (HBr), and hydriodic (HI). The salts corresponding to these four acids end in *ide*, *e.g.* chloride, fluoride, bromide, and iodide. Sometimes the compound commonly known as hydrogen sulphide (H_2S) is called an acid, and its salts are called sulphides.

Oxygen is a constituent of most acids and salts, and the names of the oxy-acids and oxy-salts are related, especially the suffixes. This relation can be best illustrated by the chlorine acids that contain oxygen. These acids are hypochlorous (HClO), chlorous (HClO_2), chloric (HClO_3), and perchloric (HClO_4). In forming the names of the corresponding salts the suffix *ous* becomes *ite*, while *ic* be-

comes *ate*; the prefixes are not changed. Thus, the names of the corresponding sodium salts are sodium hypochlorite, chlorite, chlorate, and perchlorate respectively. In the case of the acids of some elements the body of the name is modified, *e.g.* sulphuric becomes sulphate (not sulphurate!), and phosphoric becomes phosphate (not phosphorate!). Hence we may say briefly, *ous* becomes *ite* and *ic* becomes *ate* in changing names of acids to the corresponding salts.

Bases are distinguished by placing the name of the metal before the word *hydroxide*, *e.g.* sodium hydroxide (NaOH), calcium hydroxide (Ca(OH)_2).

167. Conclusion.—More will be learned about acids, bases, and salts, especially in Chapter XVIII and under typical examples of these compounds.

EXERCISES

1. Prepare a summary of this chapter.
2. State some characteristics of (a) acids, (b) bases, (c) salts.
3. How are acids, bases, and salts related?
4. Give the name and formula of three common (a) acids, and (b) bases. (c) Of five salts.
5. Define and illustrate neutralization.
6. What is hydroxyl?
7. Give the name and formula of the sodium salt of hydrochloric acid. Also of the corresponding salt of potassium, aluminium, lead, silver, antimony, manganese, zinc, and barium.
8. Apply Exercise 7 to (a) nitric acid, (b) nitrous acid, (c) hypochlorous acid.
9. Apply Exercise 7 to (a) sulphuric acid, (b) sulphurous acid, (c) permanganic acid.
10. Give the name and formula of the hydroxide of the metals enumerated in Exercise 7.
11. Give the name of these: (a) potassium salt of chloric acid (b) calcium salt of hypophosphorous acid, (c) sodium salt of carbonic acid, (d) lead salt of chromic acid, (e) zinc salt of hydriodic acid, (f) potassium salt of perchloric acid, (g) iron salt of hydrochloric acid, (h) sodium salt of hydrofluoric acid, (i) calcium salt of persulphuric acid,

(j) potassium salt of hydrobromic acid, (k) calcium salt of hydrofluoric acid, (l) sodium salt of hypophosphorous acid.

12. Classify into acids, bases, and salts: KOH, HBr, NH_4OH , NaNO_3 , H_3PO_4 , Ag_2SO_4 , $\text{Ca}(\text{OH})_2$, HI, $\text{Pb}(\text{OH})_2$, FeCl_3 , $\text{Zn}(\text{NO}_3)_2$, $\text{Cu}(\text{OH})_2$, KClO_4 , Na_2CO_3 , BaSO_4 , BaCl_2 , $\text{Al}(\text{OH})_3$.

PROBLEMS

1. Calculate the per cent of hydrogen in (a) hydrochloric acid, (b) sulphuric acid, (c) nitric acid.

2. Calculate the per cent of hydroxyl in (a) sodium hydroxide, (b) potassium hydroxide, (c) ammonium hydroxide, (d) calcium hydroxide.

3. How many grams of hydroxyl correspond to (a) 35 gm. of $\text{Al}(\text{OH})_3$, (b) 80 gm. of barium hydroxide?

4. What weight of nitric acid is needed to neutralize 27 gm. of the base corresponding to (a) Ca, (b) sodium, (c) K?

5. Two solutions are well mixed. One contained 75 gm. of sulphuric acid, and the other 75 gm. of sodium hydroxide. What will be the weight of the compounds (other than water) in the final solution?

6. Complete and balance: (a) $\text{BaO} + \text{---} = \text{Ba}(\text{OH})_2$; (b) $\text{NH}_4\text{I} + \text{---} = \text{AgI} + (\text{NH}_4)_2\text{SO}_4$; (c) $\text{Pb}(\text{NO}_3)_2 + \text{---} = \text{PbCl}_2 + \text{---}$.

7. Calculate the formula corresponding to: (a) $\text{Ca} = 29.41$, $\text{S} = 23.52$, $\text{O} = 47.05$; (b) $\text{Na} = 39.31$, $\text{Cl} = 60.68$.

8. What weight of the salt is formed in these cases of neutralization? (a) Hydrochloric acid and 10 gm. of potassium hydroxide; (b) sulphuric acid and 37 gm. of sodium hydroxide.

9. Suppose 37.5 cc. of a hydrochloric acid solution neutralize 30 cc. of a sodium hydroxide solution, and that each cc. of the sodium hydroxide solution contains 0.003 gm. of the base. What weight of hydrochloric acid is contained in the acid solution?

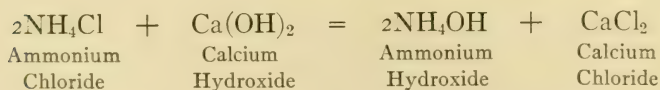
CHAPTER XIII

AMMONIA — AMMONIUM HYDROXIDE — AMMONIUM COMPOUNDS

168. Introduction. — The term *ammonia* includes both the gas (NH_3) and its solution in water (NH_4OH). Sometimes the solution is called ammonia water, though its scientific name is ammonium hydroxide. Ammonium hydroxide is an example of a base (**163**).

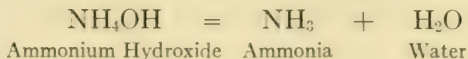
169. Formation of ammonia. — When vegetable and animal matter containing nitrogen decays, the nitrogen and hydrogen are usually liberated as the compound ammonia. The odor of ammonia can be detected near stables. If animal substances containing nitrogen are heated (especially with lime or soda-lime), ammonia is given off. (The formation of ammonia in this way is a test for **combined nitrogen**. See **114**.) Soft coal contains combined nitrogen and hydrogen, and when the coal is heated, as in making illuminating gas, ammonia is liberated. This is one source of commercial ammonium hydroxide.

170. Preparation of ammonia gas in the laboratory. — Ammonia gas is prepared in the laboratory by heating ammonium chloride with a base, usually moist calcium hydroxide. The equation for the reaction is: —



The ammonium hydroxide is unstable, especially when

heated, and quickly decomposes into ammonia and water, thus: —



The gas is very volatile, and is usually collected by upward displacement, *i.e.* by allowing the gas to flow upward into a bottle and displace the air (Fig. 71). The solution is prepared by conducting the gas into water.

171. Manufacture of commercial ammonium hydroxide. — The ammonia gas from which commercial ammonium hydroxide is manufactured is obtained mainly from the illuminating gas works. When coal is heated in closed retorts, a mixture of gases is liberated containing ammonia. The ammonia is separated from the other gases by dissolving it out with water (326). This impure solution, which is called ammoniacal liquor or gas liquor, is treated with lime to liberate the ammonia, which is absorbed in tanks containing hydrochloric acid or sulphuric acid. This solution upon the addition of a base (*e.g.* calcium hydroxide) gives up its ammonia, which is dissolved in distilled water, forming thereby the ammonium hydroxide of commerce.

Some ammonia is obtained from the gases liberated from coke ovens. Ammonia is also manufactured by the direct combination of nitrogen and hydrogen (174, 175).

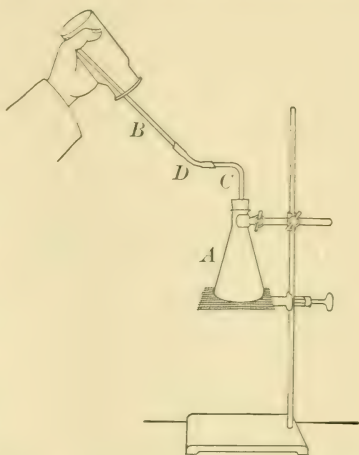


Fig. 71. — Apparatus for preparing ammonia in the laboratory

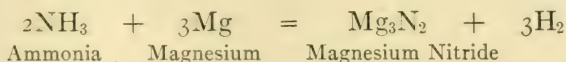
172. Properties of ammonia. — Ammonia gas is colorless. It has an exceedingly pungent odor, and if inhaled suddenly or in large quantities, it brings tears to the eyes and may cause suffocation. It is a light, volatile gas, being about one half (0.59) as heavy as air. A liter of the gas at 0° C. and 760 mm. weighs 0.77 gm. Ammonia gas is easily liquefied — 0° C. and 4.2 atmospheres (*i.e.* 4×760 mm.) being the usual conditions. **Liquefied ammonia** is often called anhydrous ammonia, because it contains no water. It boils at -34° C. Hence, if it is exposed to the air or warmed in any way, it changes into the gas, and in so doing absorbs considerable heat. This fact has led to the extensive use of liquid ammonia in refrigeration and in the manufacture of ice (177).

Ammonia gas is very soluble in water, even more so than hydrogen chloride; and its solubility can be shown by the "fountain" experiment. (See Fig. 68.) A liter of water at 0° C. dissolves 1148 l. of gas (measured at 0° C. and 760 mm.), while at ordinary temperature 1 l. of water dissolves about 700 l. of gas. This solution of the gas is often called ammonia, though other names, *e.g.* ammonium hydroxide and ammonia water are sometimes applied to it (168); it gives off the gas freely, when heated, as may be easily discovered by the odor or by the formation of dense white fumes of ammonium chloride (NH_4Cl) when the solution is exposed to hydrochloric acid (156). The commercial solution called ammonia is lighter than water (its specific gravity being about 0.88) and contains approximately 35 per cent (by weight) of the compound NH_3 .

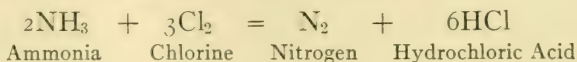
173. Chemical conduct of ammonia. — Ammonia gas will not burn in air under ordinary conditions, nor will it support combustion, as the term is usually used; but if the

air is heated or if its proportion of oxygen is increased, a jet of ammonia gas will burn in it with a yellowish flame. When electric sparks are passed through ammonia gas, it decomposes to some extent into nitrogen and hydrogen; whereas nitrogen and hydrogen form a small amount of ammonia under the same conditions (174, 175).

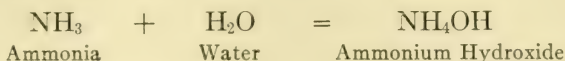
Ammonia reacts with certain elements. Dried ammonia gas and heated magnesium form magnesium nitride and hydrogen, thus:—



Ammonia and chlorine interact, thus:—

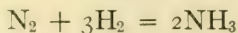


Ammonia combines directly with water, forming ammonium hydroxide, thus:—

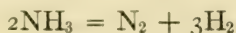


It also combines with certain gases, *e.g.* hydrogen chloride (HCl), thereby forming ammonium chloride (NH₄Cl). This reaction serves as a **test for ammonia gas**. (Compare 156.)

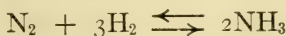
174. Synthesis of ammonia from its elements.—Nitrogen and hydrogen unite if electric sparks are passed through a mixture of these gases. The equation is:—



The amount of ammonia formed in a given case, however, is only a small per cent of that indicated by the equation. The small yield is due partly to the fact that ammonia itself decomposes into nitrogen and hydrogen. Thus, we may write this equation:—



If we compare these equations, we see that one is the reverse of the other. This means that one reaction undoes the work of the other. When the experiment is done in a closed tube, the two reactions proceed at the same time — one reversing the other. Such a complete reaction is called a **reversible reaction**. The equation for a reversible reaction contains oppositely pointed arrows in place of the equality sign. The equation for this reversible reaction is : —



This equation is read: nitrogen and hydrogen react reversibly to form ammonia.

A reversible reaction under a given set of conditions proceeds to **equilibrium**. This means that the amounts of the substances involved in both reactions increase or decrease until the quantity of any one substance formed equals the quantity of it which is transformed. In the case of ammonia, the mixture at equilibrium is only about 2 per cent ammonia (and 98 per cent nitrogen and hydrogen). If the ammonia is removed by adding acid or water to the apparatus, or by some other device, its removal displaces the equilibrium and the reaction proceeds to completion, *i.e.* all, or practically all, the nitrogen and hydrogen combine. (See also 196.)

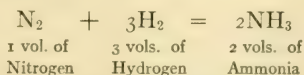
175. Manufacture of ammonia from nitrogen and hydrogen. — The reaction described in 174 for the manufacture of ammonia proceeds too slowly. To be profitable commercially, the reaction must be hastened, that is, its velocity must be increased so that more ammonia will be formed *in a given time*. Several factors affect the velocity of a reaction, *e.g.* temperature, pressure, and experimental conditions. In manufacturing ammonia, the best conditions

are a temperature of about 450°C . and a pressure of about 200 atmospheres (*i.e.* 200×760 mm.). This reaction, as well as many others, is further hastened by passing the heated and compressed gases over a catalyst (53) — in this case essentially finely divided iron.

The mixture of ammonia, nitrogen, and hydrogen is passed, still under pressure, through water, which dissolves the ammonia, while the other gases are returned to the apparatus. The ammonia solution is drawn off when it becomes saturated (under ordinary pressure and temperature). Ammonia made directly from its elements is called **synthetic ammonia**.

176. Composition of ammonia. — Experiments show that ammonia is a compound of nitrogen and hydrogen, especially its synthesis from these elements. By utilizing the fact that ammonia and chlorine react and liberate nitrogen, the volumetric composition of ammonia can be shown to be nitrogen is to hydrogen as 1 to 3. A supplementary experiment shows that two volumes of ammonia are formed by the union of one volume of nitrogen and three volumes of hydrogen.

The volumetric composition of ammonia may be expressed thus: —



The simple volumetric relation of these three gases is a good example of Gay-Lussac's law (93, 157).

In demonstrating the volumetric composition of ammonia, a tube of known volume (Fig. 72) filled with chlorine is provided with a funnel through which concentrated ammonium hydroxide is slowly dropped into the chlorine, until the reaction ceases. After the ex-



Fig. 72. — Apparatus for determining the volumetric composition of ammonia gas by the interaction of ammonium hydroxide and chlorine

cess of ammonium hydroxide is neutralized with sulphuric acid, the volume of nitrogen left is found to be one third of the original volume of chlorine. Now hydrogen and chlorine combine in equal volumes (157). Hence the volume of hydrogen withdrawn from the ammonia must be equal to the original volume of chlorine. But this volume is three times the volume of the nitrogen, therefore there must be three times as much hydrogen as nitrogen in ammonia gas.

177. Ammonia as a refrigerant. — The use of ammonia in producing low temperatures depends upon the fact that liquefied ammonia (not ordinary ammonia solution) changes rapidly into a gas when its pressure is reduced, and in so doing absorbs heat from the surrounding air or liquid. Hence,

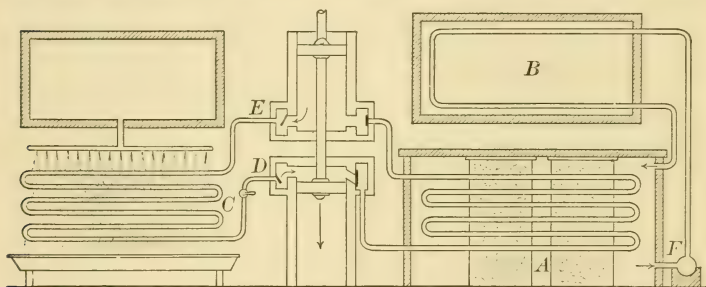


Fig. 73. — Apparatus for using liquefied ammonia to produce low temperatures

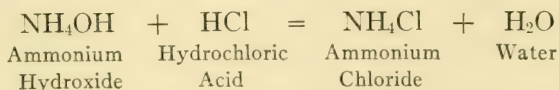
if liquefied ammonia is allowed to flow through a pipe immersed in a solution of sodium chloride or calcium chloride (technically called a brine), the ammonia evaporates in the pipe and cools the brine, which may be used directly as a refrigerant or for making ice. In some cold storage plants, packing houses, and sugar refineries, this cold brine is circulated through pipes placed in the storage rooms where a low temperature is desired.

The construction and general operation of an ice-making plant is shown in Fig. 73. Liquefied ammonia is forced from a tank into a series of pipes which are submerged in a large vat *A* nearly filled with

brine. Metal cans containing pure water to be frozen are immersed in the brine, which is kept below the freezing point of water by rapid evaporation of the ammonia in the pipes. After several hours the water in the cans is frozen into cakes of ice. As fast as the ammonia gas forms in the pipes, it is removed by exhaust pumps (*E*) into another set of pipes *C*, where it is condensed into liquefied ammonia and conducted through *D* into the other set of pipes ready for renewed use.

In cold storage plants the cold brine is circulated through pipes in the various rooms (*B*).

178. Ammonium hydroxide. — When ammonia gas is passed into water, the ammonia combines with the water to some extent and forms a solution of an unstable compound having the composition represented by the formula NH_4OH . This compound is ammonium hydroxide. Ammonium hydroxide is a base (**163**). Like other members of this class of substances it turns litmus blue. Concentrated solutions have a slippery feeling. It also neutralizes acids, thus: —



Ammonium hydroxide is widely used as a cleansing agent (especially for the removal of grease), and as a restorative in cases of fainting or of inhaling irritating gases; large quantities are consumed in dyeing and calico printing, and in the manufacture of dyestuffs, sodium carbonate and bicarbonate, and ammonium compounds.

179. Ammonium compounds contain a group of atoms which acts chemically like an atom of a metal, especially the metals sodium and potassium. This group is called **ammonium**, and its formula is NH_4 . Ammonium has never been isolated from its compounds. Ammonium, like hydroxyl (**163**), is called a radical, because it is the

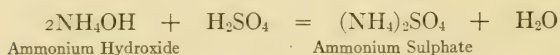
root or foundation of a series of compounds and in chemical changes passes from one ammonium compound to another.

Ammonium compounds decompose when heated with an alkali, such as sodium hydroxide or moist lime, *i.e.* calcium hydroxide (170); ammonia gas is the conspicuous product. This reaction is a **test for ammonium compounds**.

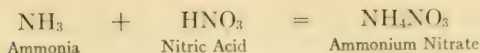
180. Ammonium chloride. — There are many ammonium salts. Thus, **ammonium chloride** (NH_4Cl) is the salt formed by the neutralization of ammonium hydroxide (a base) by hydrochloric acid (see 164). It is manufactured by passing ammonia (obtained from the ammoniacal liquor in gas works) into hydrochloric acid. The crude product is often called “muriate of ammonia” to indicate its relation to muriatic acid (the commercial name of hydrochloric acid). It is used in Leclanché batteries, as an ingredient of soldering fluids and of fertilizers.

The crude salt is purified by heating it gently in a large iron pot with a dome-shaped cover; the ammonium chloride volatilizes easily and then crystallizes in the pure state as a fibrous mass on the inside of the cover, whereas the impurities remain behind in the vessel. This process of purification is called **sublimation**. The product is a sublimate. Sublimed ammonium chloride is known as sal ammoniac.

181. Other ammonium salts. — **Ammonium sulphate** ($(\text{NH}_4)_2\text{SO}_4$) is made by passing ammonia gas into sulphuric acid, or by adding ammonium hydroxide to the acid, thus: —



The commercial salt is a grayish or yellowish solid and is obtained in large quantities as a by-product of coal gas manufacture. It is used as an ingredient of fertilizers, since it is a cheap, soluble salt containing considerable nitrogen (116). **Ammonium nitrate** (NH_4NO_3) is made by passing ammonia into nitric acid, or by allowing ammonia gas and the vapor of nitric acid to mingle, thus: —



When gently heated it decomposes into nitrous oxide (N_2O) and water, and is used in the preparation of nitrous oxide. It is also used as an ingredient of certain explosives because it decomposes readily into volatile products. **Ammonium carbonate** ($(\text{NH}_4)_2\text{CO}_3$) is used in some kinds of baking powder, to scour wool, as a medicine, and in certain smelling salts (since it gives off ammonia readily).

EXERCISES

1. Prepare a summary of ammonia.
2. How is ammonium hydroxide manufactured from (a) gas liquor, (b) nitrogen and hydrogen?
3. State the conspicuous properties of ammonia gas.
4. Describe the synthesis of ammonia.
5. Define and illustrate (by ammonia) (a) reversible reaction (b) equilibrium, (c) displacement of equilibrium, (d) catalyst.
6. State these reactions in the form of equations: (a) Preparation of ammonium hydroxide from ammonium chloride and calcium hydroxide. (b) Decomposition of ammonium hydroxide into ammonia and water. (c) Nitrogen and hydrogen react reversibly to form ammonia. (d) One volume of nitrogen and three volumes of hydrogen form two volumes of ammonia.
7. What is (a) liquid ammonia, (b) anhydrous ammonia, (c) liquefied ammonia, (d) synthetic ammonia, (e) ammonia water?
8. Describe the manufacture of ice by liquid ammonia.
9. What is the volumetric composition of ammonia gas? How is it found?
10. State the test for (a) ammonia, (b) ammonium compounds, (c) combined nitrogen.
11. Topics for home study: (a) A cold storage plant. (b) Gay-Lussac's law. (c) Uses of ammonia. (d) Uses of ammonium compounds. (e) Equilibrium.

PROBLEMS

1. How many grams of ammonia (NH_3) can be obtained from 1 kg. of ammonium chloride and sufficient calcium hydroxide?
2. A pupil prepared five 250 cc. bottles of ammonia gas at 21°C . and 755 mm. What weight of materials interacted?
3. What weight of ammonium chloride (95 per cent pure) is needed for the preparation of 60 gm. of NH_3 ? Of 60 l. at 22°C . and 767 mm.?

4. What is the weight of 32 l. of ammonia gas at 20° C. and 763 mm.? What volume will 32 gm. of ammonia gas occupy at the same temperature and pressure?

5. To what weight and what volume of NH_3 are 25 gm. of ammonium chloride equivalent (at standard conditions)?

6. What volume of ammonia gas will be liberated by the action of any base on 75 gm. of ammonium sulphate (at standard conditions)?

7. How many liters of ammonia are formed by the complete interaction of 9 l. of hydrogen and sufficient nitrogen?

8. How many grams of ammonium chloride can be made from ammonium hydroxide and 100 gm. of the necessary acid?

9. What formula corresponds to $\text{N} = 26.17$, $\text{H} = 7.48$, $\text{Cl} = 66.35$?

10. Complete and balance: (a) $\text{NH}_4\text{OH} + \text{---} = (\text{NH}_4)_2\text{SO}_4 + \text{---}$; (b) $\text{NH}_3 + \text{---} = \text{N}_2 + \text{HCl}$.

CHAPTER XIV

NITRIC ACID — NITRATES — NITROGEN OXIDES

182. How nitric acid is formed. — Nitric acid (HNO_3) is formed in small quantities when electric sparks are passed through air. Hence nitric acid or its salts can be detected in the atmosphere after a thunderstorm. This chemical change is applied on a commercial scale in Norway (196). In another chemical process ammonia is oxidized (197).

183. Preparation of nitric acid. — Nitric acid is prepared in the laboratory by heating concentrated sulphuric acid with a nitrate, usually sodium nitrate (NaNO_3).

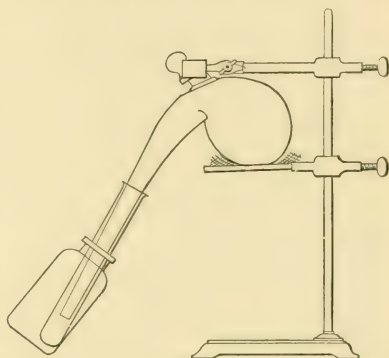
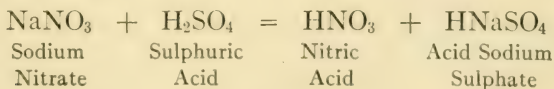


Fig. 74. — Apparatus for preparing nitric acid in the laboratory

About equal weights of sodium nitrate and concentrated sulphuric acid are put into the glass retort (Fig. 74), and gently heated. The nitric acid is much more volatile than the sulphuric acid and distills into the receiver (*e.g.* a large test tube), which is kept cool by water, ice, or moist paper.

The chemical change at a low temperature is expressed by the equation: —



But if the temperature is high and an excess of sodium nitrate is used, the equation is:—



At a high temperature part of the nitric acid decomposes; hence excessive heat is usually avoided.

184. Manufacture of nitric acid.—Nitric acid is manufactured by a process like that used in the laboratory. A sketch of the apparatus is shown in Fig. 75. Sulphuric

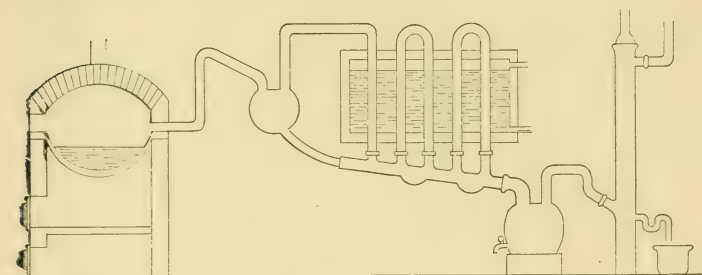


Fig. 75. — Sketch of the apparatus for manufacturing nitric acid

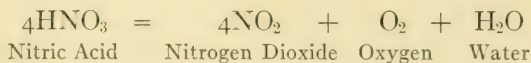
acid and sodium nitrate are heated in the cast iron retort, which is connected with glass or stoneware tubes in which the vapor is condensed by a current of cold water; the tubes are arranged so that the nitric acid first condensed runs into a reservoir, while the vapors pass up a tower, where they are dissolved by descending water and flow out at the bottom as dilute acid. (See 196, 197.)

185. Properties of nitric acid.—Pure nitric acid is a colorless liquid, but the commercial acid is yellow or reddish, due to dissolved nitrogen oxides. The acid that has been exposed to the sunlight is often yellow or brown, and if the light is intense, a brownish gas may often be seen in bottles of the acid. It is somewhat volatile, and the vapor dissolves readily in water; hence the acid forms irritating

fumes when exposed to air, especially moist air. (See 155.)

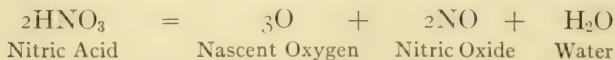
Nitric acid mixes with water in all proportions. Commercial concentrated nitric acid contains about 68 per cent of the compound HNO_3 , the rest being water. Such an acid has a specific gravity of 1.41 and boils at about 120°C .

186. Chemical conduct of nitric acid. — Nitric acid is sour, turns blue litmus red, and forms salts — the nitrates. It is an unstable substance, and decomposes readily; among the decomposition products is a brown gas, nitrogen dioxide (NO_2), which causes the yellow or brown color referred to above (185). If strongly heated, the decomposition is rapid; the equation is: —

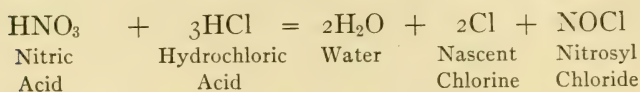


Nitric acid is a very corrosive substance and reacts readily with many substances. With organic substances like hair, feathers, wool, silk, finger nails, and skin it forms a yellow compound. Hence nitric acid stains the skin, and often the clothing, yellow. The concentrated acid causes serious burns and should not be spilled on the hands or face. With other organic compounds it forms explosives, such as nitroglycerin and nitrocellulose.

One of the decomposition products of nitric acid is oxygen. Hence nitric acid is an oxidizing agent. Usually the oxygen is not liberated as a gas, but oxidizes whatever oxidizable substance is present. In order to emphasize the fact that oxidizing oxygen is available, the equation is written thus: —



Thus, charcoal burns brilliantly in the hot acid, while straw, sawdust, hair, and similar substances are charred and even inflamed by it; some organic compounds, when heated with nitric acid, are completely decomposed into carbon dioxide and water. In the mixture of concentrated nitric and hydrochloric acids called **aqua regia**, nitric acid acts as an oxidizing agent (159). The nitric acid oxidizes the hydrochloric acid to water and leaves the chlorine in the nascent condition. (Compare end of 149.) The equation is usually written:—

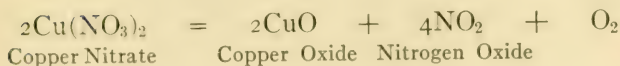
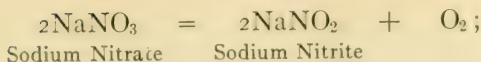


Finally, it interacts readily and often violently with metals, metallic oxides, and hydroxides. (Compare 158.) The products of these reactions vary, the essential ones being nitrates and nitrogen oxides (189).

187. Uses of nitric acid. — Nitric acid is one of the common laboratory acids. Large quantities are used in the manufacture of nitrates, dyestuffs, sulphuric acid, and explosives, and in etching copper plates.

188. Nitrates. — Nitric acid forms salts called nitrates. They are prepared by the methods usually used for salts, *i.e.* the interaction of nitric acid and metals or metallic oxides and the neutralization of hydroxides by nitric acid.

Many nitrates are white solids; those of copper, nickel, and cobalt are blue, green, and dark red respectively. The nitrates of most metals are soluble in water. Their solutions are frequently used in the laboratory. The solids behave in various ways when heated. Equations illustrating typical reactions are:—

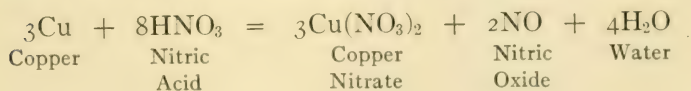


Since many nitrates, when heated, give up oxygen, they are powerful oxidizing agents. Thus, when potassium nitrate is dropped on hot charcoal, the charcoal burns vigorously. This kind of chemical action is called **deflagration**.

Nitrates are also formed in the soil by the action of bacteria on complex nitrogen compounds. This process, which is called **nitrification**, is slow; formerly this was the sole source of the potassium nitrate needed for gunpowder.

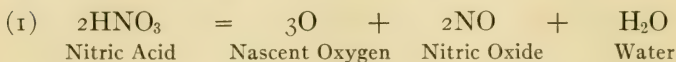
189. The interaction of nitric acid and metals. — This action is exceedingly vigorous; for this reason, probably, the alchemists called the acid *aqua fortis* — strong water. The products of the reaction vary with the metal, the concentration of the acid, and the temperature. Hydrogen as a rule is not liberated so that it can be collected, for it is oxidized at once to water by the nitric acid, whereas the nitric acid is reduced to nitrogen compounds.

The interaction of nitric acid and copper will serve as an example of the common reactions. When moderately dilute nitric acid is poured on copper, a reddish brown gas is given off, and the liquid turns blue, owing to dissolved copper nitrate. The equation for the reaction is:—



This equation is made up of three equations, and the

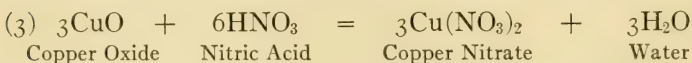
complete form conceals the way in which the reactions take place. The nitric acid first decomposes, thus:—



The nascent oxygen (149) next oxidizes the copper, thus:—

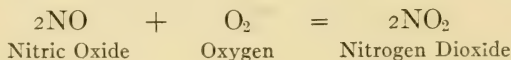


The copper oxide then reacts with the nitric acid, thus:—



Since 3O is formed in (1) and used in (2) and 3CuO likewise in (2) and (3), these two terms should not appear in the complete equation; the other terms make up the complete equation.

Nitric oxide is represented as a product of the interaction of nitric acid and copper. If the reaction takes place in an open vessel, the nitric oxide, which is a colorless gas, combines with oxygen and forms the reddish brown nitrogen dioxide gas. The equation is:—



Hence we often speak of nitrogen dioxide as a product of the interaction of nitric acid and metals, though it is usually a secondary product.

190. The test for a nitrate (and of course for **nitric acid**) is not, as customary, made by producing a precipitate. It is a color test, and is made as follows: Add to the solution of the nitrate or the nitric acid in a test tube an equal volume of ferrous sulphate solution (freshly prepared from clean ferrous sulphate and cold water); mix well. In-

cline the test tube, and pour concentrated sulphuric acid cautiously down the side of the test tube. A dark brown layer appears where the two liquids meet (Fig. 76), owing to the formation of a brown unstable compound which has the composition (approximately) $3\text{FeSO}_4 \cdot 2\text{NO}$.

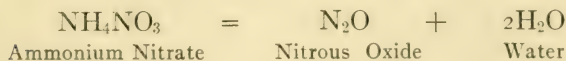


Fig. 76. — Test for nitric acid and nitrates

191. Nitrous acid (HNO_2) is not easily obtained in the free state, owing to its instability, but its salts — the nitrites — are well known. **Potassium nitrite** (KNO_2) and **sodium nitrite** (NaNO_2) are formed by removing part of the oxygen from the corresponding nitrate by heating alone (188) or with lead. Nitrites give off yellow-brown fumes (NO_2) readily when treated with sulphuric acid, and are thus easily distinguished from nitrates.

192. Nitrogen oxides. — There are five nitrogen oxides. The three important ones are nitrous oxide (N_2O), nitric oxide (NO), and nitrogen dioxide (NO_2); there is also an oxide called nitrogen tetroxide (N_2O_4), which is a special form of nitrogen dioxide.

193. Nitrous oxide (N_2O) is prepared by heating ammonium nitrate. The equation for the reaction is: —



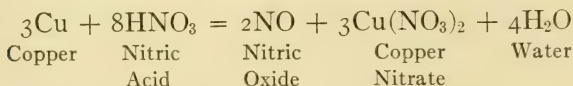
This colorless gas has a faint but pleasant odor. It is soluble in water, and the solution has a sweet taste. It is easily liquefied by reducing the temperature and applying pressure, and is often used in this form to furnish the gas.

The gas does not burn, but it supports the combustion of many well-burning substances, though not so vigorously as oxygen does. Thus, sulphur, unless well ignited, will not burn in nitrous oxide. In its power to support

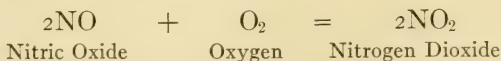
combustion it resembles oxygen. It is distinguished from oxygen by its failure to form brown fumes (NO_2) when mixed with nitric oxide (194).

The most striking property of nitrous oxide is its effect on the human system. If inhaled for a short time, it causes more or less nervous excitement, often manifested by laughter, and on this account the gas was called "laughing gas" by Davy, who first studied its properties in 1799. If breathed in large quantities, it produces temporary unconsciousness and insensibility to pain. The gas, mixed with a small proportion of air or oxygen, is often used as an anæsthetic in dentistry.

194. Nitric oxide (NO) is usually prepared by the interaction of copper and dilute nitric acid (sp. gr. 1.2). The complete equation (189) for the reaction is:—



Nitric oxide is a colorless gas. It is a little heavier than air and only slightly soluble in water. Upon exposure to air, it combines at once with the oxygen, forming reddish brown fumes of nitrogen dioxide — a striking change. The equation for this reaction is:—

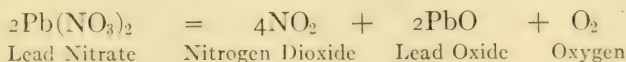


This property distinguishes nitric oxide from all other gases. It does not burn, nor support combustion, unless the burning substance (*e.g.* phosphorus or sodium) introduced is hot enough to decompose the gas into nitrogen and oxygen, and then, the liberated oxygen assists the combustion.

195. Nitrogen dioxide (NO_2) is the reddish brown gas formed by the direct combination of nitric oxide and oxy-

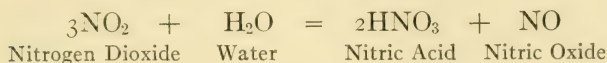
gen (189 end). It is also produced by heating certain nitrates.

Thus : —



The fumes of nitrogen dioxide usually appear when nitric acid and metals interact, but, as stated in 194, the nitrogen dioxide is produced by a second reaction, viz. the combination of nitric oxide with the oxygen of the air.

Nitrogen dioxide has a disagreeable odor, and it is poisonous if breathed in moderate quantities. It interacts with water and yields under ordinary conditions nitric oxide and nitric acid, thus : —



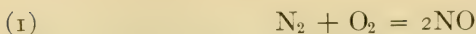
(See 196.) It also dissolves in concentrated nitric acid, forming **fuming nitric acid**, which is an oxidizing agent.

When the reddish brown gas is cooled, it gradually loses color and at about 26° C. becomes a yellow gas, which has the composition represented by the formula N_2O_4 and is called **nitrogen tetroxide**. Upon heating nitrogen tetroxide, the brown gas reappears, and at about 140° C. the gas is wholly nitrogen dioxide. Above 140° C. the brown color fades, owing to the decomposition of nitrogen dioxide into nitric oxide and oxygen. At ordinary temperatures the brown gas is a mixture of the two oxides.

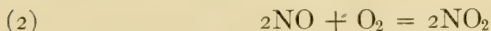
A simple demonstration of the relation between nitrogen dioxide and tetroxide is readily made by collecting some nitrogen dioxide in a glass tube, closing the tube, and immersing the lower half in ice water. The gas in the lower part becomes yellow-brown (NO_4) whereas in the upper part it remains reddish brown (NO_2).

196. Manufacture of nitric acid from nitrogen oxides. —

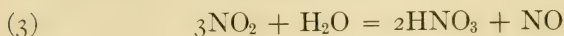
If electric sparks are passed through air, nitrogen and oxygen unite, thus : —



But the nitric oxide combines at once with oxygen, and forms nitrogen dioxide, thus:—



When nitrogen dioxide is added to water, nitric acid and nitric oxide are produced, thus:—



These reactions are the basis of modern processes of making nitric acid from nitrogen oxides and water.

Air is used in one process as a source of the nitrogen oxides. Two unusual conditions must be fulfilled in this

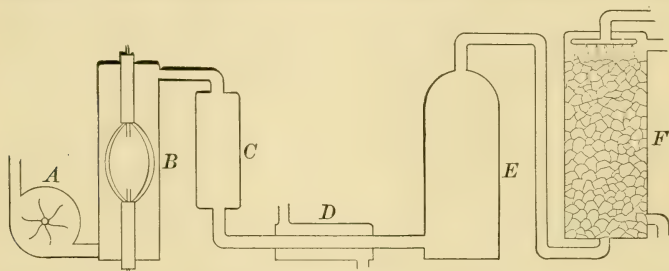
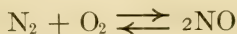


Fig. 77. — Sketch of the apparatus for the manufacture of nitric acid from nitrogen, oxygen, and water

process. First, nitrogen and oxygen must be heated to a very high temperature (about $3000^{\circ}\text{C}.$) before they will unite to an appreciable extent. Second, the mixture of gases resulting from reaction (1) must be cooled very quickly. Reaction (1) is reversible, thus:—



The maximum quantity (only about 5 per cent) of nitric oxide is obtained at about $3000^{\circ}\text{C}.$ At this temperature equilibrium is reached, *i.e.* the relative proportions remain unchanged. (Compare 174.) But just as soon as the tem-

perature becomes lower, the reverse reaction (right to left) begins and the quantity of nitric oxide rapidly decreases. However, if the mixture is cooled very quickly, enough nitric oxide is left for the reaction with water.

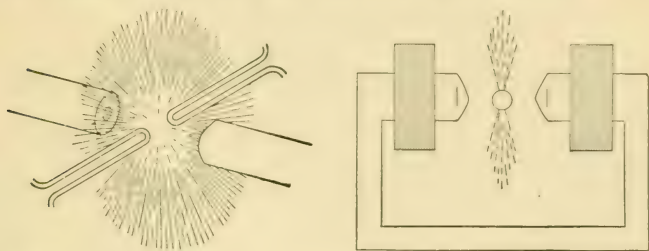
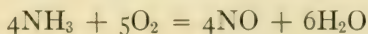


Fig. 78. — Electric arc — spread out (*left*) and end view (*right*)

A sketch of the apparatus is shown in Fig. 77 and certain parts are shown in detail in Fig. 78. Air is blown (by *A*) into the electric furnace *B*. Here it is raised to the proper temperature by passing through an electric arc. In order to provide a large heating surface, the arc is spread out by a magnet into a disk six feet in diameter (Fig. 78, *left*). The electrodes usually are hollow and are kept cool by running water; graphite electrodes are also used. An end view (Fig. 78, *right*) shows the magnets and edge of the disk. The hot gases containing the nitric oxide from the furnace are suddenly cooled in *C*, pass through boiler *D* into the oxidizing chamber *E*, where nitrogen dioxide is formed, and then into the tower *F* filled with tiles over which water trickles, where the nitric acid is produced. The dilute nitric acid is concentrated or converted (by limestone or lime) into calcium nitrate. The latter is used as a fertilizer, either alone or mixed with lime.

197. Manufacture of nitric acid from ammonia. —

In another process, ammonia is the starting point. A heated mixture of ammonia and air is passed into fire-brick-lined chambers containing a catalyst — usually platinum in the form of gauze. At about 600°C. , the reaction, expressed by the following equation, takes place: —



The nitric oxide is cooled, mixed with air, and then, as in the other process, passed into towers through which water trickles, where the nitric acid is produced, thus:—



EXERCISES

1. How is nitric acid prepared in the laboratory? State the two equations.
2. Describe the older process of manufacturing nitric acid.
3. Summarize the properties of nitric acid.
4. Explain: (a) nitric acid is an oxidizing agent; (b) nitric acid is unstable.
5. What is the test for (a) nitric acid, (b) a nitrate, (c) nitric oxide, (d) nitrous oxide, (e) nitrogen dioxide, (f) a nitrite?
6. Describe the interaction of nitric acid and copper and state the equations.
7. Summarize briefly the properties of nitrous oxide.
8. Compare nitric oxide and nitrogen dioxide.
9. How is nitrogen dioxide prepared?
10. State the relation of nitrogen dioxide and nitrogen tetroxide.
11. Describe fully the manufacture of nitric acid from (a) nitrogen oxides and (b) ammonia.
12. Interpret the equation $\text{N}_2 + \text{O}_2 \rightleftharpoons 2\text{NO}$.
13. Complete and balance: (a) $\text{CuCO}_3 + \text{---} = \text{Cu}(\text{NO}_3)_2 + \text{---}$
+ --- ; (b) $\text{HNO}_3 + \text{C} = \text{NO}_2 + \text{---} + \text{CO}_2$.

PROBLEMS

1. Calculate the percentage composition of (a) nitric acid, (b) potassium nitrite, (c) sodium nitrate.
2. Show how nitrous oxide, nitric oxide, and nitrogen dioxide illustrate the law of multiple proportions.
3. Calculate the formula and give the name of the compound corresponding to (a) O = 76.19, H = 1.58, N = 22.22; (b) O = 47.52, K = 38.61, N = 13.86.
4. If the specific gravity of a sample of nitric acid is 1.522, (a) what will 100 cc. weigh; (b) what volume must be taken to weigh 100 gm.?
5. How many liters of oxygen are needed to change 6 l. of nitric oxide to nitrogen dioxide?
6. How much sodium nitrate is needed to form a ton of commercial nitric acid? (See end of 185.)

CHAPTER XV

MOLECULAR WEIGHTS AND FORMULAS

198. Introduction. — Formulas and molecular weights have been used freely in the foregoing pages. In this chapter we shall consider the methods by which molecular weights and formulas are found by experiment.

199. Gay-Lussac's law of gas volumes. — We have seen several times that the volumes of gases involved in a chemical change can be expressed by small whole numbers (**92, 93, 157, 176**). These results may be summarized in a: —

TABLE OF THE COMBINATION OF GASES BY VOLUME

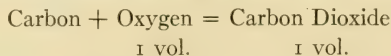
VOLUMES OF COMBINING GASES	VOLUMES OF GASEOUS PRODUCT
2 volumes of hydrogen 1 volume of oxygen	2 volumes of water vapor
1 volume of chlorine 1 volume of hydrogen	2 volumes of hydrogen chloride
3 volumes of hydrogen 1 volume of nitrogen	2 volumes of ammonia
2 volumes of nitrogen 1 volume of oxygen	2 volumes of nitrous oxide
1 volume of nitrogen 1 volume of oxygen	2 volumes of nitric oxide

It is clear from the above table that the volumes of the gases can be expressed by small whole numbers. This

simple relation is true of all gas reactions, and, as we found in studying the volumetric composition of water (92, 93), it may be stated as **Gay-Lussac's law**, thus: —

In a chemical change the volumes of the gases can be expressed by small whole numbers.

This law applies only to gases. For example, carbon is not a gas, though it is frequently involved in reactions with gases, *e.g.*: —



So we omit carbon as far as *volume* is concerned, and say carbon unites with 1 volume of oxygen (O_2) to form 1 volume of carbon dioxide (CO_2).

200. Avogadro's theory. — In 1811 the Italian physicist Avogadro proposed an explanation of the simple numerical relation of gas volumes. It is usually called **Avogadro's theory** and may be stated thus: —

Equal volumes of gases under like conditions of temperature and pressure contain the same number of molecules.

This theory means that a liter of oxygen contains just as many molecules as a liter of hydrogen, nitric oxide, or any other gas, if the temperature and pressure conditions are not altered. The actual number of molecules in the volume of the gas is not important, but the assumption that the number — whatever it may be — is the *same in equal volumes* is very important in chemistry.

201. How Avogadro's theory is used in finding relative molecular weights. — By means of Avogadro's theory we can find the relative molecular weights of gases. Let us consider carbon dioxide and oxygen. A liter of carbon dioxide weighs 1.98 gm. and a liter of oxygen 1.43 gm. at 0°C . and 760 mm. Therefore the weight of a liter of carbon dioxide is (approximately) 1.38 times that of a liter of oxygen. Since a liter of each gas contains the *same number*

of molecules, the weight of the carbon dioxide molecules is (approximately) 1.38 times the weight of the oxygen molecules. It is evident, then, that if we weigh equal volumes of gases (under like conditions of temperature and pressure), we obtain weights which are in the same relation as the weights of single molecules.

202. How we find the approximate molecular weight of a gas. — In **201** we found that carbon dioxide molecules weigh (approximately) 1.38 times the weight of oxygen molecules. Obviously, we could calculate the (approximate) molecular weight of carbon dioxide if we knew the molecular weight of oxygen. The molecular weight of oxygen is 32. (See next paragraph.) We now calculate the (approximate) molecular weight of carbon dioxide by multiplying 32 by 1.38, *i.e.* $32 \times 1.38 = 44.16$. Therefore 44.16 is the (approximate) molecular weight of carbon dioxide.

The molecular weight of oxygen is 32 for two reasons. *First*, a molecule of oxygen contains 2 atoms, as will be shown in **203**. *Second*, an atom of oxygen weighs 16, because this number has been adopted by chemists as the standard atomic weight (**215**). Hence the molecular weight of oxygen is 32 (*i.e.* 2×16).

This method of finding molecular weights is called the **vapor density method**. The steps are (1) find the vapor density referred to oxygen, and (2) multiply this value by 32. The expression *vapor density referred to oxygen* means the number found by dividing the weight of a given volume of a gas or vapor by the weight of an equal volume of oxygen (measured at the same temperature and pressure). Thus, in the example given above the number 1.38 is the vapor density of carbon dioxide (*i.e.* $1.08 \div 1.43$). •

One method of determining the approximate molecular

weight of a gas or a readily volatilized substance is now clear, viz. find the vapor density on the oxygen basis and multiply this value by 32, or

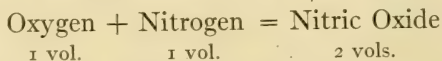
Molecular Weight = Vapor Density referred to Oxygen $\times$ 32

Molecular weights determined by this method are approximate. That is, they do not exactly equal the sum of the weights of the atoms in a molecule, *i.e.* the so-called theoretical molecular weight. The difference is due mainly to slight but unavoidable errors in the process. For example, the approximate molecular weight of carbon dioxide is 44.16, whereas the exact molecular weight is 44.00 (*i.e.* $12 + (2 \times 16)$). The slight difference in this, and other cases, does not affect the validity and use of the weights found by this method.

Some substances cannot be vaporized without decomposition. The molecular weights of such substances cannot, of course, be found by the vapor density method. If a substance dissolves without decomposition, its molecular weight can be determined by an appropriate method (244).

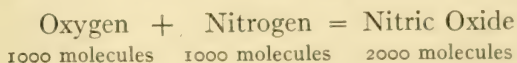
No experimental method, however, has been devised for determining the molecular weight of a substance in the solid state (*i.e.* not dissolved or vaporized); it is customary to assume that the molecular weight of such substances is the sum of the atomic weights in the simplest formula (109 and last paragraph in 206).

203. How Gay-Lussac's law and Avogadro's theory are used to find the number of atoms in a molecule. — A molecule of oxygen contains two atoms. This conclusion is based mainly on the following argument: When oxygen and nitrogen combine to form nitric oxide, the volumes used and produced can be expressed thus:—



Now according to Avogadro's theory, equal volumes of

oxygen and of nitrogen contain the same number of molecules, while the two volumes of nitric oxide contain twice this number of molecules. We do not know the actual number of molecules in any of the volumes. Suppose, however, there are 1000 molecules of oxygen; then by Avogadro's theory, there are 1000 molecules of nitrogen and 2000 molecules of nitric oxide, thus:—



Every molecule of nitric oxide must contain at least one atom of oxygen; and the 2000 molecules must contain at least 2000 atoms of oxygen. But these 2000 atoms of oxygen were provided by the 1000 molecules of oxygen. Therefore, each molecule of oxygen must contain at least two atoms of oxygen.

By a similar argument it can be shown that a molecule of nitrogen contains at least two atoms. So also it can be shown in the same way that a molecule of the common elementary gases contains at least two atoms.

Furthermore, experiment shows that there is no reaction in which a given volume of the elementary gases, oxygen, nitrogen, hydrogen, and chlorine, provides material for more than two volumes of the gaseous product. This means there is no reaction in which a molecule of these gases is divided into more than two parts. And so we conclude that the molecule of these gases contains only two atoms. Hence we write their formulas O_2 , N_2 , H_2 , and Cl_2 . It is clear now why we used these formulas in preceding sections for molecules of the gases.

204. What is a mole? — A **mole** of a substance is the number of grams numerically equal to its molecular weight. It is sometimes defined as a gram-molecular weight. Thus,

a mole of carbon dioxide is 44 grams because the molecular weight is the number 44. Similarly, a mole of oxygen is 32 grams, of carbon monoxide is 28 grams, and of nitric oxide is 30 grams.

The volume occupied by one mole of oxygen (at 0° C.

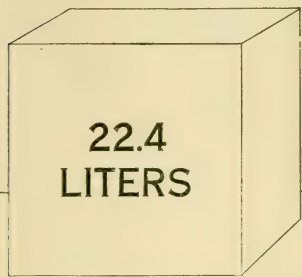


Fig. 79. — A box holding 1 mole or 22.4 liters of a gas (actual length of one edge is 28.2 cm.)

and 760 mm.) is 22.4 liters.

Suppose we construct a box holding 22.4 liters (Fig. 79)

and fill it with oxygen (at 0° C and 760 mm.), the gas will weigh 32 grams.

This must be so. One liter of oxygen weighs 1.43 grams.

Therefore the volume occupied by 32 grams of oxygen will be $32 \div 1.43$,

or 22.4 liters. Simple division shows that 1 mole of a gas occupies 22.4 liters (in round numbers), *e.g.* carbon monoxide, $28 \div 1.25 = 22.4$.

This volume (22.4 liters) is sometimes called the gram-molecular volume, since it is the volume of the gram-molecular weight. It is also called a molar volume, because it is the volume of one mole. So it is clear that 1 mole of a gas and 22.4 liters of the same gas are equal — one being the weight and the other the volume of the same mass of gas.

205. Calculation of molecular weight from a mole. —

Suppose we construct several cubical boxes each holding 22.4 liters (Fig. 80), weigh each box, fill each with a gas (at 0° C. and 760 mm.), and weigh again. The increase in each case is the weight of one mole of the several gases, *i.e.* it is numerically equal to the molecular weight. If the gases used, for example, were nitric oxide, carbon monoxide, hydrogen chloride, and ammonia, the numbers ob-

tained would be 30, 28, 36.5, and 17. And these numbers are the respective molecular weights of these gases.

Hence to find the molecular weight of a gas by the mole method, we find the weight of 22.4 liters of the gas. It is not necessary to use such a large volume in the actual

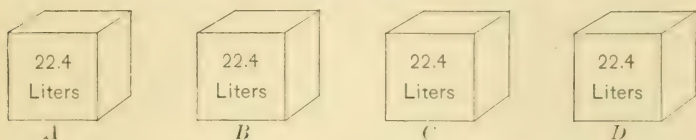


Fig. 80. — A mole of different gases occupies 22.4 liters. $A = 30$ gm. NO, $B = 28$ gm. CO, $C = 36.5$ gm. HCl, $D = 17$ gm. NH_3

experiment. We simply find the weight of any convenient volume and then calculate the weight of 22.4 liters. An example will make this clear. If 1.5 liters of carbon monoxide (at 0° C. and 760 mm.) weigh 1.88 grams, what is the molecular weight of the gas? The weight of 22.4 liters is found thus: $1.88 \div 1.5 = 1.25$; $1.25 \times 22.4 = 28$. Therefore 28 is the molecular weight of carbon monoxide.

206. Correct formulas of compounds. — A formula of a compound expresses composition. That is, it represents by means of symbols the *kind* and *number* of atoms in a molecule.

In 109 it was shown that the **simplest formula** of a compound can be calculated from the percentage composition, viz. by dividing the per cent of each element in the compound by the atomic weight, and then, if necessary, reducing the quotients to the smallest whole numbers. A formula thus calculated expresses in the simplest chemical way the proportions of the different elements in a compound. But it may not be its correct formula.

The **correct formula** of a compound **must represent its molecular weight**. That is, the sum of the weights rep-

resented by the kind and number of atoms in the formula must be equal, or very nearly equal, to the molecular weight found by experiment. Let us take an example. A compound was found by analysis to contain 92.3 per cent of carbon and 7.7 of hydrogen, and to have a vapor density of 2.4375. Dividing the percentages by the atomic weights, we have: $92.3 \div 12 = 7.7$, and $7.7 \div 1 = 7.7$. Since 7.7:7.7 as 1:1, the compound contains at least one atom each of carbon and hydrogen, and its simplest formula is CH. This formula corresponds to the molecular weight 13. But the vapor density 2.4375 requires the molecular weight 78 (*i.e.* 2.4375×32), which is six times the weight (13) corresponding to the formula CH. Hence the molecular formula of this compound is not CH, but C_6H_6 .

We recapitulate regarding formulas of compounds: The **simplest formula** of a compound is found by dividing the per cent of each element by its atomic weight and reducing these quotients to the smallest whole numbers (if necessary). The **molecular formula** of a compound is found by three steps: (a) Find the simplest formula, (b) divide the molecular weight by the sum of the weights of the atoms in the simplest formula, (c) multiply the whole numbers of the simplest formula by the quotient obtained in (b).

If the molecular weight of a compound cannot be found by experiment, then the simplest formula is accepted as the molecular formula. For example, a compound contains 40 per cent of calcium, 12 of carbon, and 48 of oxygen. Dividing each per cent by the proper atomic weight, we have: $40 \div 40 = 1$, $12 \div 12 = 1$, $48 \div 16 = 3$. That is, one molecule of this compound contains (at least) one atom each of calcium and carbon, and three of oxygen; therefore the simplest formula is $CaCO_3$. This is also accepted as its molecular formula, because the molecular weight cannot be found by any method known at present. (See last paragraph in 202.)

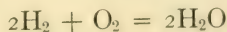
207. Molecular formulas of elements. — The molecular weights of elements, as well as of compounds, can be found by experiment (202, 205). Such determinations show several interesting facts:

(1) Several gaseous elements have molecular weights which are twice the atomic weight. This means that the molecule consists of two atoms, and their molecular formulas are, for example, O_2 , H_2 , Cl_2 , N_2 (also Br_2).

(2) The molecular weights of many metallic elements and gaseous elements are identical with their atomic weights. This shows that the molecule and atom are identical, and the molecular formula is the same as the atomic symbol, *e.g.* Na, K, Zn, Hg, Cd (cadmium), A (argon), He (helium), and Ne (neon). Such elements, especially the rare gases in the atmosphere, are often called monatomic gases to emphasize the fact that their molecules contain only one atom.

(3) Finally the molecular weights of certain elements vary with the temperature, decreasing with rise of temperature, *e.g.* at lower temperatures, molecules of iodine, sulphur, and phosphorus are represented by I_2 , S_8 , and P_4 , and at higher temperatures by I, S_2 , and P_2 .

208. Molecular equations. — Reactions involving the common elementary gases should be expressed by molecular equations. Thus, the equation for the formation of water vapor from hydrogen and oxygen is: —



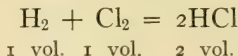
This equation is read thus: Two molecules of hydrogen unite with one molecule of oxygen to form two molecules of water vapor. Since this equation correctly represents the interacting substances as molecules, the equation is called a **molecular equation**. It should be noted that the

proportions by weight are the same as in the simpler or gravimetric equation (135, 138).

Molecular equations are sometimes called **volumetric equations** or **gas equations**, because they show the volumes of gases involved in the reaction. Thus, the equation



may be written:—



because equal numbers of molecules represent equal volumes. This equation is read: One volume of hydrogen and one volume of chlorine form two volumes of hydrogen chloride. It should be remembered that in molecular or volumetric equations a single molecule represents one volume of a gas (or vapor) and the coefficient indicates the number of volumes.

EXERCISES

1. Prepare a summary of molecules and molecular weights.
2. State and illustrate (a) Gay-Lussac's law and (b) Avogadro's theory.
3. (a) State the argument proving that a molecule of oxygen consists of at least two atoms. (b) Apply (a) to nitrogen.
4. Hydrogen and nitrogen combine in the ratio of 3 to 1 to form 2 volumes of ammonia. Show from this relation that a molecule of hydrogen contains at least two atoms.
5. What is the relation between molecular weight and vapor density? Illustrate your answer.
6. Why is the formula of water vapor H_2O and not HO or H_2O_2 ?
7. How are the molecular weights of gases determined by (a) the vapor density method, and (b) the mole method?
8. Define and illustrate (a) molecular equation, (b) mole, (c) gram-molecular weight, (d) gram-molecular volume.
9. What is a molecular formula? What is the molecular formula of oxygen, nitrogen, chlorine, hydrogen, zinc, mercury, sodium, potassium, argon, helium?

10. How is a molecular formula determined? Illustrate.
11. Express the following as volumetric equations: (a) One volume of phosphorus vapor and six volumes of chlorine form four volumes of phosphorus trichloride (PCl_3) vapor; (b) carbon and water (vapor) form hydrogen and carbon monoxide.
12. Topics for review: (a) Gay-Lussac's law (93). (b) Equations (Chapter X). (c) Atoms and molecules (101).

PROBLEMS

1. 1,000,000 molecules of hydrogen will unite with how many molecules of oxygen to form how many molecules of water vapor? What will be the relative weights of hydrogen and water vapor?
2. A liter of sulphurous oxide gas (SO_2) weighs 2.9 gm. What is the molecular weight of this compound? Compare with the theoretical molecular weight.
3. The vapor density of hydrogen chloride is 1.14. Calculate the molecular weight.
4. If 3000 cc. of a carbon oxide weigh 3.75 gm., what is the molecular weight, formula, and name?
5. Calculate the correct formula of the compound corresponding to (a) C = 39.9, H = 6.7, O = 53.4, vapor density = 1.906; (b) C = 73.8, H = 8.7, N = 17.1, vapor density = 5.03.
6. What volume of the constituent gases can be obtained by the complete decomposition of 6 l. of ammonia?
7. Write the equation for the reaction between nitric oxide and oxygen. What volume of oxygen is needed for 10 l. of nitric oxide? What will be the volume of the product?
8. What is the volume of (a) 2 moles of oxygen, (b) 0.5 mole of hydrogen chloride, (c) 22 gm. of carbon dioxide, (d) 22,400 cc. of hydrogen?
9. The correct formula of a gas is CH_4 . (a) How many grams does a mole weigh? (b) What volume does this weight occupy? (c) What is the weight of 1 l. of the gas?
10. A gas contains 69.49 per cent of oxygen and 30.51 of nitrogen. (a) What is its simplest formula? (b) If 500 cc. weigh 2.042 gm., what is the correct formula?

CHAPTER XVI

ATOMIC WEIGHTS

209. Introduction. — In this chapter we shall study the methods of determining atomic weights. But first, let us review what we have already learned about atoms and atomic weights. In Chapter VII we learned that, according to Dalton's atomic theory (100), matter consists ultimately of particles called atoms, which have the same weight if alike but a different weight if different. These atoms, furthermore, remain undivided in chemical changes. Atoms unite and form molecules. The relative weights of atoms are called atomic weights. The standard for atomic weights is oxygen = 16.

210. Determination of approximate atomic weights from molecular weights. — The approximate atomic weight of an element can be determined from the molecular weights of several of its compounds.

We have seen (202, 205) that the molecular weight of a compound can be determined by experiment. After the molecular weights of several compounds have been determined, it is only necessary to find what parts of the molecular weights should be chosen as the atomic weight of the respective elements that constitute the compounds.

The steps in this method are:—

First, determine the molecular weights of several compounds of an element.

Second, find by analysis the per cent of the element in the compounds.

Third, find the weight of the element in each molecular weight by multiplying the molecular weight by the corresponding per cent of the element.

Fourth, select the minimum value as the approximate atomic weight.

Let us find the atomic weight of carbon by this method. The steps are embodied in the accompanying table. Column 1 contains the name of each compound, column 2

DETERMINATION OF THE ATOMIC WEIGHT OF CARBON

COMPOUND	MOL. WT.	PER CENT OF CARBON	WT. OF CARBON	COMPOUND	MOL. WT.	PER CENT OF CARBON	WT. OF CARBON
Carbon Monoxide	28	42.9	12	Ethylene	28	85.7	24
Carbon Dioxide	44	27.3	12	Acetylene	26	92.3	24
Methane	16	75.0	12	Ether	74	64.0	48
Ethane	30	80.0	24	Propane	44	81.8	36

the molecular weight, column 3 the per cent of carbon in each compound, and column 4 the weight of carbon in the corresponding molecular weight. The weights in column 4 are found by multiplying the molecular weight (in column 2) of the compound (in column 1) by the corresponding per cent of carbon (in column 3); thus $28 \times 0.429 = 12$. The minimum value 12 is the atomic weight of carbon.

Obviously, the minimum weight must be the weight of a single atom, for it is highly probable that one or more compounds in a representative group will contain only one atom of a given element; and the part of the molecular weight apportioned to this element will of course be its atomic weight. In the compounds that contain a multiple of this weight, it is likewise obvious that the

molecule must contain several atoms of the element. Thus, the weight of carbon in ethane is twice that in methane, and we conclude that a molecule of ethane contains two atoms of carbon — a conclusion in harmony with other observations.

The numerical results obtained by a study of the elements oxygen, hydrogen, chlorine, nitrogen, and carbon are summarized in the accompanying table. In this table, for the sake of simplicity, whole numbers are used (except in the case of chlorine) and per cents are omitted. The minimum weight in each case is the atomic weight of the element, *e.g.* Cl = 35.5.

DETERMINATION OF APPROXIMATE ATOMIC WEIGHTS

COMPOUND	MOLECULAR WEIGHT	WEIGHT OF OXYGEN	WEIGHT OF HYDROGEN	WEIGHT OF CHLORINE	WEIGHT OF NITROGEN	WEIGHT OF CARBON
Water	18	16	2	—	—	—
Hydrogen Peroxide	34	32	2	—	—	—
Hydrogen Chloride	36.5	—	1	35.5	—	—
Ammonia	17	—	3	—	14	—
Nitric Acid	63	48	1	—	14	—
Nitrous Oxide	44	16	—	—	28	—
Nitric Oxide	30	16	—	—	14	—
Nitrogen Dioxide	46	32	—	—	14	—
Carbon Monoxide	28	16	—	—	—	12
Carbon Dioxide	44	32	—	—	—	12
Methane	16	—	4	—	—	12
Ethylene	28	—	4	—	—	24
Acetylene	26	—	2	—	—	24
Ether	74	16	10	—	—	48
Ethyl Alcohol	46	16	6	—	—	24
Chloroform	119.5	—	1	106.5	—	12
Carbon Tetrachloride . . .	154	—	—	142	—	12
Cyanogen Chloride	61.5	—	—	35.5	14	12
Minimum weight of each element . .		16	1	35.5	14	12

This method of determining approximate atomic weights

was proposed about 1858 by the Italian chemist Cannizzaro (Fig. 81).

211. Dulong and Petit's law. — Formerly the selection of the atomic weights of solid elements, especially metals, was checked by an approximate generalization commonly called the **law of Dulong and Petit**, which can be stated thus: —

The atomic weight is the quotient of 6.25 (approximately) divided by the specific heat.

As an example we take silver. Its specific heat is 0.057; if 6.25 is divided by this number, the quotient is about 109. This result shows that the atomic weight of silver is approximately 109 — not 55 or 218. The exact value (found by other methods) is 107.88.

More reliable methods are now used in determining atomic weights, although this so-called law is helpful in deciding between a number and its multiple.

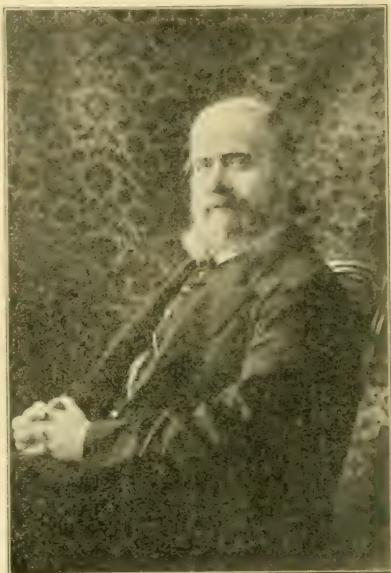


Fig. 81. — Cannizzaro (1826-1910)

212. Equivalent weights. — The term *equivalent weights* requires explanation. Equivalent weights of the elements are the weights that are chemically equivalent, provided the weights are expressed in terms of the standard for equivalent weights, viz. 8 grams of oxygen. In other words, the **equivalent weight** of an element is the weight that combines with or replaces 8 grams of oxygen. For example, magnesium and oxygen combine in the ratio of 1.5 to 1 respectively (in round numbers). Now if for the 1 we

substitute 8, then the 1.5 becomes 12; that is, 12 is the number of grams of magnesium that unites with 8 grams of oxygen. Therefore 12 is the equivalent weight of magnesium. Similarly, hydrogen and oxygen combine in the ratio of 1 to 8; therefore 1 is the equivalent weight of hydrogen.

The equivalent weights of certain elements are not found directly in terms of oxygen, but by finding the weight that combines with or replaces the equivalent weight of some other element. Thus, chlorine and hydrogen combine in the ratio of 35.5 to 1; therefore the equivalent weight of chlorine is 35.5. Sodium replaces hydrogen from water in the ratio of 23 to 1; therefore 23 is the equivalent weight of sodium. Again, 32.5 grams of zinc replace 1 gram of hydrogen from hydrochloric acid; therefore 32.5 is the equivalent weight of zinc.

These numbers are sometimes called combining numbers, combining weights, or simply equivalents. The term *equivalent weights* is preferable, because they actually are the weights chemically equivalent to each other. Thus, if we start with hydrogen chloride (HCl), 1 gm. of hydrogen — to take a convenient denomination — combines with 35.5 gm. of chlorine, and this 1 gm. of hydrogen can be replaced chemically by 32.5 gm. of zinc, 12 gm. of magnesium, 39 gm. of potassium, or 23 gm. of sodium, and so on. These elements are chemically equivalent in the ratio of these weights.

213. The relation of equivalent weights and atomic weights. — The equivalent weight of certain elements is equal to the atomic weight, *e.g.* hydrogen, chlorine, and sodium. In other cases the atomic weight is a multiple of the equivalent weight, *e.g.* 2 for oxygen, and 3 for aluminium. We say, therefore, that the atomic weight of an element is equal to its equivalent weight or a small whole

multiple of it. This relation is seen in the accompanying table (in which approximate weights are used).

TABLE OF EQUIVALENT WEIGHTS AND ATOMIC WEIGHTS

ELEMENT	EQUIVALENT WEIGHT	ATOMIC WEIGHT	MULTIPLE
Oxygen	8	16	2
Aluminium	9	27	3
Bromine	80	80	1
Calcium	20	40	2
Carbon	3	12	4
Chlorine	35.5	35.5	1
Hydrogen	1	1	1
Magnesium	12	24	2
Potassium	39	39	1
Silver	108	108	1
Sodium	23	23	1
Sulphur	16	32	2
Zinc	32.5	65	2

The equivalent weight of an element can be very accurately determined by experiment. Hence if we wish to determine the atomic weight accurately, we determine the equivalent weight and then multiply it by the correct whole number.

214. Accurate determination of atomic weights. — The method of determining atomic weights discussed in **210** involves finding the vapor density. But since the vapor density cannot be found accurately, atomic weights determined by the vapor density method have only approximate values. The accurate value of an atomic weight is determined by painstaking analysis of very carefully purified substances. The general method can be illustrated by an actual case kindly furnished by the American chemist Richards (Fig. 82), who has made exceptionally accurate determinations of atomic weights. In determining the

atomic weight of chlorine he found that 28.26299 gm. of silver chloride were formed from 21.27143 gm. of silver. He accepted AgCl as the formula of silver chloride and 107.880 as the atomic weight of silver, and calculated the atomic weight of chlorine thus:—

$$28.26299 - 21.27143 = 6.99156$$

Wt. of silver	:	Wt. of chlorine	:	At wt. of silver	:	At. wt. of chlorine
21.27143	:	6.99156	:	107.880	:	x
$x = 35.458$						

The international atomic weight (35.46) is based on this and other determinations made by this same chemist.

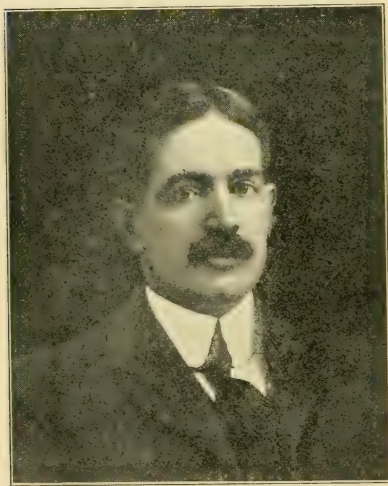


Fig. 82. — Richards (1868—)

215. International atomic weights.—An international committee selects the most accurate atomic weights of the elements. This committee selected 16 as the atomic weight of oxygen (from several values formerly used). The weights are embodied in a table published at frequent intervals and called the International Table of Atomic Weights. The table is given on the in-

side of the back cover of this book. In this table the adopted atomic weights are placed in one column and the approximate weights in another. The approximate atomic weights are sufficiently accurate for general refer-

ences and in making chemical calculations; they may be used in solving the problems in this book.

216. Review of methods of determining atomic weights. — The methods and principles used in determining the atomic weight of an element can be reviewed by following the steps necessary in determining the atomic weight of zinc (if its atomic weight were unknown).

(a) When zinc interacts with dilute hydrochloric acid, hydrogen is liberated; and if a known weight of zinc is used, the weight of zinc needed to liberate 1 gm. of hydrogen is easily calculated. This number is the equivalent weight of zinc. Now if one atom of zinc replaces one atom of hydrogen, the atomic weight of zinc and the atomic weight of hydrogen will have the same ratio as the weight of zinc and the weight of hydrogen found by experiment. According to experiment the equivalent weight of zinc is about 32.5. This is its relation, atom for atom, to hydrogen, and thus far, is its atomic weight.

(b) When zinc and hydrochloric acid interact, zinc chloride is formed. If it is analyzed, the proportion of zinc to chlorine is about 32.5 to 35.5. Now if the elements combine, atom for atom, the atomic weight of zinc is 32.5 (assuming 35.5 as the atomic weight of chlorine).

(c) However, when zinc is burned in air, zinc oxide is formed. If this compound is analyzed, the proportion of zinc to oxygen is about 65 to 16. If the elements combine, atom for atom, the atomic weight of zinc is about 65 (assuming 16 as the atomic weight of oxygen).

(d) According to these three determinations, the atomic weight of zinc is 32.5 or 65. We have assumed that the elements unite, atom for atom, in each compound. This is an incorrect assumption, because an atom of zinc cannot have two different weights — 32.5 and 65. If the atomic weight is 32.5, zinc oxide must consist of one atom of oxygen and two of zinc. But if the atomic weight is 65, zinc chloride must consist of two atoms of chlorine and one of zinc, and two atoms of hydrogen must have been replaced by one of zinc.

(e) The molecular weight of zinc-chloride is found by the vapor density method to be about 136. Zinc chloride contains 47.8 per cent of zinc. Therefore 47.8 per cent of 136, or 65.08, is zinc; that is, 65.08 is the approximate weight of the smallest part of zinc in zinc chloride, and it may be the approximate weight of one atom. If

zinc chloride consists of two atoms of chlorine and one of zinc (weighing 65), its molecular weight is about 136. In other words, it is evident that our assumption regarding the number of atoms in zinc chloride is probably correct.

(f) We are not absolutely positive, however, that the zinc in a molecule of zinc chloride may not be one atom weighing 65, or two atoms weighing 32.5 each. But the approximate atomic weight of zinc determined by applying the law of specific heats is 66.4 (*i.e.* $6.25 \div 0.094$). This shows clearly that the atomic weight of zinc is approximately 65 (and not 32.5).

(g) Accurate analyses of pure zinc compounds show that the atomic weight of zinc is 65.37.

EXERCISES

1. Prepare a summary showing the relation of atomic weights to (a) molecular weights and (b) equivalent weights.
2. State the three steps in finding atomic weights by the "minimum weight" method. Illustrate by carbon.
3. Describe Dulong and Petit's method of finding atomic weights.
4. What is an equivalent weight? Illustrate by aluminium.
5. State exactly the meaning of "chemically equivalent."
6. What is the equivalent weight of (a) oxygen, hydrogen, chlorine, carbon, sulphur, bromine, and (b) aluminium, calcium, magnesium, potassium, silver, sodium, zinc?
7. Describe the process of finding an exact atomic weight.
8. Why is 16 the atomic weight of oxygen?
9. What is the atomic weight of (a) Al, Ba, Br, Ca, C, Cl, Cu, F, Au, H; (b) I, Fe, Pb, Mg, Mn, Hg, N, O, P, K; (c) Si, Ag, Na, S, Sn, Zn?

PROBLEMS

1. If 2 gm. of potassium chloride yield 3.84 gm. of silver chloride, calculate the atomic weight of potassium.
2. If 91.46 gm. of metallic silver, when heated in chlorine, yield 121.4993 gm. of pure silver chloride, calculate the atomic weight of chlorine.
3. Calculate the equivalent weights of the respective metals from the following data: (a) 0.5 gm. of calcium unites with 0.2 gm. of oxygen to form calcium oxide (CaO). (b) 15 gm. of mercury unite with 1.2 gm. of oxygen to form mercuric oxide (HgO).
4. Calculate the equivalent weight of sodium from the following:

(a) 2.3 gm. of sodium liberate 0.1 gm. of hydrogen from water.
 (b) 1.15 gm. of sodium liberate 555.5 cc. of hydrogen (at standard conditions).

5. If 0.03 gm. of magnesium yields 30.4 cc. of hydrogen at 20° C. and 750 mm., what is the equivalent weight of magnesium?

6. Suppose 4.86111 gm. of ferric oxide (Fe_2O_3) yield 3.39995 gm. of iron, what is the atomic weight of iron?

7. If 4.59507 gm. of phosphorus trichloride (PCl_3) give by precipitation 14.38118 gm. of silver chloride, what is the atomic weight of phosphorus?

8. In the synthesis of hydrogen bromide, 0.8606 gm. of hydrogen combined with 68.25033 gm. of bromine. Calculate the atomic weight of bromine.

9. By experiment, 14.36691 gm. of mercuric bromide (HgBr_2) yield 14.9694 gm. of silver bromide. Calculate the atomic weight of mercury.

10. Assume that 1.70563 gm. of strontium bromide (SrBr_2) require 1.48707 gm. of silver to precipitate the bromine as AgBr . What is the atomic weight of bromine?

11. (a) What is the atomic weight of phosphorus, if the specific heat is 0.189? (b) Of potassium, if the specific heat is 0.166? (c) Of manganese, if the specific heat is 0.122? (d) Of tin, if the specific heat is 0.054? Compare each with the exact atomic weight.

12. It was found that 4.58644 gm. of calcium bromide (CaBr_2) require 4.95025 gm. of silver to precipitate the bromine as AgBr . What is the atomic weight of calcium?

CHAPTER XVII

VALENCE

217. What is valence? — Formulas obtained by the methods discussed in Chapter XVI show certain regularities. Let us take as examples the following groups:—

I. *Hydrogen Compounds*

HCl	H ₂ O	NH ₃	CH ₄
HBr	H ₂ S	PH ₃	SiH ₄

II. *Oxides*

Na ₂ O	CaO	Al ₂ O ₃	SO ₂	P ₂ O ₅	SO ₃
K ₂ O	MgO	P ₂ O ₃	CO ₂	As ₂ O ₅	CrO ₃

III. *Acids and Salts*

HCl	HNO ₃	H ₂ SO ₄	H ₃ PO ₄
NaCl	NaNO ₃	Na ₂ SO ₄	Na ₃ PO ₄
CaCl ₂	Ca(NO ₃) ₂	CaSO ₄	Ca ₃ (PO ₄) ₂
AlCl ₃	Al(NO ₃) ₃	Al ₂ (SO ₄) ₃	AlPO ₄

IV. *Bases*

NaOH	Ca(OH) ₂	Al(OH) ₃
KOH	Ba(OH) ₂	Bi(OH) ₃

These groups might be greatly extended. Careful comparison of these and many other formulas shows two significant facts. (1) Atoms of elements differ in the number of atoms or atomic groups of the other elements with which they combine. Thus, one atom each of chlorine and bromine combines with one of hydrogen; while one atom

each of oxygen and sulphur combines with two of hydrogen ; and so on. (2) One atom of certain elements unites with only one atom or atomic group of certain other elements, with only two atoms or two atomic groups of certain others, and so on. Thus, one atom of calcium combines with one atom of oxygen, two of chlorine, with two NO_3 groups, one SO_4 group, and two OH groups. Hence, we conclude that atoms of elements have definite combining capacity.

The number which expresses the combining capacity of an atom of an element is called the **valence** of the element (Table A, 221).

218. Valence of radicals. — Strictly speaking, valence is a property of atoms. But many atomic groups often act chemically like individual atoms, *e.g.* they pass as a whole from one compound to another. Hence it is customary to assign a valence to atomic groups like SO_4 , NO_3 , NH_4 , and OH. Such groups are called radicals (163, 179); occasionally the term *radical* is applied by analogy to a single atom, *e.g.* Cl in chlorides, C in carbides, S in sulphides (as in Table B, 221). In a word, a radical has a valence just as an element does.

219. Valence terms. — An element or radical which has the valence 1 is called a monad; those which have the valence 2 are called dyads; similarly, those elements or groups which have the valence 3, 4, 5, 6 are called respectively triads, tetrads, pentads, and hexads. The corresponding adjectives are univalent, bivalent (or divalent), trivalent, quadrivalent (or tetravalent), quinquivalent (or pentavalent), and hexavalent.

220. How valence is represented. — The valence of an element or radical may be represented by writing a small Roman numeral slightly above the symbol, *e.g.* H^{I} , O^{II} , Al^{III} , SO_4^{IV} , OH^{I} . Other ways are given in 226.

221. Tables of valence. — The valence of certain elements and radicals is shown in Tables A and B. These tables are very useful in writing formulas (225).

TABLE A.—VALENCE OF CERTAIN ELEMENTS

NAME	SYMBOL	VALENCE	NAME	SYMBOL	VALENCE
Aluminium . .	Al	3	Iron (ous) . .	Fe	2
(Ammonium) .	(NH ₄)	1	Iron (ic) . . .	Fe	3
Antimony (ous)	Sb	3	Lead	Pb	2
Antimony (ic) .	Sb	5	Magnesium . .	Mg	2
Arsenic (ous) .	As	3	Mercury (ous) .	Hg	1
Arsenic (ic) . .	As	5	Mercury (ic) .	Hg	2
Barium	Ba	2	Phosphorus (ous)	P	3
Bismuth	Bi	3	Phosphorus (ic)	P	5
Calcium	Ca	2	Potassium . .	K	1
Carbon	C	4	Silicon	Si	4
Copper (ous) .	Cu	1	Silver	Ag	1
Copper (ic) . .	Cu	2	Sodium	Na	1
Gold (ous) . .	Au	1	Tin (ous) . . .	Sn	2
Gold (ic) . . .	Au	3	Tin (ic)	Sn	4
Hydrogen . . .	H	1	Zinc	Zn	2

TABLE B.—VALENCE OF CERTAIN RADICALS

GROUP NAME OF COMPOUND	SYMBOL OR FORMULA	VALENCE	GROUP NAME OF COMPOUND	SYMBOL OR FORMULA	VALENCE
Acetate	C ₂ H ₃ O ₂	1	Iodide	I	1
Bromide	Br	1	Manganate	MnO ₄	2
Carbide	C	4	Nitrate	NO ₃	1
Carbonate	CO ₃	2	Nitrite	NO ₂	1
Carbonate (acid)	HCO ₃	1	Oxide	O	2
Chlorate	ClO ₃	1	Permanganate . .	MnO ₄	1
Chloride	Cl	1	Phosphate (ortho)	PO ₄	3
Chromate	CrO ₄	2	Silicate (meta) . .	SiO ₃	2
Dichromate . . .	Cr ₂ O ₇	2	Sulphate	SO ₄	2
Ferricyanide . .	Fe(CN) ₆	3	Sulphate (acid) . .	HSO ₄	1
Ferrocyanide . .	Fe(CN) ₆	4	Sulphide	S	2
Fluoride	F	1	Sulphite	SO ₃	2
Hydroxide . . .	OH	1	Sulphite (acid) . .	HSO ₃	1

For convenience in using or learning the usual valence of certain elements and the valence of radicals, the valences given in Tables A and B may be rearranged as follows: —

1. Monads (valence 1) — Ag, Au (ous), Br (ide), Cl (ide), ClO_3 , Cu (ous), F (ide), H, HCO_3 , HSO_3 , Hg (ous), I, K, MnO_4 (per), Na, NH_4 , NO_2 , NO_3 , OH.
2. Dyads (valence 2) — Ba, Ca, CO_3 , CrO_4 , Cr_2O_7 , Cu (ic), Fe (ous), Hg (ic), Mg, MnO_4 (ate), O, Pb, S (ide), SO_3 , SO_4 , SiO_3 , Sn (ous), Zn.
3. Triads (valence 3) — Al, As (ous), Au (ic), Bi, Fe (ic), $\text{Fe}(\text{CN})_6$ (i), P (ous), PO_4 , Sb (ous).
4. Tetrads (valence 4) — C, C (ide), $\text{Fe}(\text{CN})_6$ (o), Si, Sn (ic).
5. Pentads (valence 5) — As (ic), P (ic), Sb (ic).

222. Variable valence. — Most elements and radicals have a fixed valence. But the valence of some elements varies with the combining element and the conditions under which the combination occurred. For example, iron, copper, mercury, and a few other elements form two series of compounds in which these elements have a different valence. These series are designated as *-ous* and *-ic* (see 502). Thus, iron forms *ferrous* compounds (*e.g.* ferrous sulphate) in which iron has the valence 2, and *ferric* compounds (*e.g.* ferric chloride) in which iron has the valence 3. (See 228.)

223. Interpretation of valence by combination. — Elements which have the *same* valence combine with each other unit for unit. This is a general rule. For example, sodium and chlorine each has the valence 1; hence one atom of sodium combines with one atom of chlorine to form one molecule of sodium chloride (NaCl).

Elements which have a *different* valence usually combine with each other so that the total valence of the atoms of each element in a molecule is equal. This is also a general rule. In other words, the valence of the two parts must balance. For example, two atoms of hydrogen (each having the valence 1) combine with one of oxygen (having the valence 2) to form one molecule of water (H_2O); similarly two atoms of aluminium (each having the valence 3)

combine with three atoms of oxygen (each having the valence 2) to form one molecule of aluminium oxide (Al_2O_3).

The two rules just given apply to radicals. Thus, ammonium and hydroxyl each has the valence 1; so one NH_4 radical combines with one OH radical to form one molecule of ammonium hydroxide (NH_4OH). Similarly, two NH_4 radicals combine with one S_4O radical (having the valence 2) to form one molecule of ammonium sulphate ($(\text{NH}_4)_2\text{SO}_4$). So also, three atoms of calcium (each having the valence 2) combine with two PO_4 radicals (having the valence 3) to form one molecule of calcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$).

224. Interpretation of valence by displacement or substitution. — Just as atoms and radicals of the *same* valence combine, unit for unit, and those of *different* valence combine so that the valence of the two parts (element or radical) balances, so also atoms and radicals displace each other — unit for unit if the valence is the same, or equivalently if the valence is different. Let us take several examples: (1) When silver displaces hydrogen in hydrochloric acid, one atom of silver (having the valence 1) displaces one atom of hydrogen (having the valence 1), thereby forming silver chloride (AgCl). (2) Similarly, one atom of chlorine (having the valence 1) displaces one OH radical (having the valence 1) from sodium hydroxide, thus producing sodium chloride (NaCl). (3) So also, when aluminium is substituted for the hydrogen in sulphuric acid, two atoms of aluminium (each having the valence 3) are needed to balance the three SO_4 radicals (each having the valence 2) in the aluminium sulphate ($\text{Al}_2(\text{SO}_4)_3$) formed.

225. Writing formulas from valence. — Formulas of many compounds may be written by using the tables of valence.

(1) Suppose we wish to write the formula of

magnesium chloride. From Table A the valence of magnesium is found to be 2, and from Table B the valence of chlorine in chlorides is found to be 1. Remembering the *fundamental rule* that in most compounds the total valence of each of the two parts must be equal, it is clear that the formula must contain one atom of magnesium and two atoms of chlorine; hence the formula is MgCl_2 .

(2) Suppose we wish to know the formula of lead nitrate. From the tables, the valence of lead is 2 and of the NO_3 radical is 1; so it is necessary to have two NO_3 radicals for one atom of lead; the formula, therefore, is $\text{Pb}(\text{NO}_3)_2$.

(3) Similarly, the formula of aluminium oxide is Al_2O_3 , because 2 and 3 are the least number of atoms of Al and O which give a balanced valence (6 in each case).

Formulas of salts are frequently needed. These can be readily written by learning the formulas of the common acids and substituting the correct number of atoms for the hydrogen. Thus, the formula of sulphuric acid is H_2SO_4 . Therefore, all sulphates will have one or more SO_4 radicals as one part of the formula and one or more atoms of a metal for the other part. If the metal has the valence of 1, the formula will contain two atoms of the metal, *e.g.* Na_2SO_4 , K_2SO_4 , Ag_2SO_4 ; if the valence is 2, there will be only one atom, *e.g.* CaSO_4 , BaSO_4 , CuSO_4 . Whereas if the valence is 3, there will be two atoms of the metal and three SO_4 radicals, *e.g.* $\text{Al}_2(\text{SO}_4)_3$. Similarly, all nitrates have NO_3 (one or more), all chlorides have Cl (one or more), all phosphates have PO_4 (one or more), and so on. It is not necessary to learn by heart formulas of salts; they can be written by applying the valence rules.

226. Representation of valence. — The valence of elements and radicals may be represented in various ways. One has already been

given, viz. H^I , O^{II} , PO_4^{III} . Sometimes short lines are used, *e.g.* $H-$, $O=$, $-O-$, $Al\equiv$, etc. If lines are used to represent valence in compounds, a single line answers for two elements. Thus, the formula of water is written $H-O-H$ rather than $H- -O- -H$. Simi-

larly, ammonia gas is $N \begin{array}{l} \diagup H \\ \diagdown H \\ \diagup H \end{array}$ and calcium hydroxide is $Ca \begin{array}{l} \diagup OH \\ \diagdown OH \end{array}$ or

$Ca \begin{array}{l} \diagup O-H \\ \diagdown O-H \end{array}$. Such formulas are called **structural** or **graphic formulas**,

for they show the probable arrangement of the atoms in the molecules. Thus, the graphic formula of nitric acid is usually written

$H-O-N \begin{array}{l} \diagup O \\ \diagdown O \end{array}$, because this arrangement of atoms not only shows

the correct valence of each element but it also represents certain facts about nitric acid, *e.g.* that the hydrogen is not combined directly with nitrogen. Structural formulas are useful, especially in organic chemistry (Chapter XXIII), but it must not be forgotten that they are merely representations; the lines are intended to indicate the numerical value of the valence and not the strength of the combination of the atoms.

227. Determination of valence from atomic and equivalent weights. — We learned in 213 that the atomic weight is equal to the equivalent weight or is a small whole multiple of it. The number (1 or a small multiple) expressing the relation of the atomic and equivalent weight of an element is the valence. Hence the valence of an element is found by dividing its atomic weight by its equivalent weight, that is: —

$$\text{Valence} = \text{Atomic Weight} \div \text{Equivalent Weight}$$

Thus, the atomic weight of magnesium is 24, and its equivalent weight is 12. Therefore the valence is $24 \div 12$, or 2.

228. Exceptional compounds. — The formulas of certain compounds apparently do not conform to the simplified conception of valence discussed above. Carbon monoxide (CO), calcium carbide

(CaC_2), lead tetroxide (Pb_3O_4), magnetic iron oxide (Fe_3O_4), hydrogen peroxide (H_2O_2), acetylene (C_2H_2), and ethylene (C_2H_4) are apparent exceptions. Interpretations of these apparent exceptions must be sought in a larger textbook. (See, however, 503, 573.)

229. Importance of valence. — Valence is very useful in writing formulas and in understanding analogous compounds. The valence of the common elements and radicals should be learned and used. (See especially Exercises 1, 3, 4, 8, 9, below.)

EXERCISES

1. What is the valence of these elements and radicals? (a) H, O, C, Cl; (b) Ag, K, Na, NH_4 ; (c) NO_3 , OH; (d) Ba, Ca, Cu, Fe (ous), Mg, Pb, Zn; (e) CO_3 , SO_4 , S (ide); (f) Al, Fe (ic), PO_4 .

2. State the fundamental rule for writing formulas from valence.

3. Write the formula of the chloride of potassium, sodium, silver, copper (ous), copper (ic), mercury (ous), mercury (ic), iron (ous), iron (ic), zinc, tin (ous), tin (ic), calcium, barium, magnesium, bismuth, aluminium, ammonium, lead.

4. Write the formula of the sulphate of K, Na, Ag, Cu, Fe (ous), Zn, Pb, Ca, Ba, Mg, Cr, Al, NH_4 .

5. Write the formula of the following compounds and indicate the valence of each element or radical by Roman numerals: ammonium fluoride, sodium silicate, potassium manganate, barium phosphate, zinc iodide, ammonium chromate, silver chromate, magnesium oxide, sodium dichromate, aluminium chloride, ferrous bromide, calcium phosphate, mercurous nitrate.

6. Write the formulas of the following (as in Exercise 5): ferrous carbonate, aluminium phosphate, calcium fluoride, sodium permanganate, phosphoric acid, silicic acid, sulphurous acid, nitrous acid, chromic acid, hydriodic acid, carbonic acid.

7. Define and illustrate the term *equivalent weight*. What is the equivalent weight of hydrogen, oxygen, sulphur, zinc, copper, magnesium, silver, potassium, aluminium? State the relation of each to its atomic weight.

8. Write the formula of the nitrate of calcium, silver, iron (ic), mercury (ous), barium, magnesium, aluminium.

9. Write the formula of the oxide of Al, Sb (ous and ic), As (ous and ic), Ba, Bi, Ca.

10. Write the formula of (a) the carbonate of Cu (ic), Ba, Ag; (b) the iodide of Hg (ous and ic), Pb, Ag, Na, Fe (ous and ic), Al; (c) the chlorate of Na, Ba, Ag.

11. Write the formula of (a) the dichromate of Pb, Na, Al, Ag; (b) the manganate of Na, Ca, Ag; (c) the nitrate of Pb, Ca, Cu (ous and ic).

12. Write the formula of (a) the nitrite of Na, Ca, Pb, Cu (ic); (b) the permanganate of Na, Ag, H, K; (c) the sulphate, chloride, nitrate, carbonate, sulphite, bromide of H.

CHAPTER XVIII

IONS AND IONIZATION

230. Introduction. — Many properties of solutions and the general properties of acids, bases, and salts have already been enumerated (161–165). Considerable attention has also been given to examples of acids, bases, and salts, viz. hydrochloric and nitric acids, ammonium hydroxide, and chlorides and nitrates. In this chapter we shall consider more in detail the properties of dilute solutions of acids, bases, and salts.

231. Theory of ionization. — Solutions of acids, bases, and salts differ conspicuously in certain properties from solutions of other substances (*e.g.* sugar, glycerin, alcohol). That is, we have two classes of solutions. One class — acids, bases, and salts — is active chemically, conducts an electric current, and behaves abnormally when boiled or frozen. Whereas the other class — not acidic, basic, or salty — is not active chemically, does not conduct an electric current, and behaves normally when boiled or frozen.

The properties of solutions, especially solutions of acids, bases, and salts, are explained more or less acceptably by the **theory of ionization**, which was proposed in 1887 by the Swedish chemist Arrhenius (Fig. 83). We shall state and explain the theory first, and then show how the theory helps us understand the properties of dilute solutions of acids, bases, and salts. The theory is usually stated as follows : —

Acids, bases, and salts, when dissolved in water, decompose into particles charged with electricity.

This theory means that a solution of sodium chloride, for example, consists of water throughout which are dis-



Fig 83. — Arrhenius (1859-)

tributed some molecules of sodium chloride together with particles of electrically charged sodium and chlorine into which the other molecules of sodium chloride have dissociated.

232. What are ions?

— The decomposition, or dissociation, of acids, bases, and salts when in solution is called **ionization**. The electrically charged particles formed by ionization are called **ions**. Each ion is a por-

tion of a molecule. Two kinds of ions are present in every electrolytic solution, viz. electro-positive ions, or **cations**, and electro-negative ions, or **anions**.

Ions, although formed by the dissociation of molecules, must not be confused with atoms. *Ions are electrically charged atoms or radicals.* The electric charge changes the atom or radical, so that the properties of ions are quite different from those of atoms. For example, in a solution of sodium chloride the electro-positive sodium ions move about in the water without producing any apparent chemical change; whereas ordinary sodium interacts violently with water, as we have already seen (49). Similarly, the chloride

ions circulate freely in water and exhibit none of the effects of chlorine on water (145, 146). It must be understood that the electric charges on the ions in a solution do not come from the electricity that may subsequently be passed through the solution. The ions are electrically charged just as soon as the molecules decompose in the solution (238).

233. How ions are represented. — Ions are represented by chemical symbols *supplemented by the sign that designates the kind and amount of the electric charge*. Thus, the ions formed by sodium chloride are Na^+ and Cl^- . In sodium chloride solution a molecule of sodium chloride dissociates into one ion each of sodium and chlorine. Hence the number of sodium ions equals the number of chloride ions; and the sum of the positive charges on all the sodium ions equals the sum of the negative charges on all the chloride ions.

On the other hand in calcium chloride solution (CaCl_2), each molecule dissociates into two chloride ions and one calcium ion. Hence the ions formed by the dissociation of calcium chloride are designated Ca^{++} and 2Cl^- (*not* Cl_2^-).

Since the sum of each kind of electric charge must be equal (*i.e.* the total positive equals the total negative), the charge on each calcium ion must be twice the charge on each chloride ion. Similarly, the ions formed by calcium hydroxide ($\text{Ca}(\text{OH})_2$) are Ca^{++} and 2OH^- , and by calcium sulphate are Ca^{++} and SO_4^{--} .

In ordinary chemical formulas, atoms and radicals are represented as united, *e.g.* Cl_2 , CaCl_2 , $\text{Ca}(\text{OH})_2$. But when the molecule dissociates, independent particles (ions) are formed. Therefore we represent ions as separate particles. That is, the Cl_2 in CaCl_2 becomes 2Cl^- or $\text{Cl}^- + \text{Cl}^-$, but not Cl_2^- .

234. A new definition of acid and base. — Specific prop-

erties are exhibited by solutions of typical acids and bases. Thus, acids have a sour taste and turn litmus red; bases have a bitter taste and turn litmus blue. When these properties are interpreted by the theory of ionization, interesting and important conclusions result. Acids, bases, and salts are electrolytes. Hence their solutions contain ions, and the properties of such solutions are ascribed to the ions. According to the theory of ionization, then, **an acid** is a compound whose solution contains hydrogen ions (H^+), while **a base** is a compound whose solution contains hydroxyl ions (OH^-). These definitions should be compared with those previously given (161–165).

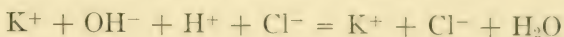
235. Salts and ionization. — Salts may be defined in several ways. For example, they are compounds (other than water) resulting from neutralization of acids and bases. Again, they are formed by substituting (1) a metal for the hydrogen of an acid or (2) a non-metal for the hydroxyl of a base (163–165).

According to the theory of ionization, salts may be defined in two ways. *First*, salts are electrolytes which in solution yield neither hydrogen nor hydroxyl ions. *Second*, salts are compounds finally formed by the union of the positive ion of a base and the negative ion of an acid. Later we shall study different kinds of salts. (See 273, 293.)

236. A new definition of neutralization. — In 164 we saw that neutralization is a chemical change in which an acid and a base interact and form a salt and water. **Neutralization**, interpreted by the theory of ionization, is the combining of hydrogen and hydroxyl ions to form molecules of water. Suppose solutions of hydrochloric acid and potassium hydroxide are mixed in the proper proportions. The mixture at first contains ions of hydrogen, chlorine, potassium, and hydroxyl. But the hydrogen

and hydroxyl ions immediately unite to form molecules of water, because water does not dissociate to any appreciable extent. The final solution is thus rendered neutral by the removal of the hydrogen and the hydroxyl ions — the acidic and basic constituents respectively.

The ionic equation expressing the neutralization of potassium hydroxide by hydrochloric acid is: —



The potassium and chloride ions move freely about in the solution. If the solution is evaporated, the ions unite as it becomes concentrated until nothing remains except the neutral salt potassium chloride. Since neutralization is the combining of hydrogen and hydroxyl ions to form water, the general ionic equation for neutralization is: —



237. Interpretation of certain facts by the theory of ionization. — The theory of ionization, like other theories, must meet one important requirement, *i.e.* it must explain facts derived from experiment. We shall now interpret certain facts by this theory.

238. Behavior of solutions toward an electric current. — Water itself conducts electricity very slightly indeed. If solutions are subjected to the action of an electric current, the results vary. Solutions of some substances do not conduct electricity. Whereas solutions of certain substances conduct electricity readily; these substances are acids, bases, and salts.

A simple experiment enables us to find out what substances are **electrolytes** and what are **non-electrolytes**, *i.e.* what substances form conducting solutions and what form non-conducting. The apparatus is shown in Fig. 84. It consists of a beaker A containing the

solution, into which dip two pieces of platinum, *B* and *C*, called electrodes, through which the current enters and leaves the solution. The wire from the electrode *C* and the wire *E* from the electric light bulb *D* are connected with the electric light system. The wire from

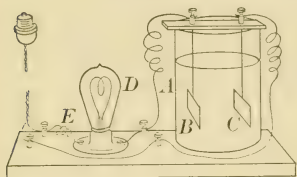


Fig. 84. — Apparatus for showing that only solutions of acids, bases, and salts conduct an electric current

the electrode *B* is also connected with the electric light bulb *D*. When the current is turned on, the bulb glows if the solution contains an electrolyte. For example, if solutions of hydrochloric acid, sodium hydroxide, and calcium chloride are tried in succession, the bulb glows brightly. But the bulb does not glow if solutions of sugar, alcohol, or glycerin are used.

Thus we see that *only solutions of acids, bases, and salts are electrolytes*. This fact is readily interpreted by the theory of ionization. Solutions of acids, bases, and salts, according to the theory, contain electrically charged particles — ions. Whereas solutions of other substances do not. Hence, when an electric current is introduced into solutions of acids, bases, or salts, particles *already charged with electricity* are there to conduct the current. No such particles are in solutions of other substances; hence such solutions cannot conduct an electric current.

239. Chemical reactions in solutions of acids, bases, and salts. — Dry potassium chloride and dry silver nitrate do not interact chemically, but if their solutions are mixed, a precipitate of silver chloride is immediately produced. Furthermore, *any* dissolved chloride will interact in the same way with silver nitrate or *any* soluble silver salt.

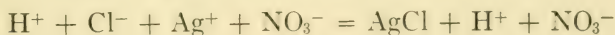
Let us interpret this fact by the theory of ionization. Solutions of potassium chloride and silver nitrate contain potassium ions (K^+), chloride ions (Cl^-), silver ions (Ag^+),

and nitrate ions (NO_3^-). Now when certain ions are introduced into the same solution, they react chemically. Thus, silver ions and chloride ions, if brought into the same solution, always combine to form insoluble silver chloride; and this precipitate serves as evidence of the chemical change. According to the theory, the source of the silver ions and the chloride ions is immaterial. And it is a fact that hydrochloric acid and solutions of different chlorides precipitate silver chloride from a solution containing silver ions, whether the silver ions are furnished by silver nitrate, silver sulphate, or any other soluble silver salt. This is the explanation offered by the theory of ionization for the precipitation of silver chloride, which you will recall is the usual test for hydrochloric acid and all soluble chlorides (160). The test is a test for ions (Cl^- and Ag^+).

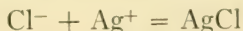
The ordinary equation for this test is: —



The corresponding **ionic equation** is: —



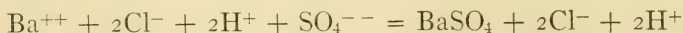
A general form of this equation is: —



On the other hand, substances quite similar in name and related in composition do not react alike. Thus, no chemical action is observed when solutions of potassium *chlorate* and silver nitrate are mixed, despite the fact that the solutions contain ions and that chlorine is a constituent of potassium chlorate. This apparent contradiction is readily explained by the theory. Potassium chlorate solution contains potassium ions (K^+) and chlorate ions (ClO_3^-), and when silver nitrate solution is added, the solution con-

tains two more kinds of ions — silver ions (Ag^+), and nitrate ions (NO_3^-). But compounds which might be formed by the various combinations of these ions are soluble. Hence the ions remain uncombined, for the most part, in the solution. Silver nitrate is effective in testing for chlorine compounds which yield chloride ions but not for other chlorine compounds, such as potassium chlorate (KClO_3).

Similarly, the test for sulphuric acid and all soluble sulphates is the formation of insoluble barium sulphate (BaSO_4) upon the addition of a solution of barium chloride or any other soluble barium compound. Sulphuric acid and sulphate solutions contain sulphate ions (SO_4^{--}), which combine with barium ions (Ba^{++}) furnished by the soluble barium compound. But this test is not applicable to other sulphur compounds, such as sulphides, sulphites, and thio-sulphates, because solutions of these sulphur compounds do not contain sulphate ions. The ionic equation for the usual test for a sulphate is: —



In the laboratory many of our common tests involving acids, bases, and salts are ionic reactions, *i.e.* reactions in which certain ions formed by dissociation reunite into a precipitate.

240. Electrolysis. — The simple experiments with solutions of acids, bases, and salts described in **238** (in which the bulb glowed) are examples of electrolysis. **Electrolysis** is the term applied to the series of changes accompanying the passage of an electric current through a solution of an acid, base, or salt. The facts connected with electrolysis can be adequately interpreted by the theory of ionization.

If hydrochloric acid is put in the Hofmann apparatus (provided with carbon instead of platinum electrodes), and an electric current is passed through the acid, bubbles

of gas rise from each electrode — hydrogen from one and chlorine from the other.

Let us interpret this example of electrolysis by the theory of ionization.

(1) The solution of hydrochloric acid contains hydrogen chloride molecules, hydrogen ions (H^+), and chloride ions (Cl^-). These ions are in the solution before the electric current is turned on.

(2) When the electric current is turned on, the electrodes become charged with electricity — the anode positively (+) and the cathode negatively (-).

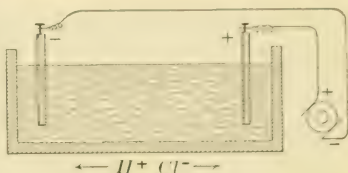


Fig. 85. — Sketch to illustrate the electrolysis of hydrochloric acid

(3) According to an old principle, bodies charged with the same kind (*e.g.* plus) of electricity repel each other; whereas bodies charged with different kinds (*i.e.* plus and minus) attract each other. In other words, the negative electrode (cathode) attracts the positive ions (cations) and repels the negative ions (anions). At the same time the positive electrode (anode) attracts the negative ions (anions) and repels the positive ions (cations). As a result of this attraction and repulsion the ions actually move toward the electrodes and, of course, carry their electric charges with them. Anions go to the anode and cations to the cathode.

In this case, hydrogen ions (H^+) go to the cathode and chloride ions (Cl^-) go to the anode (Fig. 85). This migration of ions, as it is called, was first studied carefully by the English scientist Faraday (Fig. 86), who named the charged particle “ion” from a Greek word meaning wanderer. The term *ion* thus emphasizes the fact that in an electrolytic solution the charged particles move about; when the

current of electricity is passed through the solution, these movements are regulated, so to speak, negative ions migrating to the positive electrode and positive ions to the negative electrode.

(4) As soon as the ions come in contact with their respective electrodes they

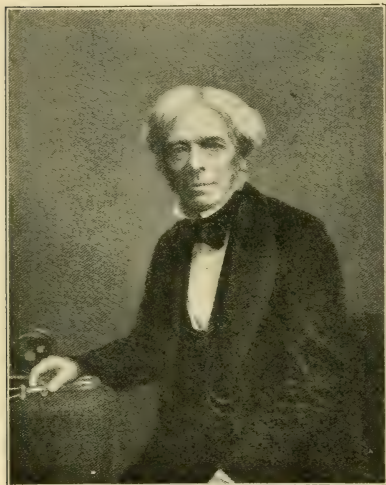


Fig. 86. — Faraday (1791-1867)

act in accordance with another long-established principle; that is, they lose their electric charges. In other words, when the positive ions, or cations (H^+), touch the cathode, the electric charges on the ions are neutralized. Electric charges, equal in quantity, but opposite in kind, are lost by the cathode; but are constantly renewed by the battery or dynamo. The

hydrogen ions (H^+) once deprived of their electric charges do not regain them but immediately become ordinary, uncharged hydrogen atoms (H) which combine and escape as molecules of hydrogen gas (H_2). Similarly, the negative ions, or anions (Cl^-), migrate to the anode, lose their charges, become chlorine atoms (Cl), and escape as chlorine gas (Cl_2). As a final result of the electrolysis of hydrochloric acid, hydrogen and chlorine are the sole products.

241. Electrolysis sometimes yields secondary products. — When a solution of sodium hydroxide undergoes electrolysis, hydrogen is liberated at the cathode and oxygen

at the anode. The electrolysis proceeds as usual, the cations (sodium ions — Na^+) migrate to the cathode and the anions (hydroxyl ions — OH^-) to the anode. As the ions are discharged, chemical changes take place. The sodium atoms (Na) which are produced at the cathode, react with the water (in the solution), forming hydrogen and sodium hydroxide. The unstable hydroxyl radicals (OH) which are produced at the anode break down into oxygen (O_2) and water (H_2O). Hence the final result is the production of two secondary products, viz. hydrogen at the cathode and oxygen at the anode. We might summarize the process as follows:—

(1) Ionization, $\text{NaOH} = \text{Na}^+ + \text{OH}^-$

(2) At the cathode, $2\text{Na} + 2\text{H}_2\text{O} = \text{H}_2 + 2\text{NaOH}$

(3) At the anode, $4\text{OH} = \text{O}_2 + 2\text{H}_2\text{O}$

The electrolysis of copper sulphate adds one more point. In a copper sulphate solution the ions are copper ions (Cu^{++}) and sulphate ions (SO_4^{--}). When the electric current is passed through the solution, the copper ions (Cu^{++}) migrate to the cathode, lose their electric charges, become copper atoms (Cu), and adhere as metallic copper to the cathode. The sulphate ions (SO_4^{--}) lose their electric charges at the anode and immediately interact with the water around the anode, forming sulphuric acid (H_2SO_4) and oxygen atoms (O), which unite into molecules (O_2) and escape from the solution as a gas. But the sulphuric acid mingles with the solution and dissociates into its ions, and continues to participate in the process.

The so-called electrolysis of water (88) is interpreted as follows: Water itself does not conduct electricity to an extent which is comparable with the behavior of an electrolytic solution, because water dissociates only inappreciably and therefore gives only an exceedingly

small number of ions. However, if sulphuric acid is added, the solution will be provided with hydrogen ions (H^+) and sulphate ions (SO_4^{--}). When an electric current is passed through this solution, hydrogen ions migrate to the cathode, lose their electric charges, become hydrogen atoms (H) and escape as hydrogen gas (H_2). The SO_4 ions migrate to the anode, lose their electric charges, and interact with the water to form sulphuric acid and oxygen. The oxygen (O_2) escapes as a gas, while the sulphuric acid continues to play the usual part in the process.

After the electrolysis has proceeded some time, the solution will be found to contain the same weight of sulphuric acid but less water — in fact, the decrease in the weight of water equals the weight of the liberated gases.

242. Another definition of electrolysis. — We may now re-define or describe **electrolysis** as ionic migration induced by the electric current, the ions moving to their respective electrodes, where they are transformed into atoms or radicals which escape wholly or in part as elements, or which form various products by interaction with the water of the solution.

243. Practical applications of electrolysis. — Electrotyping and electroplating consist in depositing a thin film of metal upon a surface. The process of **electrotyping** is substantially as follows: The page of type, for example, is first reproduced in wax. This exact impression is next covered with powdered graphite to make it conduct electricity. The coated mold is then suspended as the cathode in an acid solution of copper sulphate; the anode is a plate or bar of copper. When the electric current is passed through the solution, electrolysis occurs, and copper is deposited upon the mold in a film of any desired thickness. The exact copper copy is stripped from the mold, backed with metal, and used instead of the type for printing. The process of **electroplating** differs from electrotyping in only one essential, viz. in electroplating the deposited film is not removed from the object.

244. Boiling and freezing points of solutions. — Solutions boil at a higher temperature and freeze at a lower temperature than water. When 1 mole (*i.e.* the number of

grams numerically equal to the molecular weight — 204) of a non-electrolyte, such as alcohol, is dissolved in 1000 grams of water, the boiling point is raised from $100^{\circ}\text{C}.$ to $100.52^{\circ}\text{C}.$, and the freezing point is lowered from $0^{\circ}\text{C}.$ to $-1.86^{\circ}\text{C}.$ Whereas when solutions of electrolytes, *i.e.* acids, bases, and salts, are experimented with, the boiling point is higher and the freezing point is lower than that produced by non-electrolytes under parallel conditions. Thus, 1 mole of sodium chloride will cause a change in temperature nearly twice that produced by alcohol. Solutions of all electrolytes behave in the same way, though they differ in the amount of change. To sum up the results of experiments, we may say that **acids, bases, and salts cause abnormal raising of the boiling point and abnormal lowering of the freezing point.**

According to the theory of ionization, solutions of non-electrolytes contain only molecules, while solutions of electrolytes contain molecules *and ions* — the number of particles depending on the substance and the concentration of the solution. Hence the number of particles (molecules and ions) moving about freely in the electrolytic solution is greater than in the non-electrolytic solution. Ions have the same effect as molecules on the boiling and freezing points of a solution. Hence the greater the number of particles the greater should be the raising of the boiling point and the lowering of the freezing point. This is the fact. In other words, the theory of ionization furnishes an acceptable explanation of the abnormal boiling and freezing points of solutions of acids, bases, and salts.

The agreement between fact and theory is still further confirmed when molecular weights are determined by the freezing point or the boiling point method — a method too complicated to explain here. It is found that the molec-

ular weights of non-electrolytes agree with the values found by other methods, whereas in the case of electrolytes (*i.e.* acids, bases, and salts), not only do the values disagree with those found by other methods but the values also vary with the concentration of the solution.

245. What ions are in a solution? — As a rule, the ions formed by an electrolyte are the charged atom or group corresponding to the two parts of the compound. Thus, nitric acid consists of the two parts H and NO_3 , and the ions are H^+ and NO_3^- . Similarly, the parts of sodium hydroxide are Na and OH, and the ions are Na^+ and OH^- .

The ions normally formed by the ionization of acids, bases, and salts are given in the accompanying table of ions.

TABLE OF IONS

ELEMENT OR RADICAL	ION	ELEMENT OR RADICAL	ION	ELEMENT OR RADICAL	ION
Ammonium . . .	NH_4^+	Barium . . .	Ba^{++}	Aluminium	Al^{+++}
Hydrogen . . .	H^+	Calcium . . .	Ca^{++}	Antimony	Sb^{+++}
Mercury (ous)	Hg^+	Copper . . .	Cu^{++}	Bismuth . . .	Bi^{+++}
Potassium . . .	K^+	Iron (ous) . .	Fe^{++}	Iron (ic) . . .	Fe^{+++}
Silver	Ag^+	Lead	Pb^{++}		
Sodium	Na^+	Magnesium	Mg^{++}		
Bromide	Br^-	Mercury (ic)	Hg^{++}	Tin (ic)	Sn^{++++}
Chlorate	ClO_3^-	Tin (ous) . . .	Sn^{++}		
Chloride	Cl^-	Zinc	Zn^{++}		
Hydroxyl	OH^-	Carbonate . . .	CO_3^{--}		
Iodide	I^-	Chromate . . .	CrO_4^{--}		
Nitrate	NO_3^-	Dichromate	$\text{Cr}_2\text{O}_7^{--}$		
		Sulphate	SO_4^{--}		
		Sulphide	S^{--}		

246. What electric charges are on ions? — As repeatedly stated, certain ions (cations) carry a positive charge and others (anions) a negative charge. These can be selected,

of course, from the table of ions. It is convenient, however, to remember these simple rules regarding the *kind* of charge:—

(1) Hydrogen and metals form positive ions or cations (*e.g.* H^+ , Cu^{++}).

(2) Non-metals—except hydrogen—form negative ions or anions (*e.g.* Cl^-).

(3) Characteristic radicals of electrolytes form negative ions or anions (*e.g.* NO_3^- , SO_4^{--} , OH^-).

Special kinds can be found in the table or often under the compound itself. It is well to remember that the ion corresponding to the common radical ammonium (NH_4) is NH_4^+ .

The *number* of electric charges on an ion is equal to the valence of the corresponding atom or radical (221). Thus Na^I and Na^+ , Ba^{II} and Ba^{++} , SO_4^{II} and SO_4^{--} , Al^{III} and Al^{+++} . Moreover, just as the total valences of the two parts of a compound are equal, so the total number of each kind of charges (+ and −) is equal. For example, Na^ICl^I and Na^+ , Cl^- ; $\text{Al}_2^{III\ III}(\text{SO}_4)_3^{II\ II\ II}$ and 2Al^{+++} , 3SO_4^{--} . We may define **the valence of an ion** as the number of electric charges it carries.

247. Degree of ionization of acids, bases, and salts.—Except in unusual cases solutions of acids, bases, and salts contain both molecules and ions. That is, not all the molecules dissociate into ions. The degree of dissociation depends upon the concentration of the solution and also upon the electrolyte itself. In concentrated solutions the number of molecules is large. As the solution is diluted, more and more molecules dissociate into ions. Thus, in sodium hydroxide solution containing about 40 gm. in a liter the per cent of the ionized base is 73, whereas it is 90 in a solution containing 4 gm. in a liter. In contrast

to this, the degree of dissociation of acetic acid solutions containing respectively 60 gm. and 6 gm. in a liter is only 0.4 and 1.3 per cent of ionized acid. This means that acetic acid is weak; it contains a small per cent of ions. Whereas sodium hydroxide is strong; it contains a large per cent of ions. In contrast, nitric acid is a strong acid and ammonium hydroxide is a weak base.

Strong acids and bases are almost completely dissociated in dilute solutions, and weak ones are only slightly dissociated. We do not call salts "weak" or "strong," because they dissociate to about the same degree (unless they undergo hydrolysis (452)).

The approximate per cent of dissociation of certain acids, bases, and salts in solutions of the same relative concentration and at the same temperature is shown in the accompanying Table of Per Cent of Ionization.

TABLE OF PER CENT OF IONIZATION

SUBSTANCE	IONS	PER CENT OF IONIZATION
Hydrochloric Acid	H^+, Cl^-	90
Nitric Acid	H^+, NO_3^-	90
Sulphuric Acid	H^+, HSO_4^-	60
Acetic Acid	$H^+, C_2H_3O_2^-$	1.3
Potassium Hydroxide	K^+, OH^-	90
Sodium Hydroxide	Na^+, OH^-	90
Ammonium Hydroxide	NH_4^+, OH^-	1.4
Potassium Chloride	K^+, Cl^-	86
Silver Nitrate	Ag^+, NO_3^-	86
Barium Chloride	$Ba^{++}, 2Cl^-$	72

EXERCISES

1. Prepare a summary of this chapter.
2. State the theory of ionization. Illustrate it. State briefly the facts that support the theory.

3. Define and illustrate ion, anion, cation, electrode, anode, cathode, positive electrode, negative electrode.
4. Distinguish between an atom and an ion of potassium. How is each represented?
5. Name the ions in a solution of (a) hydrochloric acid, (b) sodium chlorate, (c) calcium hydroxide, (d) sodium nitrate, (e) zinc sulphate.
6. Learn the chemical expression for these ionized elements or radicals: (a) Hydrogen, sodium, potassium, silver, ammonium; (b) chloride, nitrate, hydroxyl; (c) calcium, barium, copper, zinc, magnesium, lead, iron (ous); (d) sulphate, carbonate; (e) aluminium, iron (ic).
7. Interpret neutralization by the theory of ionization. Write the fundamental equation for neutralization.
8. Interpret by the theory of ionization (a) test for a chloride; (b) test for a sulphate.
9. Define acid, base, and salt in terms of the theory of ionization.
10. Define electrolysis. Interpret electrolysis of (a) hydrochloric acid, (b) sodium hydroxide, (c) copper sulphate by the theory of ionization.
11. Write ionic equations for (a) potassium chloride and silver nitrate form silver chloride and potassium sulphate, and (b) barium nitrate and sodium sulphate form barium sulphate and sodium nitrate.
12. Describe fully the electrolysis of sodium sulphate solution.
13. What is the difference between strong and weak electrolytes?
14. Topics for review and home study: (a) Electroplating, (b) Arrhenius, (c) Valence, (d) Faraday's work on electrolysis, (e) Prepare a list of the new chemical words in this chapter and define each, (f) Degree of ionization of acids, bases, and salts.

PROBLEMS (REVIEW)

1. If 36 gm. of copper are heated in air until there is no farther increase in weight, what is the name, formula, and weight of the product?
Ans. 45.07 gm.
2. Equal weights of sodium and calcium interact with water, and the liberated gas is collected. Which metal yields the larger volume? Write the equation for each reaction.
3. How many grams of zinc must be used with hydrochloric acid to produce 750 cc. of dry hydrogen at 20° C. and 765 mm.? *Ans.* 2.05 gm.
4. At what temperature will 1 l. of chlorine weigh the same as 1 l. of hydrogen? (Assume constant pressure.)
5. One gram of a metal liberated 1.242 l. of hydrogen from hydrochloric acid. The specific heat of the metal was found to be about 0.23. Calculate (a) the equivalent weight and (b) atomic weight of the metal. What is the name of the metal? What is its valence?

CHAPTER XIX

SULPHUR AND SULPHIDES

248. Introduction. — Sulphur is a familiar and useful element. This element, its compounds, and the various chemicals derived from it play a fundamental, and often indispensable, part in many industries. It is an ingredient of gunpowder. Considerable is used in the manufacture of fireworks. Large quantities are consumed in the rubber industry, especially in making automobile tires. In the paper industry, sulphur is employed in making the sulphite needed to convert the wood into pulp. Sulphur is a constituent of mixtures for killing insect pests. These mixtures, *e.g.* lime-sulphur spray, liberate sulphur upon the injurious insect. Sulphur itself is also used as an insecticide, especially for killing *Phylloxera* — an insect which destroys grapevines.

Large quantities of sulphur are used in making sulphur compounds, such as sulphur dioxide (SO_2), sulphur monochloride (S_2Cl_2), carbon disulphide (CS_2), and especially sulphuric acid (H_2SO_4).

249. Occurrence. — Large deposits of free sulphur occur in volcanic regions, such as Japan and Mexico. Other deposits, as in Sicily, were doubtless formed by the action of microorganisms on calcium sulphate.

Sulphur compounds are abundant, *e.g.* lead sulphide (galena, PbS), zinc sulphide (sphalerite or zinc blende, ZnS), mercuric sulphide (cinnabar, HgS), copper sulphide (chalcocite, Cu_2S , and chalcopyrite, CuFeS_2), iron sulphide

(iron pyrites, FeS_2), and calcium sulphate (gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$).

Volcanic gases often contain sulphur dioxide (SO_2), and hydrogen sulphide (H_2S) is found in the water of sulphur springs. Sulphur is a constituent of certain organic compounds present in onions, horseradish, mustard, and eggs. Some varieties of coal and petroleum contain sulphur compounds.

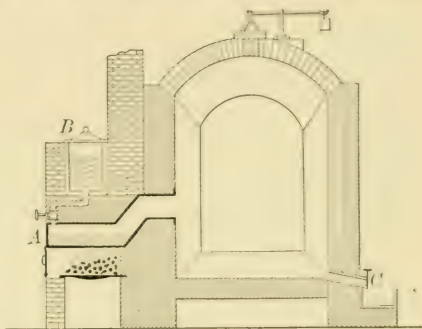


Fig. 87. — Apparatus for purifying sulphur by distillation

250. The sulphur industry. — Until about 1903 Sicily furnished most of the sulphur. Enough sulphur for domestic and foreign uses is now readily obtained from the large deposits in Louisiana and Texas.

In Sicily the deposits are not deep. The sulphur deposit is dug and removed from the mine by hand labor. The mass, which contains a large per cent of rock and earth, is piled loosely in a heap and ignited at the bottom. Some of the sulphur burns and the heat melts the rest, which drains away from the impurities.

The crude sulphur may be purified by distillation in an apparatus like that shown in Fig. 87. The melted sulphur flows from the reservoir *B* into the retort *A*, where it is boiled. The vapors pass into the large brick chamber and condense upon the cold walls as a fine powder, called **flowers of sulphur**. As the operation continues, the walls become hot, and the sulphur collects on the floor as a liquid; this is drawn off through the tap *C* into cylindrical wooden molds and allowed to cool. These sticks are called **roll sulphur** or **brimstone**.

In the United States the sulphur deposits are from 500 to 1000 feet deep. The sulphur is brought to the surface

by an ingenious method devised by American chemists. A hole is drilled through the overlying soil, sand, and rock into the sulphur deposits below. The well, as it is called,

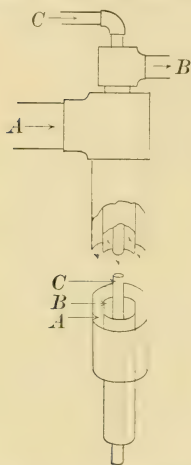


Fig. 88. — The system of pipes used in the United States to melt sulphur and bring it to the surface

is equipped with a set of pipes, one inside the other. The pipes, inclosed in a casing, are driven down through the hole (Fig. 88). The outermost pipe is the casing (not shown in the figure). The remaining pipes are the essential ones; let us call them *A*, *B*, and *C*. Through *A* water at 170°C . and under 100 pounds pressure is forced down to the bottom; this very hot water flows out into a large area around the well and melts the sulphur, which collects in a pool at the bottom of the pipes. Through *C* (the smallest pipe) hot air is forced down and forms a froth with the sulphur. This froth, owing to the pressure of the hot water and air, rises through *B*

(the middle of the three pipes) and flows out at the surface into a large wooden bin, where it cools and solidifies into huge blocks (Fig. 89).

A single well often produces over 500 tons of sulphur a day. Some of the blocks contain as much as 100,000 tons of sulphur. When the whole block is cold, the wooden sides of the bin are removed, the sulphur is blasted into fragments, and loaded into cars by steam shovels (Fig. 90). The American sulphur industry is conducted on a prodigious scale, and yields large quantities of sulphur, which is so pure (about 99.5 per cent) it can be used without further treatment.

251. Properties of sulphur. — Sulphur is a pale yellow, brittle solid, which sometimes has a faint odor. It is insoluble in water and most acids. Most varieties dissolve

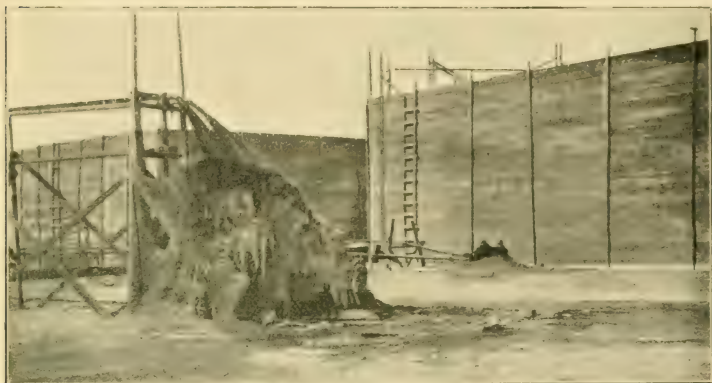


Fig. 89. — Sulphur flowing from a well (*left*). Huge block of solidified sulphur (*right*)

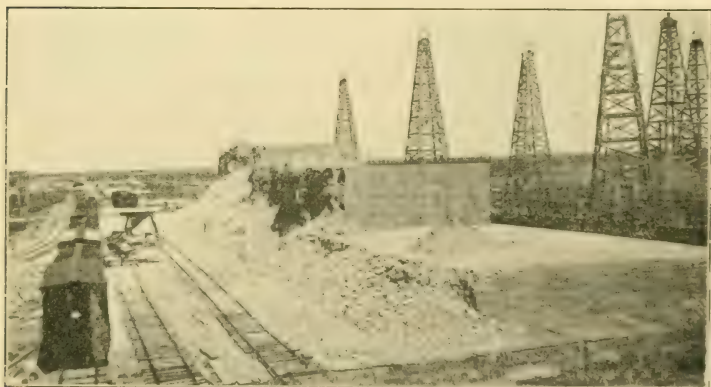


Fig. 90. — Loading sulphur into cars by a steam shovel (*left*), partly removed blocks of sulphur (*center*) derricks for drilling machinery (*right*)

readily in carbon disulphide and in sulphur chloride (*i.e.*, sulphur “monochloride,” S_2Cl_2). Sulphur does not

conduct electricity at all well. Its conductivity is lower than that of practically any other solid substance; this fact is sometimes expressed by saying sulphur is a good insulator. Nor does it conduct heat well, its heat conductivity being but one half that of cork and one quarter that of ice. The specific gravity of the solid is about 2, *i.e.* it is about twice as heavy as water.

When heated, sulphur melts at about 114° C. to a thin, pale yellow liquid. As the temperature rises, the liquid darkens and thickens; at about 160° C. it is dark brown and viscous, at about 230° C. it is black and too thick to flow from the vessel, while at about 445° C. it becomes thin again, boils, and turns into yellow sulphur vapor.

Sulphur molecules contain eight atoms (S_8) at low temperatures of the vapor, while at 800° C. the molecules contain two atoms (S_2). At about 2000° C., sulphur is monatomic (S).

252. Chemical conduct of sulphur. — Sulphur is an active element, especially when heated. It combines readily and directly with many elements. Thus, it ignites readily in the air and burns with a pale blue flame, forming sulphur dioxide gas (SO_2); if burned in oxygen, a little sulphur trioxide (SO_3) is also formed. Moist sulphur is oxidized, slowly, by the oxygen of the air. Thus: —



It combines directly with most metals, forming sulphides; the reaction is often accompanied with much heat and light, as in the case of zinc, copper, and iron (3). It also combines directly with carbon to form carbon disulphide (258), and with chlorine to form sulphur chloride (S_2Cl_2).

253. Different modifications of sulphur. — If sulphur is dissolved in carbon disulphide and the solution evaporated slowly, the sulphur is deposited as small crystals. Well-

formed crystals have eight sides and belong to the orthorhombic system (Fig. 91). It is called **orthorhombic**, or sometimes **rhombic**, sulphur. Crystallized native sulphur is orthorhombic. Roll sulphur and flowers of sulphur also are orthorhombic, though the crystals are so interlaced or so small that their shape is obscured.

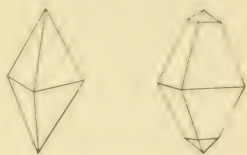


Fig. 91. — Orthorhombic crystals of sulphur

Another variety, called **monoclinic**, is obtained by letting melted sulphur cool slowly. If sulphur is melted in a crucible and the excess of liquid poured off as soon as crystals shoot out from the walls near the surface, the interior of the crucible is found to be lined with long, dark yellow, shining needles (Fig. 92). They are monoclinic crystals of sulphur. In a few days they turn dull and opaque, and in time change into small orthorhombic crystals. If monoclinic sulphur is kept above 96°C. , it does not change.



Fig. 92. — Section of a crucible showing monoclinic crystals of sulphur

These two modifications of sulphur have different physical properties. Orthorhombic sulphur has the specific gravity 2.07 and melts at 112.8°C. (if heated rapidly). The corresponding values of monoclinic sulphur are 1.96 and 119.25°C.

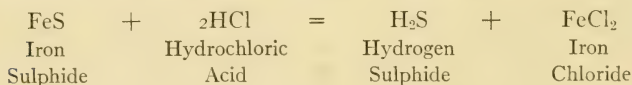
If sulphur is boiled or heated above the viscous stage and then cooled quickly by pouring into water, a tough, rubberlike, amber-colored solid is formed. It is called **amorphous** or **plastic** sulphur. It is insoluble in carbon disulphide. Plastic sulphur when first formed is non-crystalline and for this reason is called amorphous ("without form"). It is unstable, and soon becomes hard, brittle,

and yellow; after considerable time it changes in part into orthorhombic crystals. Its specific gravity is 1.89.

The different modifications of sulphur are elementary sulphur, though they have different properties. Each burns to sulphur dioxide, and the same weight of each yields the same weight of sulphur dioxide (*i.e.* 32 grams of each yields 64 grams of sulphur dioxide). An element which has different forms is called an **allotropic element**, and the different forms are called **allotropic forms** (278).

254. Hydrogen sulphide (H_2S) is the gaseous compound of sulphur and hydrogen with a notoriously bad smell. It occurs in the waters of some "sulphur springs" and in some volcanic gases. The air near sewers and cesspools often contains this gas, since it is one product of the decay of animal substances which contain sulphur. The albumin in the white part of eggs contains sulphur, and when eggs decay, hydrogen sulphide is formed; hence the bad smell.

255. Preparation of hydrogen sulphide. — The gas is usually prepared in the laboratory by the interaction of dilute hydrochloric or sulphuric acid and ferrous sulphide. The equation is: —

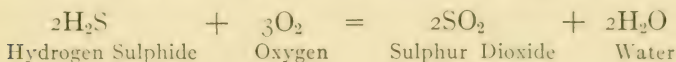


The apparatus shown in Fig. 13 may be used. All experiments involving hydrogen sulphide should be done in a hood.

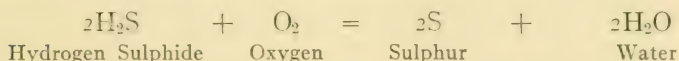
256. Properties of hydrogen sulphide. — Hydrogen sulphide is a colorless gas. It has the odor of rotten eggs. It is poisonous. A little, even if diluted with air, often produces headache and nausea, and a large quantity of the gas may prove fatal. One volume of water dissolves about three volumes of hydrogen sulphide gas at ordinary temperatures. The solution is often called **hydrogen sulphide water**, and can be used instead of the gas in many chemical

experiments; it has a weak acid reaction, and is sometimes called **hydrosulphuric acid**. In terms of the ionic theory the solution contains few ions (H^+ and S^{--}). Like all acids it forms salts; the salts are called **sulphides** (257).

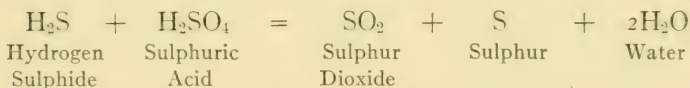
Hydrogen sulphide gas catches fire easily and burns with a bluish flame, forming sulphur dioxide and water thus:—



If the supply of air is insufficient, combustion is incomplete, and sulphur and water are formed, thus:—



Hydrogen sulphide reduces nitric acid and sulphuric acid; the equation for the latter reaction is:—

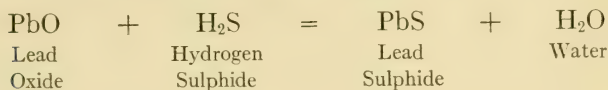


257. Sulphides may be regarded as salts of the weak acid hydrogen sulphide, though they are not always prepared directly from hydrogen sulphide. They can be produced by the direct union of sulphur and metals, as in the case of iron sulphide previously mentioned (3), or by exposing metals to the moist gas.

Sulphides are usually prepared in the laboratory by precipitation. That is, the gas is passed into solutions of certain salts, or hydrogen sulphide water is added.

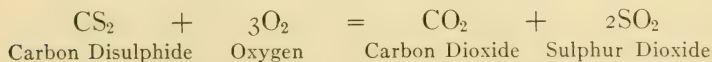
Many sulphides are black, one (zinc sulphide) is white, and several have a characteristic color. Thus, arsenic sulphide is pale yellow, manganese sulphide is flesh colored, and antimony sulphide is orange red. The color often affords a ready means of identifying each sulphide.

Copper, tin, lead, and silver react readily with hydrogen sulphide and are rapidly tarnished by exposure to the gas. Silverware turns brown or black, especially in houses heated by coal and lighted by coal gas, probably owing to the small quantity of hydrogen sulphide from these sources. A brown film (silver sulphide) also coats silver spoons which are put into mustard, eggs, and some vegetables, such as cauliflower. Lead compounds are blackened by this gas, owing to the formation of lead sulphide, thus: —



For this reason buildings painted with “white lead” paint often become dark, and, similarly, oil paintings are discolored. The blackening of paper moistened with a solution of lead nitrate or acetate is the customary **test for hydrogen sulphide**.

258. Carbon disulphide (CS_2) when pure, is a clear, colorless, heavy liquid, with an agreeable odor, but the commercial substance is yellow and has an exceedingly offensive smell. It is poisonous. It vaporizes very readily and is highly inflammable. The equation for its combustion is: —



Since its vapor burns readily and catches fire easily, the liquid must be used with care. No flames should be near when carbon disulphide is being evaporated or used as a solvent.

Carbon disulphide is practically insoluble in water. It is a useful solvent because it dissolves rubber, gums, fats,

iodine, camphor, and some forms of sulphur. It is a highly refracting liquid, and hollow glass prisms filled with it are used to decompose light. Considerable is used to kill insects on both living and dried plants (*e.g.* in museums), and to exterminate ants, mice, moles, and woodchucks.

Carbon disulphide is manufactured from carbon and sulphur by an electrothermal process. A diagram of the furnace is shown in Fig. 93. Several groups of carbon electrodes (*EE*) are set into the base of the furnace, coke is packed loosely between them, and the body of the furnace is filled with charcoal (*C*). Sulphur is introduced at suitable points (*S, S, S*), and coke is fed in through *K, K*. When the electric current passes, the heat caused by the resistance offered by the coke melts the sulphur (*Z*), which rises and unites with the heated carbon above the electrodes. The vapors of the carbon disulphide escape through a large pipe (*P*) and are condensed in a special apparatus.

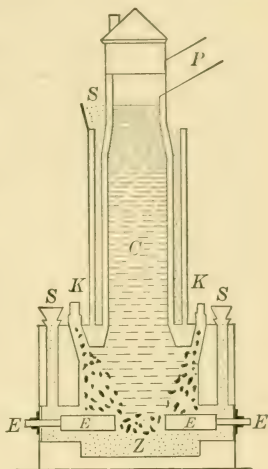


Fig. 93. — Electrothermal furnace for manufacturing carbon disulphide

EXERCISES

1. Where is free sulphur found? Name five or more native compounds of sulphur.
2. Give the name and formula of five metallic sulphides.
3. Summarize (*a*) the physical properties, and (*b*) the chemical conduct of sulphur.
4. State the uses of sulphur.
5. How is sulphur obtained from deposits in the United States? Draw (from memory) a diagram of the system of pipes.
6. Given several yellow powders, how would you prove by experiment which one is sulphur?
7. What is (*a*) roll sulphur, (*b*) brimstone, (*c*) rhombic sulphur, (*d*) monoclinic sulphur, (*e*) amorphous sulphur, (*f*) monatomic sulphur?
8. Compare rhombic and monoclinic sulphur.

9. How is hydrogen sulphide prepared? State the equation.
10. Summarize the properties of hydrogen sulphide.
11. State one or more tests for hydrogen sulphide.
12. Write these equations in the ordinary and the ionic form:
(a) Lead nitrate and hydrogen sulphide form lead sulphide and nitric acid. (b) Copper sulphate and hydrogen sulphide form copper sulphide and sulphuric acid.
13. Describe the manufacture of carbon disulphide. Draw (from memory) a diagram of the furnace.
14. Write the volumetric equation for the combustion of (a) hydrogen sulphide (with excess of air), and (b) carbon disulphide.

PROBLEMS

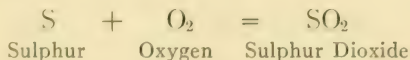
1. What is the approximate weight of sulphur in a bin 200 feet long, 80 feet wide, and 90 feet high? (NOTE. — A cubic foot of water weighs approximately 62 pounds.)
2. Calculate the weight of sulphur in (a) 500 gm. of pure FeS_2 , (b) a kilogram of CS_2 .
3. Calculate the weight of sulphur in (a) 77 gm. of pure H_2SO_4 , (b) 77 l. of H_2S at 20°C . and 755 mm.
4. Hydrochloric acid solution having the specific gravity of 1.2 contains 39.86 per cent of HCl (by weight). What (a) weight and (b) volume of hydrogen sulphide (at standard conditions) will be produced by the interaction of iron sulphide (FeS) and 2 l. of this acid?
5. If 100 cc. of hydrogen sulphide are burned in air, what volume of (a) oxygen is consumed and (b) sulphur dioxide produced?
6. Suppose a liter of carbon disulphide vapor burns in air. (a) What volume of oxygen is consumed? (b) What is the volume of each product?
7. Write the formula of the sulphide of hydrogen, sodium, silver, calcium, zinc, lead, aluminium, potassium, copper, NH_4 , Sn (ous).
8. Calculate the simplest formula corresponding to (a) $\text{S} = 30$, $\text{As} = 61$; (b) $\text{S} = 20.0$, $\text{As} = 70.1$.
9. Calculate the atomic weight of sulphur from (a) 10 gm. of silver yield 11.4815 gm. of silver sulphide (assume Ag_2S and $\text{Ag} = 107.88$); (b) 2 gm. of lead yield 2.0284 gm. of lead sulphate (make the correct assumptions).
10. Complete and balance (a) $\text{H}_2\text{S} + \text{---} = \text{CuS} + \text{---}$; (b) $\text{CdCl}_2 + \text{---} = \text{CdS} + \text{---}$

CHAPTER XX

SULPHUR OXIDES, ACIDS, AND SALTS

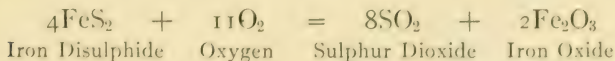
259. Introduction. — Sulphur forms two oxides — sulphur dioxide (SO_2) and sulphur trioxide (SO_3). There are two acids corresponding to these oxides — sulphurous acid (H_2SO_3) and sulphuric acid (H_2SO_4). Both acids form numerous salts.

260. Formation and preparation of sulphur dioxide. — When sulphur burns in air (or oxygen), sulphur dioxide is formed, thus: —



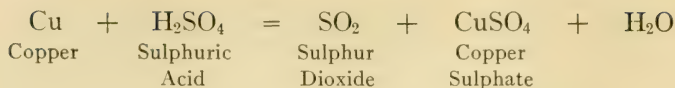
Many sulphur compounds, when burned, yield sulphur dioxide. The gas is also formed when certain sulphur compounds, *e.g.* sulphuric acid, are decomposed.

On an industrial scale, the gas is prepared by burning sulphur or by roasting metallic sulphides, especially iron disulphide (iron pyrites, FeS_2) in air, thus: —

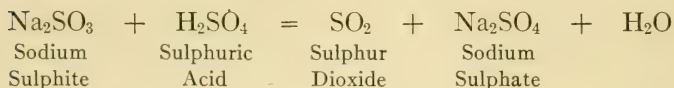


Both of these reactions (sulphur and sulphide) are utilized on a large scale in the manufacture of sulphuric acid.

In the laboratory two methods of preparation are used. (1) If copper and concentrated sulphuric acid are heated, a series of complex changes results finally in the evolution of sulphur dioxide. The equation may be written: —



(2) More commonly dilute sulphuric (or hydrochloric) acid is dropped upon a sulphite. The equation is:—



The sulphite method is safer and more convenient, especially for liberating a steady current of the gas. Sometimes the gas is obtained from a cylinder of liquid sulphur dioxide (Fig. 94).

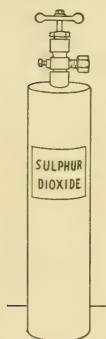


Fig. 94. — Cylinder of liquid sulphur dioxide

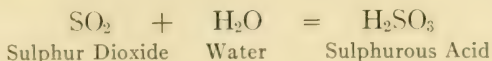
261. Properties of sulphur dioxide.— Sulphur dioxide is a colorless gas. Its odor is suffocating, being the well-known odor associated with burning sulphur. The gas is a little more than twice as heavy as air. A liter at 0° C. and 760 mm. weighs 2.9 gm. Sulphur dioxide is readily liquefied; the liquid is a common article of commerce and can be more conveniently used than similar liquids (*e.g.* chlorine or ammonia). The gas is very soluble in

water; at ordinary temperatures one volume of water dissolves about forty volumes of gas. This solution is sour and reddens blue litmus; besides sulphur dioxide it contains **sulphurous acid** (262).

Sulphur dioxide does not burn and will not support ordinary combustion.

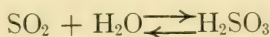
262. Sulphurous acid (H_2SO_3) is prepared by dissolving sulphur dioxide in water. The gas combines with the

water to some extent. The simplest equation expressing this fact is:—

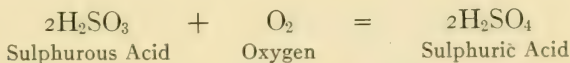


Sulphur dioxide is often called sulphurous anhydride, because it is the anhydride of sulphurous acid. Anhydrides of non-metals are acid anhydrides, *i.e.* non-metallic oxides which unite with water to form acids (266).

Sulphurous acid is unstable and decomposes readily into sulphur dioxide and water, especially when the solution is heated; solutions of sulphurous acid smell strongly of sulphur dioxide. The formation and decomposition may be represented as a reversible equation, thus:—



Sulphurous acid is readily oxidized. Solutions of the acid, if exposed to air, soon give a test for sulphuric acid, which is formed by the combining of the sulphurous acid with oxygen from the air. Oxidizing agents, such as potassium permanganate, produce this change quickly. The oxidation of sulphurous acid to sulphuric acid is expressed by this equation:—

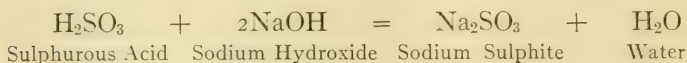


We can also describe this chemical change by saying sulphurous acid is a reducing agent.

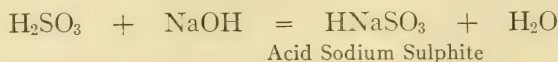
263. Salts of sulphurous acid.—Sulphurous acid forms two classes of salts—the normal and the acid **sulphites**. When the two atoms of hydrogen in sulphurous acid are replaced by a metal, the product is a **normal sulphite**. But if only one atom is replaced, the product is an **acid sulphite**.

Acids like sulphurous acid, which have two replaceable hydrogen atoms, are called **dibasic acids**.

Normal sodium sulphite (Na_2SO_3) is formed when sulphurous acid is neutralized by sodium hydroxide, thus:—



Acid sodium sulphite (HNaSO_3), often called bisulphite of soda, is formed when only half as much base is used, thus:—



Both kinds of salts yield sulphur dioxide by interaction with an acid (260 (2)). The acid salt is sometimes used as the antichlor to remove the excess of chlorine from bleached cotton cloth (150). It is also used in tanning, and in making starch, sugar, and paper.

Acid calcium sulphite ($\text{Ca}(\text{HSO}_3)_2$) is extensively used in one process of making paper from wood. The chips of wood are “cooked” in large vessels with a solution of acid calcium sulphite which dissolves the lignin and leaves cellulose (352, 354).

264. Uses of sulphur dioxide and sulphurous acid.—

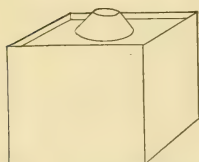


Fig. 95. — Sulphur candle for local fumigation

Vast quantities of sulphur dioxide are used in manufacturing sulphuric acid (267) and acid calcium sulphite (263). Infected clothing and rooms are sometimes fumigated with sulphur dioxide; the gas for household use may be obtained by burning a “sulphur candle” (Fig. 95). Dried fruits, canned corn, cherries, and nuts are bleached by sulphur dioxide or sulphurous acid. The moist gas—really a weak sulphurous acid

solution — is used to bleach silk, hair, straw, paper, wool, and other substances which would be injured by chlorine. The effect of the moist gas can be shown by putting a wet colored flower into a bottle in which sulphur is burning; the flower soon loses its color. In some cases the bleached article, *e.g.* a straw hat, partially regains its color or becomes yellow. The effect of sulphur dioxide on organic matter is seen in localities where considerable gas escapes, *e.g.* near smelters and chemical works; trees, shrubs, and other kinds of vegetation are blighted or destroyed.

265. Preparation of sulphur trioxide. — Sulphur trioxide (SO_3) is produced to a slight extent when sulphur burns in air or in oxygen; it causes the white fumes often seen during the combustion. The reaction between sulphur dioxide and oxygen is very slow. It can be hastened by passing a mixture of sulphur dioxide and oxygen (or air) over hot platinum or asbestos coated with platinum. Other substances also hasten the chemical change. The platinum, as far as we know, does not participate in this reaction. It hastens a very slow chemical reaction.

As we have seen (**53**), substances which hasten a chemical reaction but are unchanged at the end of the process are called **catalyzers** or catalytic agents. Such a chemical reaction is said to be due to **catalysis** or catalytic action.

266. Properties of sulphur trioxide. — Above 15°C . sulphur trioxide is a liquid, which boils at 46°C . Below 15°C . it is a white solid. When exposed to moist air, it fumes strongly, owing to the formation of sulphuric acid; and when dropped into water it dissolves with a hissing sound and evolution of heat. The equation for the combination of sulphur trioxide and water is: —



Sulphur trioxide is called sulphuric anhydride. (Compare **261**.)

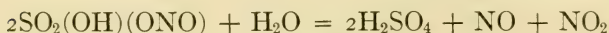
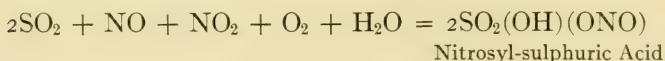
267. Manufacture of sulphuric acid. — Enormous quantities of sulphuric acid are manufactured by two processes, known as the lead chamber process and the contact process. In each process sulphur dioxide is oxidized to sulphur trioxide, which with water forms sulphuric acid. A general equation for the essential chemical change is: —



In the lead chamber process the oxidation is accomplished by nitrogen oxides; and in the contact process it is hastened by a catalyst.

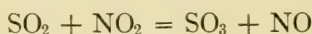
In the **lead chamber process** sulphur dioxide, air, steam, and nitrogen oxides are introduced into large lead chambers. These gases react and produce sulphuric acid, which collects on the floors of the lead chambers.

The chemical changes involved in this process are complex and variable. The two main reactions may be represented thus: —



According to some authorities, nitrogen trioxide (N_2O_3) is the active oxide. The interpretation is simpler, however, if we assume the presence of nitric oxide (NO) and nitrogen dioxide (NO_2).

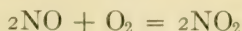
The main changes are three: (1) The sulphur dioxide is oxidized to sulphur trioxide by nitrogen dioxide, thus: —



(2) The sulphur trioxide with water forms sulphuric acid, thus: —



(3) The nitric oxide unites with oxygen (from air) and forms nitrogen dioxide, thus:—



Hence, nitric oxide acts as a carrier of oxygen, so to speak, from the air to the sulphur dioxide. Some authorities speak of the nitric oxide as a catalyst.

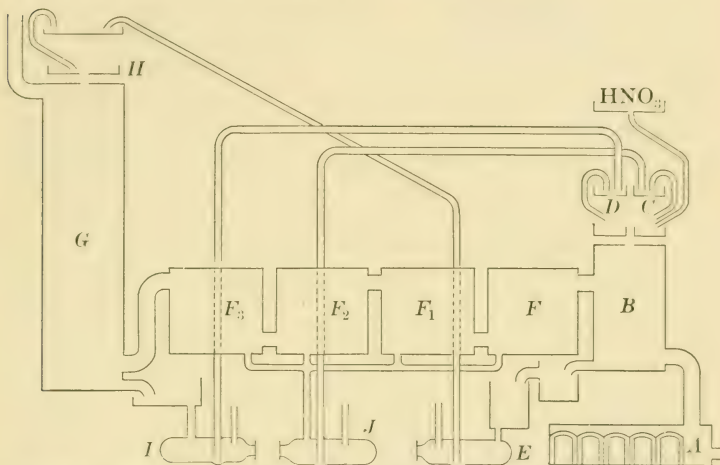


Fig. 96. — Diagram of plant for chamber process of manufacturing sulphuric acid

These equations show that the oxides of nitrogen play an important part in the manufacture of sulphuric acid. Theoretically only a small quantity of nitrogen oxides is needed to form an unlimited quantity of sulphuric acid. However, some escapes and must be replaced; this is done by putting nitric acid into the top of the Glover tower or injecting it into the chambers.

268. The construction and operation of a chamber acid plant. — The plant (Fig. 96) consists of two main parts: (a) the furnace for producing sulphur dioxide, and (b) the lead chambers together with the Glover and Gay-Lussac towers for changing the gaseous mixture into sulphuric acid.

The manufacturing operation is somewhat as follows: (1) Sulphur

or iron disulphide (FeS_2) is burned in a furnace (*A*) with enough air to change the sulphur into sulphur dioxide and to furnish the proper amount of oxygen for later changes. In some works the furnace is provided with "niter pots" to produce nitric acid vapor (*i.e.* nitrogen oxides).

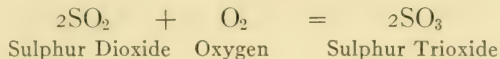
(2) The mixture of sulphur dioxide, nitrogen oxides, and air passes from the furnace into the bottom of the Glover tower (*B*). This is a tall tower filled with stones or pieces of earthenware over which flow two streams of sulphuric acid, one dilute (*C*) and the other (*D*) containing nitrogen dioxide (obtained from the Gay-Lussac tower acid). These acids cool the ascending gases; at the same time the dilute acid is deprived of water and the Gay-Lussac tower acid of its dissolved nitrogen dioxide. Hence concentrated acid flows out of the bottom of the Glover tower (*B*) into the "strong acid" blower (*E*), from which it is forced to the top of the Gay-Lussac tower for use as explained below; while from the top of the Glover tower sulphur dioxide, nitrogen oxides, and air pass into the first lead chamber (*F*). Here steam and nitric acid are introduced. The main chemical changes occur in this and the second chamber.

These chambers are huge boxes often having a total capacity of 150,000 cubic feet; the walls and floors are of sheet lead supported on a wooden framework, lead being a metal which is only slightly attacked by the chamber acid.

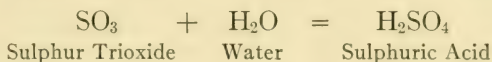
The nitrogen (from the original air) and the unused gases pass on (from the last chamber) into the bottom of the Gay-Lussac tower (*G*). This tower is filled with coke or earthenware over which flows concentrated sulphuric acid (*H*) (obtained from the blower *E* connected with the Glover tower), which absorbs the unused nitrogen dioxide. The "nitrose" acid flows from the bottom of the Gay-Lussac tower into a blower (*I*), whence it is forced to the top of the Glover tower, where, as stated above, the nitrogen dioxide is liberated.

(3) The acid produced in the chambers, which flows into *J*, contains from 60 to 70 per cent of the compound H_2SO_4 . For some uses, *e.g.* the manufacture of fertilizers, this acid needs no further treatment. Much of the acid, however, is concentrated by evaporation. It is first heated in lead-lined pans until the concentration is about 77 per cent, and finally in platinum, cast iron, or fused quartz vessels until the acid contains about 94 per cent of H_2SO_4 and has a specific gravity of 1.84.

269. Manufacture of sulphuric acid by the contact process. — In this process sulphur dioxide and air, well purified and heated to about 400°C. , are brought in contact with a catalyst, — platinum, or, in some plants, iron oxide (Fe_2O_3). The sulphur dioxide is thereby quickly oxidized to sulphur trioxide, thus:—



The sulphur trioxide is conducted into sulphuric acid containing a little water, because it is not absorbed quickly enough by water alone. The sulphur trioxide combines with the water, thereby producing sulphuric acid, thus:—



270. The construction and operation of a contact acid plant. — A sketch of the apparatus is shown in Fig. 97. The blower *A* forces

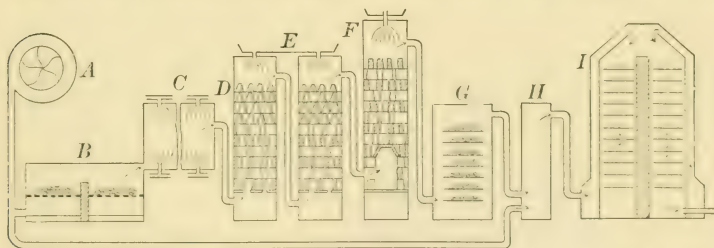


Fig. 97. — Sketch of the apparatus for making sulphuric acid by the contact process

air into the burner *B*, where the sulphur dioxide is formed by burning iron pyrites (FeS_2) or sulphur. The gases pass into the dust chamber *C*, where they are freed from sulphur dust and other solid impurities; this is an important step, for dust reduces the transforming power of the catalytic agent. The gases, cooled by the pipe *D*, are further cleaned in the scrubbers, which contain coke wet with water (*E*) and with sulphuric acid (*F*). The next step is the removal of arsenic compounds in the purifier *G*. During the combustion of

iron pyrites, arsenic compounds are liberated; traces of such compounds "poison" the platinum used as a catalytic agent and stop the formation of sulphur trioxide. The purified gases (mainly sulphur dioxide) then enter the mixer and heater *H*. Here a large excess of air is introduced from the blower and the whole mixture is heated to 400°C . This temperature is carefully regulated because at 400°C . the yield of sulphur trioxide is maximum (98–99 per cent).

The purified and heated mixture of sulphur dioxide and air passes into the contact chamber *I*. Here the gases come in contact with the catalyst and form sulphur trioxide. The catalyst, if platinum, consists of asbestos fibers coated with a very thin layer of metallic platinum and is spread out on plates or mixed with porous material in order to provide a large contact surface.

The final step is the transformation of the sulphur trioxide into sulphuric acid by combining with water; the trioxide is passed into the absorber (not shown). This is a large earthenware jug partly filled with sulphuric acid containing 2 to 3 per cent of water. In this liquid, all the sulphur trioxide combines with water; the supply of water is replenished to maintain the required concentration in the absorber.

271. Properties of sulphuric acid. — Sulphuric acid is an oily liquid, colorless when pure, but often brown from the presence of charred organic matter, such as dust and straw. The specific gravity of the commercial acid is about 1.84; thus it is nearly twice as heavy as water. It boils at about 338°C ., decomposing to some extent and forming dense, white, suffocating fumes.

When sulphuric acid is mixed with water, much heat is evolved. *The acid should always be poured into the water and the mixture should be stirred*, otherwise the intense heat may crack the vessel or spatter the hot acid. This tendency to absorb water is shown in many ways. The concentrated acid absorbs moisture from the air and from gases passed through it. It is often used in the laboratory to dry gases. Organic substances, such as wood,

paper, sugar, starch, and cotton, are charred by sulphuric acid (Fig. 98). Such compounds contain hydrogen and oxygen in the proportion to form water; these two elements are abstracted and carbon alone remains. Sulphuric acid also disintegrates the flesh, often causing serious burns, and if accidentally spilled on the hands or spattered on the face should be washed off immediately.

The interaction of sulphuric acid and metals varies. With many metals, dilute sulphuric acid forms hydrogen and the corresponding metallic sulphate. Thus, hydrogen is usually prepared in the laboratory from zinc and sulphuric

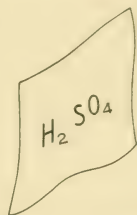
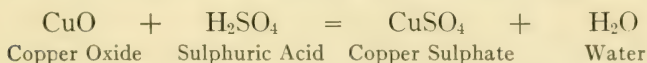
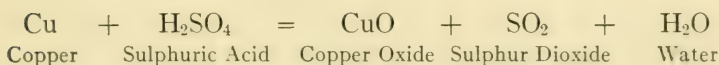


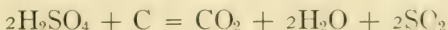
Fig. 98. — Paper charred by sulphuric acid

acid. Concentrated acid, especially if hot, converts most metals into an oxide, which is then transformed into the corresponding sulphate. Thus, the equations expressing the reactions with copper are:—



Iron is the only common metal that is not readily attacked by the concentrated acid, and advantage is taken of this property in transporting acid in bulk in iron tank cars.

Sulphuric acid unites with ammonia (NH_3) to form ammonium sulphate ($(\text{NH}_4)_2\text{SO}_4$). Hot concentrated acid oxidizes sulphur and carbon to sulphur dioxide and carbon dioxide. Thus:—



Owing to its high boiling point, sulphuric acid by inter-

action with the proper salt liberates acids having a low boiling point, *e.g.* hydrochloric and nitric acids (**153**, **183**).

Dilute solutions of sulphuric acid contain an abundance of hydrogen ions (H^+) and sulphate ions (SO_4^{--}). The HSO_4 ion is in solutions of certain concentration (**247**).

272. Uses of sulphuric acid. — Sulphuric acid is one of the most important substances. Directly or indirectly it is used in hundreds of industries upon which the comfort, prosperity, and progress of mankind depend. It is used in the manufacture of many acids. It is essential in one process for the manufacture of sodium bicarbonate, which has many uses. The petroleum industry requires large amounts. Enormous quantities are consumed in making fertilizers, alum, and other sulphates, nitroglycerin, glucose, dyes, and in various parts of such fundamental industries as dyeing, bleaching, metal cleaning, refining, and metallurgy.

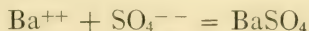
273. Sulphates. — Sulphuric acid is dibasic and forms two classes of salts — the **normal sulphates**, such as sodium sulphate (Na_2SO_4), and the **acid sulphates** (or bisulphates), such as acid sodium sulphate (HNaSO_4).

Most sulphates are soluble in water; only the sulphates of barium, strontium, and lead are insoluble, while calcium sulphate is but slightly soluble. Important sulphates are calcium sulphate (gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), barium sulphate (barite, barytes, heavy spar, BaSO_4), zinc sulphate (ZnSO_4 , and white vitriol, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$), copper sulphate (CuSO_4 , and blue vitriol or blue stone, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), iron sulphate (FeSO_4 , and green vitriol, copperas, or ferrous sulphate, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), sodium sulphate (Na_2SO_4 , and Glauber's salt, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$), and magnesium sulphate (MgSO_4 , and Epsom salts, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$). Sulphates are used in many industries.

274. The test for sulphuric acid or a soluble sulphate is the formation of white, insoluble barium sulphate upon the addition of barium chloride solution. Thus:—



Since sulphuric acid and solutions of sulphates contain SO_4 ions and barium chloride (or nitrate) contains Ba ions, the ionic equation for the reaction is:—



An insoluble sulphate fused on charcoal is reduced to a sulphide, which blackens a moist silver coin, owing to the formation of silver sulphide (Ag_2S); this is the usual **test**.

275. Fuming sulphuric acid ($\text{H}_2\text{S}_2\text{O}_7$), is made by mixing sulphur trioxide with sulphuric acid. This is the acid called sulphuric acid by the alchemists, who made it by heating moist ferrous sulphate. It is sometimes called Nordhausen sulphuric acid. It is a thick, brown liquid, which fumes strongly in the air, owing to the escape of sulphur trioxide. It is used in gas analysis to absorb ethylene and other illuminants, and in dyeing to dissolve indigo. If the fuming acid is cooled to 0°C ., crystals separate; they are called **pyro-sulphuric acid**. Its salts are called pyrosulphates.

276. Sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3$) is a salt of an unstable acid. It is sometimes incorrectly called sodium hyposulphite, or simply “*hypo*.” It is a white, crystalline solid, very soluble in water. The solution, used in excess, dissolves certain compounds of silver, *i.e.* AgCl , AgBr , AgI ; hence its extensive use in photography (589).

EXERCISES

1. Describe the lead chamber process of making sulphuric acid.
2. Starting with sulphur, how would you prepare successively sulphur dioxide, sulphur trioxide, sulphuric acid, hydrogen sulphide, and sulphur?
3. Describe the contact process of manufacturing sulphuric acid.
4. Enumerate the important uses of sulphuric acid.

5. What is (a) gypsum, (b) white vitriol, (c) green vitriol, (d) blue vitriol, (e) Glauber's salt, (f) oil of vitriol, (g) "hypo," (h) calcium bisulphite?

6. State the test for (a) sulphuric acid, (b) sulphurous acid, (c) a soluble sulphate, (d) an insoluble sulphate, (e) a sulphite, (f) H_2S .

7. Essay topics: (a) Uses of sulphuric acid. (b) Normal and acid sulphates. (c) Bleaching with sulphur dioxide.

8. Show how the two oxides of sulphur illustrate the law of multiple proportions.

9. Explain the following: (a) Bottles of concentrated sulphuric acid sometimes have a white deposit inside the bottle and a black one outside. (b) Dishes of concentrated sulphuric acid are often left inside of a chemical balance.

10. Write the formula of (a) the sulphite, (b) the acid sulphite, (c) the sulphate, (d) the acid sulphate of K, NH_4 , Ca, Pb, Ag, Ba, Zn.

PROBLEMS

1. Write the equation for the interaction of sodium sulphite and sulphuric acid. What weight and what volume (standard conditions) of sulphur dioxide can be prepared from 25 gm. of sodium sulphite (92 per cent pure)?

2. In Problem 1 what volume of sulphuric acid solution is needed, if the acid used has the specific gravity 1.45 and contains 55.07 per cent of H_2SO_4 by weight?

3. How much sulphur (99 per cent pure) is needed to manufacture 100 tons of sulphuric acid containing 5 per cent of water?

4. An oxide of sulphur contains 50 per cent of each element. If the atomic weights of oxygen and sulphur are respectively 16 and 32, what is the molecular formula of the compound?

5. A flask filled with water was found to weigh 72 gm., the flask alone weighing 22 gm. The flask filled with sulphuric acid weighed 114 gm. Calculate the specific gravity of the sulphuric acid.

6. Suppose a manufacturer of H_2SO_4 starts with 100 tons of sulphur and obtains the theoretical yield in each case: (a) What weight of oxygen is needed to burn the sulphur to sulphur dioxide? (b) What additional weight of oxygen to convert the sulphur dioxide to sulphur trioxide? (c) What weight of water to convert the sulphur trioxide to sulphuric acid? (d) And how much sulphuric acid is obtained?

7. What weight of pure H_2SO_4 can be manufactured from 150 tons (2000 lb. each) of iron pyrites containing 92 per cent of FeS_2 ?

8. What weight of sulphuric acid having a specific gravity of 1.84 is contained in a cylindrical tank 20 m. long and 1.3 m. in diameter?

9. What weight and what volume of sulphur dioxide (at standard conditions) will sulphuric acid and 57 gm. of copper produce?

10. Calculate the weight of sulphur in (a) 2000 lb. of sulphuric acid solution (93.19 per cent pure), and (b) 2 kg. of nitrosylsulphuric acid.

11. What weight of pure sulphuric acid can be made from 1000 tons of pure sulphur? From 1000 tons of pure FeS_2 ?

12. Calculate the atomic weight of sulphur from the following analyses of sulphur compounds: (a) S = 40 per cent, molecular weight = 80; (b) S = 23.529, m. w. = 136; (c) S = 20.125, m. w. = 159.

13. Calculate the simplest formulas corresponding to (a) S = 36.36, Fe = 63.63; (b) S = 53.33, Fe = 46.66; (c) S = 32.65, O = 65.31, H = 2.04; (d) S = 39.02, O = 58.53, H = 2.44.

14. How many liters of oxygen are needed (a) to form 10 liters of sulphur dioxide (from sulphur), and (b) to transform 10 liters of sulphur dioxide to sulphur trioxide?

CHAPTER XXI

CARBON (*Continued*) — CARBONIC ACID — CARBONATES

277. Introduction. — In Chapter III we found that carbon is a useful and an important element. We studied, also, carbon dioxide (CO_2) and carbon monoxide (CO). So important are carbon and these two compounds it would be well to read Chapter III carefully before continuing the study of this fundamental element.

In this chapter we shall study carbon more in detail, its only acid (carbonic acid), the carbonates, and one carbide (calcium carbide, CaC_2). In the three succeeding chapters we shall study fuels and flames, other carbon compounds, and food.

278. Carbon is an allotropic element. — Carbon exists in different modifications. The two **crystalline** varieties are diamond and graphite. **Amorphous** carbon includes many kinds of familiar substances, *e.g.* charcoal, coal, lampblack, and coke. Although the crystalline and amorphous varieties have quite different properties, they are elementary carbon. They can be changed into one another. Indeed, graphite is manufactured from coal (**280**). Diamonds, too, have been made from charcoal. Each modification burns in oxygen and yields only carbon dioxide. Furthermore, a given weight of each yields the same weight of carbon dioxide. Carbon, like sulphur, is an **allotropic element** (**253**).

279. Diamond is pure crystalline carbon. As found in nature, diamonds are rough-looking stones, which must be ground, or “cut,” into special shapes and polished to bring out the luster and make them sparkle in the light (Fig. 99).

Diamond has the high specific gravity of 3.5. It is one of the hardest substances known, and can be "cut" and

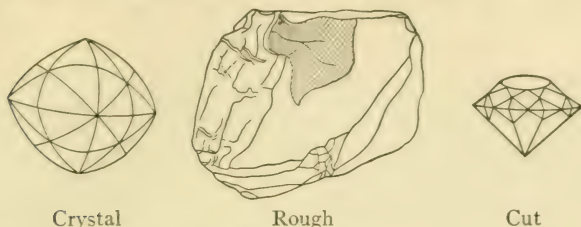


Fig. 99. — Diamonds

polished only by other diamonds (with sharp edges) or by diamond powder.

Diamonds that are badly flawed or are black are used to cut glass and as the cutting part of the diamond drill. The inner surface of the entering end of the drill is set with black diamonds. The drill in passing through rocks and hard deposits cuts a solid core, which is brought to the surface for examination.

Diamond resists the action of most chemicals, though it combines with oxygen when the two elements are heated together to a high temperature. Diamond is carbon, for when pure diamond is burned in oxygen, the only product is carbon dioxide. Diamonds have been made from carbon. The French chemist Moissan in 1893 dissolved pure charcoal in melted iron, and suddenly cooled the molten mass in water. The pressure caused the cooling carbon to crystallize into very small crystals of diamond.

The largest diamond thus far found was called the Cullinan. It was found in 1905 in South Africa, where many diamonds are mined. It weighed about 3025 carats (1.37 lb. avoirdupois).¹ Stones cut from it are among the crown jewels of England.

280. Graphite is another variety of crystalline carbon. It is a soft, friable, dark lead-colored, shiny solid, which

¹ The international carat, which is the unit of weight used in weighing and selling diamonds, is equal to 200 milligrams.

is smooth and greasy to the touch. Pure graphite is carbon; but it is sometimes called "black lead," or plumbago, because it was formerly supposed to contain lead. Unlike diamond, graphite is a good conductor of electricity and is often used to coat molds in electrotyping (243). It is so soft that it readily wears away; hence it blackens the fingers and leaves a black mark on paper when drawn across it. This property is indicated by the name graphite, which is derived from a Greek word meaning to write. It resembles diamond in its insolubility in liquids at the ordinary temperature. Its specific gravity is 2.2, being considerably lighter than diamond.

Graphite changes into carbon dioxide when heated intensely in oxygen; but it can be heated to a very high temperature in the air without melting or undergoing appreciable change.

Graphite is used to make stove polish and protective paints. As a solid lubricant it is used where oil might be decomposed by heat or might clog machinery. It is the principal ingredient of the mixture (graphite and clay) which is made into graphite crucibles; these crucibles can be heated to a high temperature, and certain metals, *e.g.* steel, are made in them. Some varieties of artificial graphite can be ground into very fine particles. If ground with tannin (or a similar substance), and mixed with oil or water, this graphite is converted into the colloidal state (86). Such mixtures of graphite make excellent lubricants.

In making **lead pencils**, the graphite is washed free from impurities, ground to a fine powder, mixed with more or less clay, and then pressed through perforated plates, from which the "lead" issues in tiny rods. These are dried, cut into the proper lengths, baked to remove all traces of moisture, and then inserted in the wooden case. Soft pencils contain more graphite and less clay than hard ones.

Graphite occurs abundantly, the famous localities being Ceylon and Siberia. Considerable **graphite** is also **manufactured** at Niagara Falls by heating a special grade of hard coal out of contact with air in an electric furnace. The

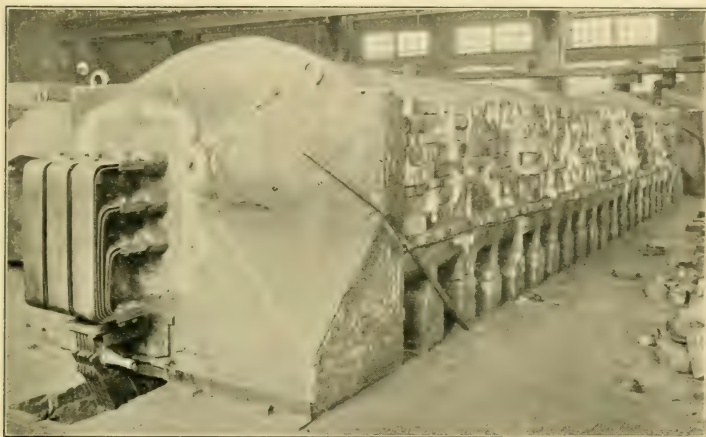


Fig. 100. — An electric furnace for making graphite

process is electrothermal, *i.e.* the chemical change is brought about by the intense heat produced by passing an electric current through the materials (Fig. 100). Articles of almost any size can now be made of artificial graphite, which is so compact that it can be further shaped by tools. This kind of graphite is especially suitable for the electrodes used in electrolytic and electrothermal apparatus.

281. Amorphous carbon includes all varieties of coal and charcoal, lampblack, coke, and gas carbon. They are the non-crystalline forms of impure carbon. The word amorphous (**253**) means without crystalline form; it is often used to designate soft, powdery, and uncrystallized substances.

282. There are many varieties of coal. — It is customary to speak of two principal kinds of coal, though several vari-

eties of each are common articles of commerce. (1) **Bituminous coal** (soft coal) contains about 70 per cent of carbon. It burns with a smoky flame, and is used to make illuminating gas, coke, and as a fuel for steam. (2) **Anthracite coal** (hard coal) contains 90 per cent or more of carbon. It ignites with difficulty, burns with little or no flame, and produces considerable heat. It is used mainly for domestic purposes — heating and cooking — especially in eastern United States. Some varieties of coal, such as **lignite** or brown coal, contain only a small proportion of carbon, as low as 20 per cent. Yet they are used as fuel in some localities.

Besides carbon, coal contains moisture, ash or mineral matter; and soft coal, especially, contains considerable volatile matter, which consists mainly of compounds of carbon with hydrogen, nitrogen, and sulphur.

283. How coal was formed. — Ages ago the vegetation was exceedingly dense and luxuriant upon the land slightly raised above the

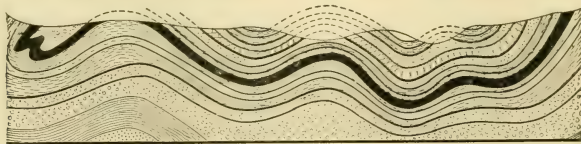


Fig. 101. — Section of the earth's crust showing layers of coal

sea. In process of time this vegetation decayed, accumulated, and slowly became covered with sand, mud, and water. This vegetable matter was then slowly changed into more or less impure carbon, moisture, and gaseous and liquid compounds called hydrocarbons. The geological and chemical changes were repeated, and as a result we find in the earth layers or seams of carbonaceous matter varying in thickness and composition (Fig. 101). These are the coal beds. Coal beds contain proofs of their vegetable origin, viz. impressions of vines, stems, and leaves of plants, and similar vegetable substances.

(Fig. 102). A thin section of coal examined through a microscope reveals a distinct vegetable structure (Fig. 103).

284. Charcoal is obtained by heating wood, bones, and other organic matter in closed vessels, or by partially

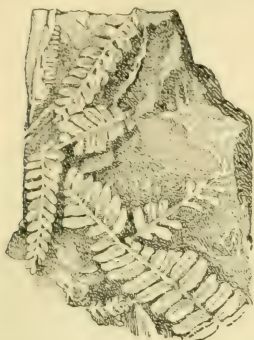


Fig. 102. — Fossil found in a coal bed

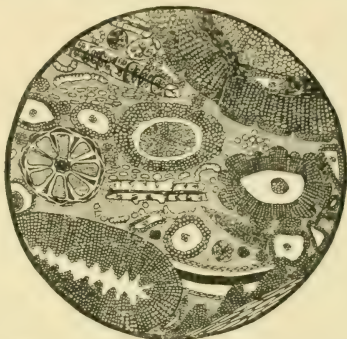


Fig. 103. — Section of coal as seen through a microscope

burning them in the air. Besides carbon, charcoal contains mineral matter.

285. Wood charcoal is a black, brittle solid, and often retains the form of the wood from which it is made. It is insoluble, though its mineral impurities can be removed by acids. It burns without flame or much smoke, and leaves a white ash which consists of mineral substances. The compact varieties conduct heat and electricity, but porous charcoal is a poor conductor. It resists the action of moisture and many chemicals; hence fence posts, telegraph poles, and wooden piles are often charred before being put into the ground.

Most varieties are very porous, and are excellent absorbers of gases. Sewers, cisterns, and foul places are sometimes purified by charcoal. It will also absorb colored substances from solutions. Foul air and water may be

partially purified by charcoal, which forms the essential part of many water filters in houses and air filters in large buildings. Charcoal used for such a purpose, however, must be frequently renewed or often heated to redness; otherwise it becomes clogged and contaminated. Large quantities of charcoal are used as a fuel and in the manufacture of steel and of gunpowder.

Wood charcoal is made either in charcoal pits or in large iron furnaces. Where wood is plentiful, it is loosely piled into a conical shape, and covered with turf. The wood is lighted, and as it slowly burns care is taken to regulate the supply of air so that the wood will smolder but not be entirely consumed. The volatile matter escapes and charcoal remains.

Much charcoal is made by heating wood in closed furnaces, no air whatever being admitted. By this method, which is called **dry distillation**, the yield of charcoal is about 30 per cent. From the volatile matter we obtain acetic acid and methanol (or "wood alcohol").

More or less charcoal may be obtained by heating a compound of carbon, *e.g.* sugar or starch, the charring being a **test for carbon**.

286. Animal charcoal or boneblack is made by heating bones and animal refuse in a closed vessel. The animal charcoal from bones contains only about 10 per cent of carbon, but this carbon is distributed throughout the porous mineral matter of the bone (largely calcium phosphate). Animal charcoal is used as a pigment, especially in making shoe-blackening. It is also extensively used to remove the color from sugar sirups.

287. Coke is made by expelling the volatile matter from bituminous coal, somewhat as charcoal is made from wood. It is left in the retorts when coal is distilled in the manufacture of coal gas (**326**). On a large scale it is made by heating a special grade of soft coal in huge brick ovens from which air is excluded after combustion begins. Owing

to the loss of valuable by-products, the older kinds of ovens are being replaced by closed furnaces, called by-product ovens (Fig. 104), constructed so as to save the by-products,

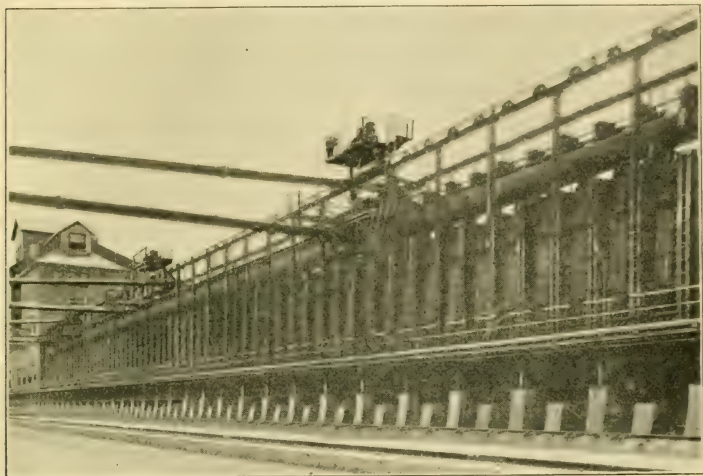


Fig. 104. — A battery of by-product coke ovens at one of the Ford automobile plants

e.g. ammonia, tar, organic compounds, and combustible gases.

Coke is a grayish, porous solid, harder and heavier than charcoal. It burns with no smoke and a feeble flame. Its most extensive use is in the iron industry (489).

288. Gas carbon is a variety of amorphous carbon which is deposited on the inside of the retorts used in the manufacture of illuminating gas (326). It is a black, heavy, hard solid, and is almost pure carbon. It is a good conductor of electricity, and is extensively used for the manufacture of the carbon rods of electric lights and for plates of electric batteries.

289. Lampblack is prepared by burning gas, oil, or oily substances rich in carbon in a limited supply of air. The dense smoke, which is finely divided carbon, is passed through a series of condensing chambers, where it is collected upon coarse cloth or a cold surface.

Lampblack is one of the purest forms of amorphous carbon, and it is used in making printer's ink and certain black paints.

290. Chemical conduct of carbon. — Carbon does not interact with acids or bases. At ordinary temperatures carbon is inactive, but it is active at high temperatures. Thus, carbon heated with oxygen forms carbon dioxide and carbon monoxide, and with sulphur, carbon disulphide (258). Carbon unites with many metals and some non-metals in the electric furnace, thereby forming carbides, *e.g.* calcium carbide (CaC_2) and carborundum (silicon carbide, CSi) (295, 392). At high temperatures carbon is a reducing agent; extensive application of this property is made in producing metals from ores, *e.g.* iron from iron oxide (489).

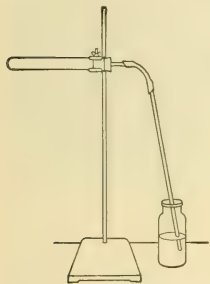
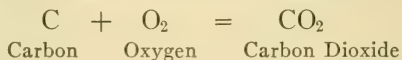


Fig. 105. — Reducing copper oxide with carbon

A simple experiment can be made to illustrate the reducing action of carbon. A mixture of powdered charcoal and copper oxide is put in a test tube fitted with a one-hole stopper and a delivery tube bent at a right angle. The test tube is clamped to an iron stand so that the end of the delivery tube dips into a bottle half full of limewater (Fig. 105). When the mixture is heated, carbon dioxide is evolved and produces a white precipitate (CaCO_3) in the limewater. Metallic copper (not easily seen) is left in the test tube. The equation is: —



291. Carbon dioxide — review and extension. — Carbon dioxide is one product of ordinary combustion, respiration of animals, fermentation, and decay. The equation for the combustion of carbon in air or oxygen is: —

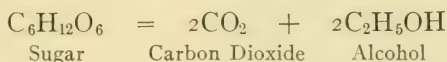


The fact that carbon dioxide is formed by the free com-

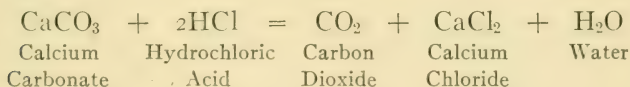
bustion of carbon and carbon compounds may be shown by bubbling the smoke from these burning substances through calcium hydroxide solution.

The continuous oxidation of the tissues of the body also produces carbon dioxide (27). If we exhale the breath through a glass tube into calcium hydroxide solution (Fig. 12), the carbon dioxide that is in the breath turns the solution milky — the usual **test for carbon dioxide**.

Many kinds of organic matter ferment, especially those containing certain varieties of sugar. By alcoholic fermentation the sugar changes into carbon dioxide and alcohol, thus: —



Carbon dioxide is usually **prepared** by the interaction of a carbonate and an acid. Calcium carbonate (limestone or marble) and hydrochloric acid are ordinarily used, thus: —



Carbon dioxide has a slight taste but no color. It is heavier than air (1.5 to 1), and a liter under standard conditions weighs 1.98 gm. This gas dissolves readily in water — especially under pressure — a property utilized in manufacturing beverages (Figs. 14, 15).

Carbon dioxide does not burn nor support combustion. This property is utilized in fire extinguishers. It combines to some extent with water, forming carbonic acid (292).

The gas is not poisonous, but its presence in the air of a room to any extent is objectionable. Carbon dioxide bears an impressive relation to the life of plants and animals.

Plants absorb it and transform it into starch, while animals eat and assimilate starch, and exhale carbon dioxide into

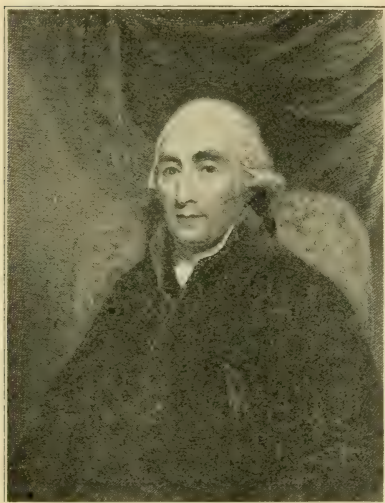


Fig. 106 — Black (1728–1799)

the atmosphere ready for the plants again (39). This relation, which is often called the cycle of carbon and oxygen, is shown by a diagram in Fig. 17.

One of the first to study carbon dioxide was the Scotch chemist Black (Fig. 106). He not only observed and recorded its properties but also showed the relation of the gas to carbonates.

292. Carbonic acid. —

Carbon dioxide is often called carbonic acid gas, or simply carbonic acid. These terms are incorrect when applied to carbon dioxide, and should be used only as the name of the compound H_2CO_3 . If carbon dioxide is passed into water, it combines to some extent with the water and forms a weak, unstable acid, which is **carbonic acid** (H_2CO_3). The equation for this change is: —



Such a solution reddens blue litmus and decolorizes pink phenolphthalein solution, though its action is feeble. Carbonic acid in terms of the theory of ionization is a weak acid, *i.e.* it ionizes only slightly, its ions being H^+ and HCO_3^- (247). Carbonic acid is so unstable that it easily breaks up by gentle heat into carbon dioxide and water, thus: —



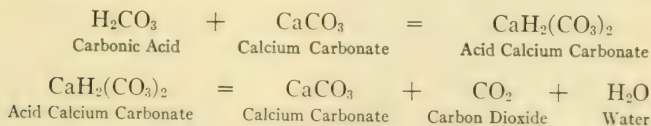
For this reason it cannot be obtained free like other acids.

Carbon dioxide is sometimes called carbonic anhydride to emphasize the fact that, like oxides of other non-metals, it unites with water to form an acid (262, 266).

293. Carbonates are salts of carbonic acid. They are common substances, but unlike the acid, are stable under ordinary conditions. The most abundant natural carbonates are those of calcium, magnesium, and iron. Immense quantities of sodium carbonate are manufactured.

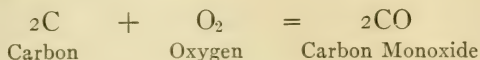
Carbonic acid is dibasic, and forms two classes of salts, the **normal** and the **acid** (263, 273). Thus, normal sodium carbonate is Na_2CO_3 , and acid sodium carbonate is NaHCO_3 ; the latter is often called sodium bicarbonate. Similarly normal calcium carbonate is CaCO_3 , and acid calcium carbonate is $\text{CaH}_2(\text{CO}_3)_2$ (or $\text{Ca}(\text{HCO}_3)_2$).

The relation between normal and acid calcium carbonate is interesting. The normal salt is almost insoluble in water; the acid salt is soluble in water and is easily decomposed by heat into the normal salt. Acid calcium carbonate is readily formed from the normal carbonate by an excess of carbon dioxide. Thus, when carbon dioxide is passed into water containing insoluble normal calcium carbonate in suspension soluble acid calcium carbonate is formed:—



An example of this reaction is seen in caves. Since many underground waters contain carbon dioxide, these waters dissolve the limestone (CaCO_3) over which they pass. When the dissolved acid calcium carbonate is decomposed (by heat or in some other way), the calcium carbonate is reprecipitated in the form of stalactites and stalagmites which adorn the interior of the caves (Fig. 162).

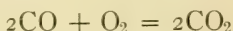
294. Carbon monoxide — review and extension.—Carbon monoxide is formed when carbon is burned in a limited supply of air, thus:—



It is also formed when carbon dioxide is reduced with carbon, thus:—

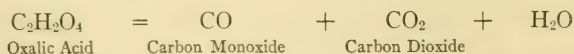


When carbon monoxide burns in air (43) or in oxygen, carbon dioxide is formed, thus:—



The oxides are, therefore, closely related, passing readily into each other (44).

Carbon monoxide is usually **prepared** by decomposing oxalic acid with hot sulphuric acid, thus:—

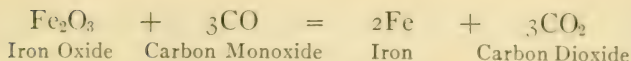


The carbon dioxide may be removed by passing the gases through a solution of sodium hydroxide.

Carbon monoxide has no color, odor, or taste, and is only slightly soluble in water.

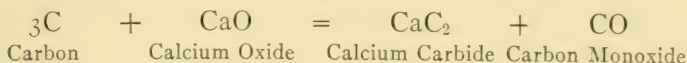
Carbon monoxide is poisonous. Air containing one part of carbon monoxide in 2000 produces unconsciousness, and ultimately causes death. Care should be taken to prevent its escape into rooms occupied by human beings (42) or into an unventilated garage.

Carbon monoxide burns in air with a bluish flame (44). At a high temperature carbon monoxide readily reduces oxides, and is an important agent in the reduction of iron ores in the blast furnace, thus:—



Carbon monoxide forms no acid and no salts. It does not turn calcium hydroxide milky, thus being readily distinguished from carbon dioxide. Its blue flame serves as a test to distinguish it from many other combustible gases.

295. Calcium carbide (CaC_2) is a brittle, dark gray, crystalline solid. It is made from coke or coal and lime (calcium oxide, CaO) in an electric furnace. The chemical change is caused solely by the intense heat and may be represented thus:—



A sketch of the furnace in which calcium carbide is made is shown in Fig. 107. The mixture of coke and lime (shown in the furnace) is introduced through the trap cover *A* and slowly sinks down into the space where the intense heat is produced by the electricity as it passes between the electrodes *G* and *E*, *E*. The liquid calcium carbide is drawn off through *F*. The carbon monoxide rises through the pipes *D*, *D* and enters the upper part of the furnace, together with air supplied through *C*, *C*; this mixture burns and heats the coke and lime. The waste gases (carbon dioxide and nitrogen) escape through *B*.

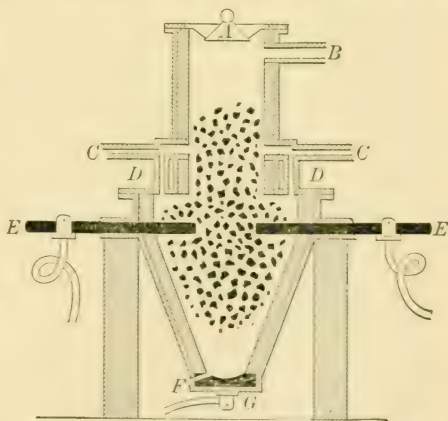
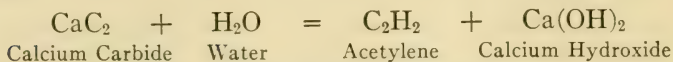


Fig. 107. — Electric furnace for making calcium carbide

The most striking and useful property of calcium car-

bide is its action with water, acetylene being formed, thus:—



Calcium carbide is used to generate acetylene, which is an illuminant (333).

EXERCISES

1. Prepare a summary of (a) the element carbon, (b) carbon dioxide, (c) carbon monoxide.
2. State the uses of (a) diamond, (b) graphite, (c) coke, (d) charcoal.
3. Prepare a summary of the chemical conduct of carbon.
4. Give a brief account of the manufacture of lead pencils. What is the literal meaning of the word graphite?
5. Describe the process of manufacturing graphite.
6. Does carbon in the amorphous varieties differ chemically from pure diamond and graphite? Why?
7. Prepare a summary of coal.
8. The specific gravity of charcoal is about 1.5. Why does it float on water?
9. Topics for home study: (a) Famous diamonds. (b) Carbon in electrical industries. (c) Carbon in paints. (d) The cycle of carbon in nature. (e) History of carbon dioxide. (f) Fire extinguishers. (g) Carbon is an allotropic element.
10. What is the relation of carbon dioxide to (a) respiration, (b) fermentation of sugar, (c) decay, (d) making lime, (e) combustion?
11. Carbon and carbon monoxide are reducing agents. Explain and illustrate by equations.
12. In what ways can carbon dioxide be prepared? Give equations for the reactions.
13. State fully the relation of carbon dioxide to carbonic acid. Give the equations for the formation and decomposition of this acid.
14. What are carbonates? Acid carbonates? Illustrate by formulas.
15. Illustrate Gay-Lussac's law by the carbon oxides.
16. Write the formulas of the normal and acid carbonates of Ca, Ba, copper, Pb, potassium, silver, zinc.

PROBLEMS

1. Calculate the per cent of carbon in (a) carbonic anhydride, (b) acid calcium carbonate, (c) carbon monoxide, (d) marble.

2. What weight of carbon is contained in 2 l. of carbon monoxide? In 2 l. of carbon dioxide? (Standard conditions.)
3. What volume at standard conditions is occupied by (a) 70 gm. of carbon dioxide, and by (b) 45 gm. of carbon monoxide?
4. Calculate the molecular weight of carbon dioxide if 10 l. weighs 19.8 gm.
5. How much oxygen by weight and by volume (standard conditions) is needed to convert the following into carbon dioxide: (a) 1 kg. of pure charcoal, (b) a diamond weighing 250 milligrams, and (c) 30 gm. of graphite?
6. Show that the two carbon oxides illustrate the law of multiple proportions.
7. Thirty grams of carbon are burned to carbon dioxide. What weight of potassium chlorate will provide the oxygen?
8. Calculate the simplest formulas from the following data: (a) 3 liters of a carbon oxide weigh 3.75 gm; (b) $C = 27.27$, $O = 72.72$; (c) an oxide of carbon contains 42.857 per cent of carbon.
9. Carbon dioxide is heated with 40 gm. of carbon. What is (a) the weight and (b) the volume of the product?
10. If 75 gm. of carbon dioxide are passed over hot carbon, what (a) weight of carbon is used and (b) volume of new gas is produced?
11. What weight of carbon (97 per cent pure) is needed to reduce 60 gm. of carbon dioxide to carbon monoxide? What volume of air (containing 21 per cent of oxygen by volume) at $19^{\circ}C$. and 758 mm. is needed to change the carbon monoxide to carbon dioxide?
12. How many cubic decimeters of carbon monoxide will be formed by the decomposition of 25 gm. of oxalic acid?
13. If one volume of carbon monoxide and two volumes of oxygen are mixed and exploded in a closed space, what will be the volume of the resulting gas or gases at the original temperature and pressure?
14. A ton of calcium carbide is needed. What weight of lime (CaO) and coke (95 per cent pure) must be used?

CHAPTER XXII

FUELS — ILLUMINATING GASES — FLAME

296. Carbon as a source of heat and light. — Carbon and many of its compounds burn readily in air and liberate considerable heat. Some compounds give also a colored flame, usually yellow. Carbon and certain carbon compounds are used as a source of heat and light, *i.e.* as fuels and illuminants, in our homes and in the industries.

297. Fuels. — Solid fuels include wood, charcoal, coke, and the various kinds of coal (282). The commonest liquid fuels are fuel oil and gasoline, though kerosene and alcohol are used to some extent. The important gaseous fuels are natural gas and producer gas, though coal gas, water gas, and acetylene are also used to some extent.

298. Illuminants are gases or readily volatilized liquids. Illuminating gas made from coal or oil is the best known gaseous illuminant (327, 329, 330). Acetylene (C_2H_2) is another gas used as an illuminant (333). Kerosene is the commonest liquid illuminant.

299. Composition of fuels. — Charcoal and coke are nearly pure carbon. Hard coal is about 90 per cent carbon, and soft coal about 70 per cent. All kinds of coal contain mineral matter, which is left as ashes when the coal is burned. Soft coal also contains considerable moisture and volatile matter. Wood is composed mainly of cellulose—a compound of carbon, hydrogen, and oxygen; water (10 to 50 per cent) and mineral matter are also present.

Liquid fuels (except alcohol) are mixtures of hydrocarbons, *i.e.* compounds of carbon and hydrogen. Alcohol is a compound of carbon, hydrogen, and oxygen (C_2H_5OH).

Gaseous fuels contain hydrocarbons (317), hydrogen, and carbon monoxide.

300. Combustion of fuels. — When heated to the proper temperature fuels burn. Chemically this means that the carbon, hydrogen, and carbon monoxide unite with oxygen furnished by air. The gaseous products of combustion are carbon dioxide, carbon monoxide, and water. The solid products are the ashes and, if combustion is incomplete, smoke. Heat is liberated when fuels burn. Indeed, the essential characteristic of a good fuel is its heat-producing capacity, especially when used to produce steam.

301. Measurement of heat produced by fuels. — Heat, like other forms of energy, is measured by a special unit. The unit used in measuring the heat produced by fuels is called the **British thermal unit** (B.t.u.). It is the amount of heat that will raise the temperature of one pound of water 1° F. Thus, coke and very good soft coal will each produce about 16,000 B.t.u. per pound. Fuel oil, now used on warships and steamships, yields about 19,800 B.t.u. per pound. Fuel gases (producer, water, and coal gas) give 145 to 600 B.t.u. per cubic foot.

Another heat unit is called the small **calorie** (cal.). It is the amount of heat required to raise the temperature of one gram of water 1° C. (usually 15° to 16°). It is convenient to know that 1 B.t.u. = 252 cal. On the calorie basis, the heat value of good soft coal is about 8700 calories per gram.

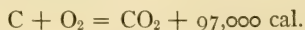
The large calorie (Cal.), which is one thousand times the small calorie, is used when the heat value is large. The heat value, often called the **fuel value**, of different kinds of food is usually expressed in large calories, *e.g.* one gram of starch in burning gives out 4 Cal-

ories and one gram of fat 9 Calories. (See also Fuel Value, Chapter XXIV.)

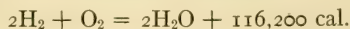
302. The calorimeter is used to find heat value. — The heat, or fuel, value of such solids as coal, charcoal, and food (dried) is measured by burning the solid in a **bomb calorimeter**. The essential part of the apparatus is a strong metal vessel, called a bomb, which is immersed in another vessel containing a known weight of water.

In making a determination, a weighed amount of the substance is put in the bomb, a looped wire is dipped into the substance and the ends of the wire are connected with the electrodes on the bomb, the cover is screwed on, and oxygen is forced into the bomb (to hasten the combustion). The bomb is next placed inside the vessel containing a known weight of water. This outer vessel is well insulated so that all the heat produced in the bomb will be absorbed by the water. The vessel is also provided with an accurate thermometer and a stirrer. The substance is ignited by passing an electric current through the looped wire. The heat from the burning substance raises the temperature of the water, and the rise is carefully noted. From the weight of the substance, the weight of the water, and the rise in temperature (together with certain allowances for the apparatus itself), the heat value of the substance can be computed.

303. Thermo-chemical equations. — The heat liberated when carbon, or a carbon compound, burns can be incorporated in the equation expressing the chemical change. Thus, the equation for the burning of charcoal in oxygen is: —



In this equation C stands for 12 grams of carbon, O_2 for 32 of oxygen, and CO_2 for 44 of carbon dioxide. Similarly: —



Here 2H_2 means 4 grams of hydrogen, O_2 32 grams of oxygen, and $2\text{H}_2\text{O}$ 36 grams of water. Such equations are called **thermo-chemical equations**.

304. Burning of coal. — When coal is burned, the products of combustion depend on the kind of coal and on

the proportion of air supplied. With an excess of air, hard coal and good soft coal produce carbon dioxide, water, and sulphur dioxide. If the air is insufficient, carbon monoxide and hydrogen sulphide are also formed, while some unburned carbon escapes as smoke. This limited combustion involves loss of heat. If too much air is supplied, heat is also lost "up the chimney."

The air needed for burning coal in stoves or under boilers is drawn in through an opening under the grate by the draft created by the natural tendency of the hot gases to rise up the chimney. To obtain the best results, the air supply should be about twice that required to change all the carbon to carbon dioxide and the hydrogen to water.

305. Smoke consists largely of unburned carbon in the form of small particles called cinders or soot; some small particles of ash are often present. In large industrial plants where soft coal is used, improper burning adds to the smoke nuisance and also causes an enormous loss of heat. Some large factories have automatic smoke consumers as a part of the boiler equipment. By this device fuel is saved and smoke is prevented. Practically complete combustion is accomplished by adding the fuel properly, regulating the supply of air, and using a special form of furnace.

306. Burning hard coal in a stove. — For domestic purposes, hard coal is usually used. In **44** we learned that both carbon dioxide and carbon monoxide are formed in a coal fire in a stove. We can now interpret this fact. (See Fig. 108.) When air enters the bottom of the grate and comes in contact with the burning coal, oxygen unites with carbon to form carbon dioxide. The carbon dioxide rises through the hot coal, and the carbon reduces the carbon dioxide to carbon monoxide. Some of the carbon monoxide usually escapes, but most of it burns with a flickering

bluish flame on the top of the fire, forming carbon dioxide with the oxygen of the air.

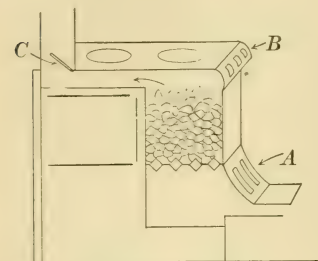


Fig. 108. — The three main changes during combustion in a coal fire

The combustion of coal in a stove or furnace in a house is regulated by **dampers**, usually three — one in the door below the grate (*A*), one in the door above the fire (*B*), and the third in pipe connected with the chimney (*C*) (Fig. 108). When the fire is built or needs to be “started up,” the dampers in the lower door and the pipe are opened but the one in the upper door is closed. This allows plenty of air to pass up through the burning coal and increase the combustion, and also creates a draft by permitting the hot products of combustion to rise and escape out of the chimney. Once started, the combustion in the fire can be regulated by closing the lower damper and opening the middle one, partly or wholly, and adjusting the chimney damper; by this arrangement most of the air goes *over* the fire instead of up *through* it.

Care must be taken to admit enough air through the lower door to burn the coal as completely as possible so the maximum quantity of heat will be liberated. Incomplete combustion is expensive. Special care should also be taken to prevent the escape of “coal gas” into the house. This gas contains carbon monoxide, which is very poisonous (294), and hydrogen sulphide, which tarnishes silverware (256).

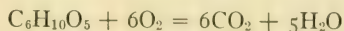
307. Combustion of fuels is hastened by increasing

the rate at which air is supplied. Before stoves were in common use, a bellows was used to "make the fire burn better." A blacksmith uses a bellows to make his fire hotter. In the laboratory we often use a foot bellows (or air blast) to force air into a blast-lamp and burn the illuminating gas completely (Fig. 29). On coal-burning steamships high speed is attained (especially on trial runs or emergency trips) by using a forced draft. That is, rapid combustion — and hence more heat — is caused by blowing air through the fire. Similar effects are produced in other ways. For example, increased draft is produced in a locomotive by forcing steam through the smokestack, in a large manufacturing plant by using a very high chimney, or an airblast (*e.g.* in making iron and steel), and in stoves and furnaces by closing the middle damper tight, opening the top damper, and leaving the lower door wide open.

308. Burning other solid carbon fuels. — Charcoal is readily ignited, burns with a slight flame, and yields no smoke. Its heat value is 12,000 to 14,000 B.t.u. per pound. Coke also burns with a small flame and without smoke. Its heat value is about 14,500 B.t.u. per pound. Both charcoal and coke find extensive use in the iron and steel industry (489, 496).

309. Burning wood. — Wood has been used as a fuel for ages. The hard varieties such as oak, ash, and maple are the best fuels. Dry wood yields from 5600 to 8000 B.t.u. per pound. A cord of seasoned hard wood has about the same heat value as a ton of bituminous coal.

The essential ingredient of wood is cellulose — a compound of unknown composition, though often expressed by the formula $(C_6H_{10}O_5)_n$. A provisional equation for its combustion is: —



310. Liquid fuels. — Three products from petroleum — fuel oil, gasolene, and kerosene — are used as fuels. They are mixtures of hydrocarbons (317). In burning, these

compounds are decomposed; the carbon forms carbon dioxide and the hydrogen forms water.

311. Fuel oil must be supplied to the furnace in the form of spray. This is produced by forcing the oil through a fine opening or by blowing it with steam or air through an atomizer.

The general principle on which the latter type of burner operates is shown in Fig. 109. Oil enters at *A* and flows through *D* into the

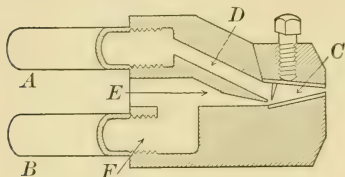


Fig. 109. — Fuel oil burner

mixing and atomizing chamber *C*. Steam enters at *B* and passes through *F* and *E* into the chamber *C*, where it cuts across the oil at an angle. Here the oil and steam mix and the pressure forces the oil as a fine spray out into the furnace, where it burns instantly.

When the spray of oil burns, a large amount of heat is liberated, as high as 19,800 B.t.u. per pound in the case of some grades of fuel oil.

Fuel oil is extensively used on warships and steamships, and in many manufactories. By using oil in place of coal to generate steam, additional space is provided for cargo, more efficient combustion is attained, speed may be greatly increased, and the cruising radius enlarged, to say nothing of the labor saved and cleanliness secured.

312. Gasolene is the fuel used in the engines of automobiles, trucks, motor boats, motor cycles, and airplanes. Gasolene is very volatile and the vapor burns readily. If the vapor is mixed with air and the mixture is ignited by an electric spark, the combustion is so rapid that it is practically an explosion; the gases, suddenly expanded, exert pressure, which is converted by the machinery into steady and continuous motion.

313. Kerosene is used as a fuel to a limited extent in engines and

cooking stoves. In some portable stoves kerosene is burned by means of a large wick (as in a lamp).

314. Alcohol. — Different kinds of **alcohol** are used as fuel, usually on a small scale. They burn without smoke and have a high heat value. **Methyl alcohol** (CH_3OH), also called wood alcohol (**285**) and methanol, boils at about 66°C . and burns with a pale blue flame. It gives about 9600 B.t.u. per pound. **Ethyl alcohol** ($\text{C}_2\text{H}_5\text{OH}$), also called grain alcohol or simply alcohol, is a colorless, volatile liquid, which boils at about 78°C . and burns with a nearly colorless flame; the heat produced is about 12,700 B.t.u. per pound.

315. The petroleum industry. — Petroleum is obtained from the earth in many parts of the world. In the United States the chief localities are Oklahoma, Kansas, Ohio, Pennsylvania, Texas, Louisiana, and California. Mexico and Russia are large producers. Some is found in Roumania, Galicia, and Japan.

Crude petroleum is an oily liquid with an unpleasant odor. Its color varies from straw to black; it is greenish in reflected light. Most kinds float on water. Its composition is complex, but all varieties are essentially mixtures of liquid and solid hydrocarbons (**317**). Certain grades contain compounds of nitrogen and of sulphur.

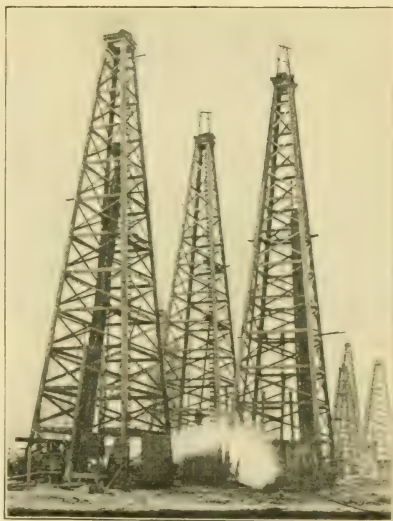


Fig. 110. — Derricks and pumps in an oil region

In some localities the oil issues from the earth, but it is usually necessary to erect a derrick, drill a deep hole, and insert a pipe into

the porous rock containing the oil (Fig. 110). Sometimes the oil "spouts" out of the well when first drilled, but after a time a pump is needed to draw it to the surface.

The oil is forced by powerful pumps through large pipes to central points for storage, or more often many miles to the refinery, where the petroleum is separated into various commercial products by **refining**. The petroleum is first cleaned by settling and filtration. Then it is distilled by heating it in huge retorts (Fig. 111, bottom), condensing the vapors in coiled pipes immersed in cold water, and collecting the distillates in separate tanks. This process is called fractional distillation, since the petroleum is separated into parts or fractions. Certain products, *e.g.* fuel oil, are obtained from the residue left in the stills.

The different distillates are further separated and purified by redistillation (Fig. 111, top). The chief commercial products obtained are petroleum ether (boiling point 40° – 70° C.), gasolene (70° – 120°), benzine (120° – 150°), kerosene (150° – 300°); there are various commercial grades of these products, which are distinguished by the range of boiling points or by the specific gravity. These liquids are mixtures of several different hydrocarbons (317). They are variously used as solvents, fuels, and illuminants.

The unusual demand for **gasolene** has led to a modification of refining in order to increase the supply. The higher boiling oils are vaporized and the vapor is heated to a high temperature (350° – 450° C.) and under increased pressure (4 to 5 atmospheres). By this treatment, which is called **cracking**, complex hydrocarbons decompose and form hydrocarbons within the gasolene range (317).

Owing to its extensive use as an illuminant, **kerosene** is carefully freed from readily inflammable liquids and gases, which might cause an explosion, and from tarry matter and semi-solid hydrocarbons, which would clog a lamp wick. This is done by agitating it successively with sulphuric acid, sodium hydroxide, and water

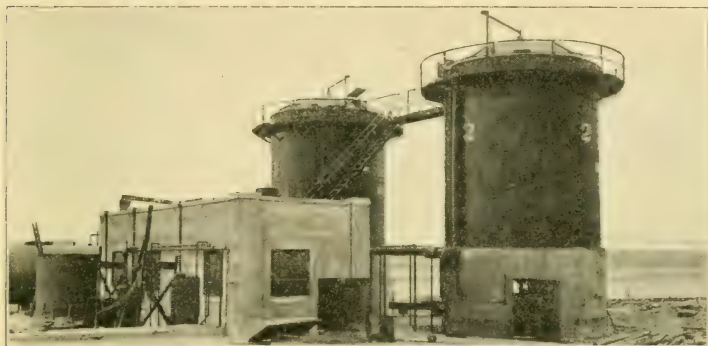
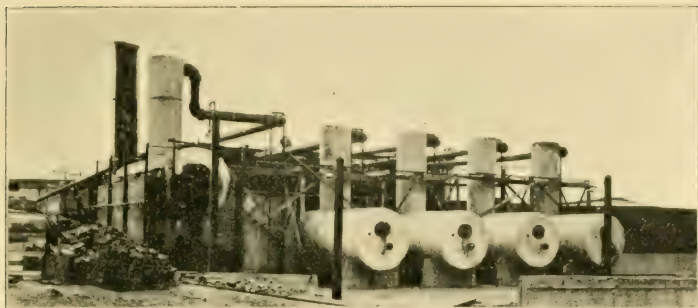


Fig. III. — Refining petroleum. Fire stills (bottom), steam stills (top), agitators (middle)

(Fig. 111, middle). Commercial kerosene must have a legal **flashing point**. This is "the temperature at which the oil gives off sufficient vapor to form a momentary flash when a small flame is brought near its surface." The legal minimum flashing point in most states is about 110° Fahrenheit (about 44° C.).

The oil left in the fire still (Fig. 111, bottom) after the removal of the low-boiling liquids including gasoline, and

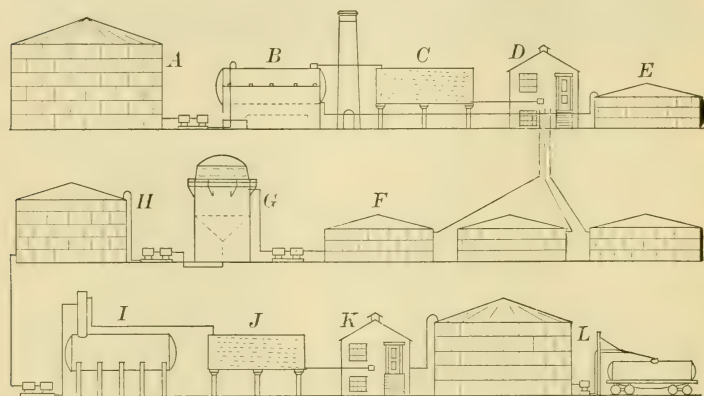


Fig. 112. — Sketch of a plant for the separation of gasoline and fuel oil from petroleum

sometimes kerosene, is the commercial **fuel oil** (316). Other oil residues, and crude petroleum to some extent, are used as fuels. Specifications prescribe the properties of fuel oil, especially its heat value, freedom from water and sulphur (compounds), and mobility.

From the residue after the distillation of the kerosene many grades of **lubricating oil** are obtained; also **vaseline** and **paraffin wax**. Petroleum oils yielding these products are said to have a paraffin base; Pennsylvania and Ohio oils are examples. Mineral lubricating oils have largely replaced animal and vegetable oils. Vaseline finds extensive use as an ointment. Paraffin wax is made into candles and into a waterproof coating for many substances. The final residue

in the still is mainly carbon and is called **petroleum coke**; it is made into electric light carbons.

Some oils, such as those from Mexico and California, leave a thick, black pitch. These oils are said to have an asphalt base.

316. Fuel oil and gasolene. — The steps in the separation of gasolene and fuel oil from petroleum are shown in Fig. 112. This figure also illustrates the general process of refining. The crude oil is pumped from the storage tank *A* into the still *B* (Fig. 111, bottom), which is heated on the bottom by a flame. The vapors pass into the condenser *C*, and the distillate flows into the receiving house *D*, where it is examined through look boxes (Fig. 113). The different portions (called fractions) are directed into the proper tank. After certain low-boiling hydrocarbons (making up gasolene and kerosene chiefly) have been boiled off in the fire still, the residue is drawn off and stored in the fuel oil tank *E*. The benzine fraction *F* is pumped to the agitator *G* (Fig. 111, middle) and then to the storage tank *H*. From here the liquid goes to the still *I*, which is heated by steam (Fig. 111, top). The vapors are condensed in *J*, the distillate received in *K*, examined, and directed into the proper tank — the main one being the gasolene tank *L*.



Fig. 113. — Look boxes in which the distillates can be examined as they flow from the condensers through the receiving house on to the special storage tanks

317. Hydrocarbons are compounds of carbon and hydro-

gen. They number over two hundred. Many of them occur in petroleum, natural gas, asphalt, and coal tar. Hydrocarbons are divided into series according to their composition. The commonest series is the **methane** or **paraffin series**. The first members in order are methane (CH_4), ethane (C_2H_6), propane (C_3H_8), butane (C_4H_{10}), pentane (C_5H_{12}), and hexane (C_6H_{14}).

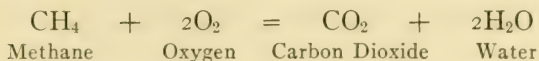
Other members have a numerical name, similar to pentane and hexane, which indicates the number of carbon atoms in the molecule. The first four members are gases. Under ordinary conditions the next ten members are liquids, and the rest are solids.

Petroleum is a mixture of many hydrocarbons, and most American varieties contain paraffin hydrocarbons. **Gasolene** is mainly a mixture of hexane (C_6H_{14}), heptane (C_7H_{16}), and octane (C_8H_{18}). **Kerosene** consists of hydrocarbons which are composed of ten to sixteen carbon atoms, **vaseline** twenty-two and twenty-three, and **paraffin wax** still higher.

318. Other series of hydrocarbons are also named from the first member, *e.g.* ethylene, acetylene, benzene, and naphthalene. **Ethylene** (C_2H_4) is a colorless gas, which burns with a yellow flame. It is the chief illuminating ingredient of coal gas (**329**). **Acetylene** (C_2H_2) is fully described in **333**. **Benzene** (C_6H_6) is a colorless liquid and **naphthalene** (C_{10}H_8) is a white, lustrous crystalline solid. They burn with a yellow flame, and, like ethylene, contribute to the luminosity of coal gas (**330**).

319. Methane occurs in coal mine gases, natural gas (**320**), and marsh gas (the mixture formed in marshy places by the decay of vegetable matter under water). It burns with a pale, hot flame, and is an essential heat-producing constituent of illuminating gas (**329**) and natural gas. A mixture of methane and air explodes violently when ignited by a spark or flame. Terrible disasters sometimes occur in bituminous coal mines from this cause. When methane

burns or explodes, carbon dioxide and water are formed, thus: —



The carbon dioxide, called **choke damp** or **black damp** by the miners, often suffocates those who escape from the explosion (29 and Fig. 11).

The miner's safety lamp was invented in 1815 by Davy to prevent explosions. It is essentially an oil lamp surrounded by a cylinder of fine wire gauze instead of the usual chimney (Fig. 114). When taken into a mine where there are explosive gases, *e.g.* methane, the gas enters the lamp and burns inside, but the flame within does not ignite the gases outside because the wire gauze keeps them cooled below their kindling temperature. When miners notice changes in the lamp flame, they usually seek a safe place. Modified forms of the Davy lamp are used at the present time.

The principle of the Davy lamp is illustrated in Fig. 115: A wire gauze is held above a Bunsen burner, the gas is turned on, and lighted above the gauze. The flame will not pass through the gauze unless the latter becomes hot.

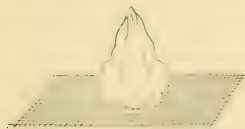


Fig. 115. — Experiment illustrating the principle of Davy's safety lamp

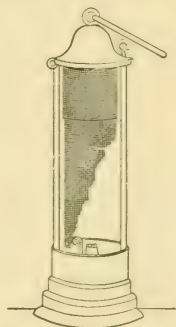


Fig. 114. — A form of Davy's safety lamp (gauze cut away to show inside)

320. Gaseous

fuels include natural gas and the various mixtures obtained from coal, *e.g.* producer gas, water gas, and coal gas. **Natural gas** exists in the earth in Pennsylvania, Ohio, West Virginia, and other parts of the United States, usually in regions where petroleum is found. It is obtained by boring wells. It

is about 90 per cent methane (CH_4), which is the chief heat-producing constituent. The gas burns with a hot flame. The heat value is about 1000 B.t.u. per cubic foot. It is used as fuel to heat houses and to generate steam in many industries, *e.g.* making steel, glass, brick, and pottery. As a fuel it is cheap and efficient. A large volume of air and a special burner are needed for its combustion.

321. Producer gas is made by forcing air (sometimes together with a little steam) through a deep coal fire in a special kind of furnace. The gaseous product contains

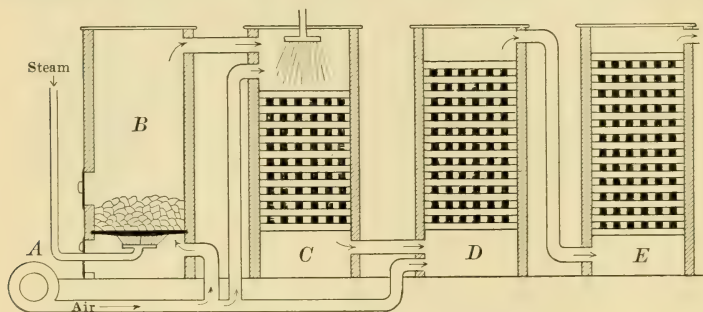


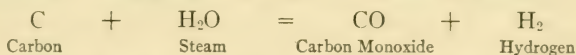
Fig. 116. — Diagram of water gas plant

25 to 30 per cent of carbon monoxide, 50 to 60 per cent of nitrogen, and 10 to 13 per cent of hydrogen (if steam is used). Its heat value is rather low, about 145 B.t.u. per cubic foot, though it varies with the process, being higher if steam is used. This value is low on account of the large proportion of nitrogen. But the cost is not great, because the gas can be quickly made and efficiently burned. Producer gas is used as a fuel in gas engines and in many industrial and metallurgical operations.

322. Water gas is made by forcing steam through a mass of hot coke or anthracite coal. It is essentially a mixture of hydrogen and carbon monoxide, and is used to

some extent as fuel. More often it is enriched by spraying in petroleum oil, and then used as an illuminant. If used as fuel, enriched water gas has a heat value of 500 to 600 B.t.u. per cubic foot.

323. Manufacture of water gas. — The essential parts of the apparatus are shown diagrammatically in Fig. 116. (1) Air is forced by a blower (*A*) through the fire in the generator (*B*), and the hot gases pass down the carburetor (*C*) up into the superheater (*D*), and escape through an opening (not shown) into the air. This operation is called the “blow.” It heats the fire brick inside the carburetor and superheater intensely hot; air is often forced in to raise the temperature. (2) The air valves and the opening at the top of the superheater are now closed, and the “run” begins. Steam is forced into the generator at the bottom. In passing through the mass of incandescent carbon, the steam and carbon interact thus: —



The mixed gases rise to the top of the carburetor, where they meet a spray of oil. And as the gaseous mixture passes down the carburetor and up the superheater, the hydrocarbons of the oil are transformed by the intense heat into gaseous hydrocarbons which do not liquefy when the final gas is cooled. (3) From the superheater the water gas passes through the purifying apparatus (*E*) into a holder. A ton of hard coal yields about 44,000 cubic feet of enriched water gas.

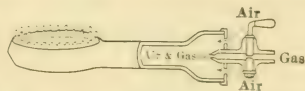


Fig. 117. — Modified Bunsen burner used on a stove to burn coal gas

324. Coal gas is made by heating coal in closed retorts and purifying the volatile product (326). It is largely hydrogen (45 to 50 per cent) and methane (30 to 36 per cent); other ingredients are hydrocarbons (ethylene, etc.), carbon monoxide and dioxide, and nitrogen. It burns with a yellow flame. When used as a fuel, considerable air is admitted and a special burner is used. In the laboratory we use the Bunsen burner (Figs. 126, 127). In

our houses the gas range burner is merely several small modified Bunsen burners arranged advantageously (Fig. 117). The heat value of coal gas varies from 525 to 600 B.t.u. per cubic foot.

325. Illuminants. — Some of the gases used as fuel are

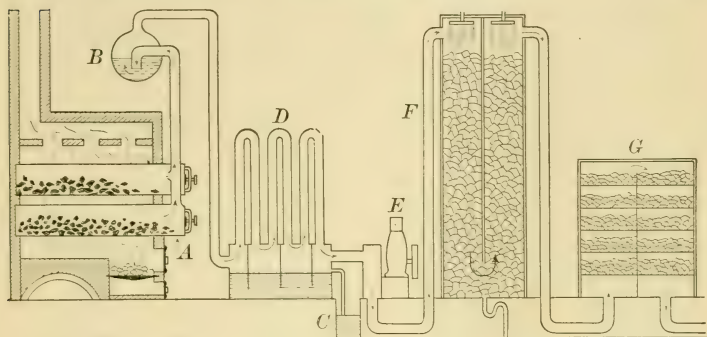


Fig. 118. — Diagram of coal gas plant

also used as a source of light, *i.e.* as illuminants. Coal gas and enriched water gas are the most important.

326. Manufacture of coal gas. — A diagram of a coal gas plant is shown in Fig. 118. (1) The coal is heated several hours in closed **retorts** (*A*). The volatile products escape from the retorts and bubble through water into the **hydraulic main** (*B*). Here some of the tar is deposited and ammonium compounds are dissolved by the water which flows constantly through the main and prevents the gas from escaping back into the retorts. The ammoniacal liquor and tar flow into the **tar well** (*C*). (2) From the hydraulic main the hot and impure gas passes through a long series of vertical pipes called the **condenser** (*D*), which cools the gas and removes tar. (3) An **exhauster** (*E*) draws or forces the gas from the condenser into the scrubber (and onward through the purifiers into the gas holder). (4) The **scrubber** (*F*) is a tall tower filled with coke or pebbles over which ammoniacal liquor and water trickle. The object of the scrubber is to remove the remaining ammonium compounds, and also carbon dioxide, hydrogen sulphide, and the last traces of tar. (5) From

the scrubber the gas passes into the **purifier** (*G*), which is a series of shallow rectangular boxes with frames loosely covered with lime or iron oxide, or both. In the purifier any remaining carbon dioxide and sulphur compounds are removed. (6) The purified gas next passes through a large **meter**, which records its volume, and then into a **gas holder** from which the gas is forced through pipes to the consumer.

A ton of good gas coal yields about 10,000 cubic feet of gas, 1400 pounds of coke (**287**), 120 pounds of tar, 20 gallons of ammoniacal liquor (**171**, **175**), and a varying amount of gas carbon (**288**).

The tar, or **coal tar** as it is often called, collected from the hydraulic main and condenser, is a thick, black, foul-smelling liquid. Some is used for preserving timber, making tarred paper and black varnishes, and as a protective paint. Most of it is separated by distillation into its important constituents (**372**).

327. The illuminating gas flame. — Luminous flames are produced when certain gases burn. Let us consider an ordinary illuminating gas flame. The gas issues from a slit in the burner tip and spreads out in a thin sheet. When the gas is ignited, the heat of the burning gases decomposes the hydrocarbons into hydrogen and carbon. The hydrogen burns to water. Part of the carbon burns at once to carbon dioxide. But some of the fine particles of carbon are heated white-hot and give the flame its illuminating power. Eventually all the carbon burns, if sufficient oxygen is supplied and the temperature is high enough.

The flame smokes or deposits free carbon, if the air supply is cut off or diminished or the temperature reduced. For example, if a bottle is held low down over the flame, smoke is given off; the same result is produced when the flame is cooled. The presence of unburned carbon in the flame can be shown by putting a cold object, such as a crayon or glass rod, in or just over the flame; a deposit of soot (carbon) soon gathers.

The flame is flattened for two purposes, viz. (1) to expose a large surface to the air so that all the carbon will be

consumed, and (2) to increase the amount of light. There are two distinct parts, or zones, to this flame (Fig. 119).

The lower part near the tip is black and consists largely of cold, non-luminous gas, while the upper part — “the flame” — is yellow-white and contains luminous particles of carbon.

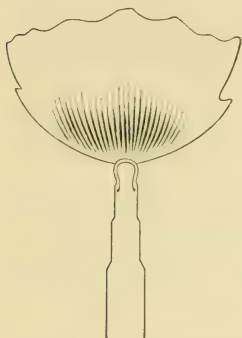


Fig. 119. — An illuminating gas flame

328. Oil gas is an illuminant made from petroleum by heating the vapor, or the vapor of some distillates, under proper conditions. The process is similar to cracking petroleum (315). The gas burns with a brilliant flame. Pintsch gas is made from oil.

329. Illuminating gas. — Coal gas is often burned alone but water gas is usually mixed with 60 or 70 per cent of coal gas. This mixture is called “illuminating gas.” Owing to the high percentage of carbon monoxide, water gas and mixtures containing it are poisonous (294).

Illuminating gases are complex mixtures. The accompanying table shows the approximate composition.

COMPOSITION OF ILLUMINATING GASES (BY VOLUME)

CONSTITUENTS	COAL GAS	WATER GAS	OIL GAS
Methane	35	17	49
Illuminants	4	9	32
Hydrogen	49	40	14
Carbon Monoxide	7	29	3
Carbon Dioxide	1	1	1
Nitrogen	4	4	1

Methane, hydrogen, and carbon monoxide burn with a feeble (non-yellow) flame; they furnish heat, but little light. The **illuminants** consist of ethylene (C_2H_4), acetylene

(C_2H_2), benzene (C_6H_6), and other hydrocarbons; they burn with a yellow flame (318).

330. The luminosity of an illuminating gas is measured by a photometer and is expressed in candles or **candle power**. The determination is made by comparing the light of the burning gas with the light produced by a standard flame (or a standard wax candle). Ordinary coal gas has about 17 candle power, water gas about 25, and oil gas 50 or more. Ordinary illuminating gas has a varying candle power (18 to 20), since it is usually a mixture of coal gas and water gas. The use of mantles has greatly improved the methods of lighting by gas (338).

331. More about luminous flames. — In an illuminating gas flame the gas itself burns in the air. In an oil lamp, *e.g.* kerosene lamp, the oil is drawn up through the wick and volatilized by heat into a gas, which burns; the air supply is increased through small holes in the burner (below the flame) or in large lamps through a central vent also. In many lighthouses the vapor from oil is burned directly (*i.e.* not through a wick). In a candle, the heat from the burning wick melts and volatilizes the wax, and this gas burns. The structure of the luminous flame is essentially the same, whether produced by burning illuminating gas, kerosene oil, or candle wax.

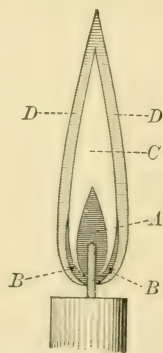


Fig. 120. — Sketch of the parts of a candle flame

332. The candle flame is more easily studied than an illuminating gas flame, and may be taken as the type. Examination of the sketch of an enlarged vertical section shown in Fig. 120 reveals four somewhat conical portions: (1) Around the wick there is a dark cone (A), filled with

combustible, but unburned gases formed from the melted wax. It is possible to draw off these gases through a small-bore glass tube and light them. (Compare Fig. 128.)

(2) Around the lower part of the dark cone is a faint bluish cup-shaped part (*B, B*). It is the lower portion of the

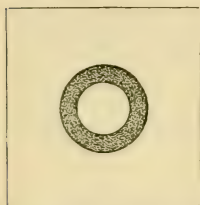


Fig. 121. — Charred paper showing the hottest part of a candle flame

exterior cone where complete combustion of the gases occurs, since plenty of oxygen from the air reaches this portion. (3) Above the dark cone is the luminous portion (*C*). It is the largest and most important part of the flame.

Combustion is incomplete here, because little or no oxygen can pass through the exterior cone. The temperature is high, however, and the hydrocarbons under-

go complex changes. Acetylene is probably formed. The most characteristic change is the liberation of small particles of carbon. This liberated carbon, heated to incandescence by the burning gases, makes the flame luminous.

(4) The exterior cone (*D, D*) is almost invisible. Here the combustion is complete, because oxygen of the air changes all the carbon to carbon dioxide. We can show that this is the hottest region of the flame by pressing a piece of stiff white paper for an instant down upon the flame almost to the wick. The paper will be charred by the hot outer portion of the flame, as shown in Fig. 121.

These four portions may be found, more or less easily, in all luminous hydrocarbon flames, whatever the shape. In ordinary gas flame the luminous part is enlarged, while the blue part cannot be seen unless the flame is turned low or looked at through a small opening (Fig. 119).

The gaseous products of the combustion of hydrocarbons, as repeatedly stated, are water vapor and carbon

dioxide. A bottle in which a candle is burning has, at first, a deposit of moisture on the inside; and if the candle is removed and calcium hydroxide solution is added, the presence of carbon dioxide is shown by the cloudiness of the solution (1).

We can readily show with a candle flame that the luminosity of hydrocarbon flames is affected by temperature. Thus, if a coil of copper wire is lowered upon a candle flame, the flame smokes, loses its yellow color, and finally goes out; but if a coil of hot wire is used, the flame burns unchanged (Fig. 122). Similarly, if a piece of wire gauze is held a few inches above a Bunsen burner and the gas is turned on and lighted *above the gauze*, the flame will not pass through the gauze until the latter becomes hot (Fig. 115). The Davy safety lamp depends on this principle (319).

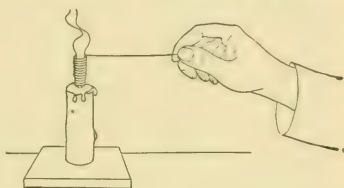
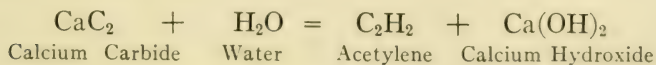


Fig. 122. — Effect of lowering the temperature of a candle flame

Not all luminous flames are hydrocarbon flames. Thus, magnesium burns with a brilliant flame. Its luminosity is due to the incandescence of solid particles of magnesium oxide. Similarly, the bright flame of burning phosphorus is accounted for by the incandescent particles of solid phosphorus pentoxide. (See also the Welsbach light, 338.)

333. Acetylene and its flame. — Acetylene (C_2H_2) is a gas, which is prepared by the interaction of calcium carbide and water, thus: —



Prepared in this way, it can be used on a small scale, as in a miner's lamp or portable lantern, or stored in tanks for lighting towns or houses. Acetylene dissolves in acetone, and cylinders in which considerable gas has

been dissolved are used to furnish gas, *e.g.* for mining camps and other localities where ordinary illuminating gas is not available.

Acetylene burns in the air with a luminous, smoky flame. But when considerable air is mixed with the gas as the

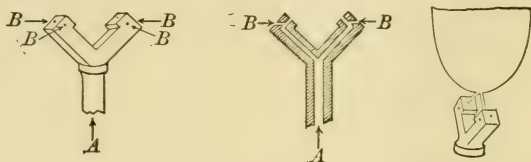


Fig. 123. — Acetylene burner and flame

latter issues from a small opening, the mixture burns with a brilliant, white flame, which does not smoke.

Ordinary gas burners cannot be used for acetylene because the flame produces soot. A common form of burner is shown in Fig. 123. The acetylene as it escapes from the supply pipe (*A*) into the burner sucks in air through the small side holes (*B*). This mixture, upon ignition, burns as a small flat flame at right angles to the burner (Fig. 123, right).

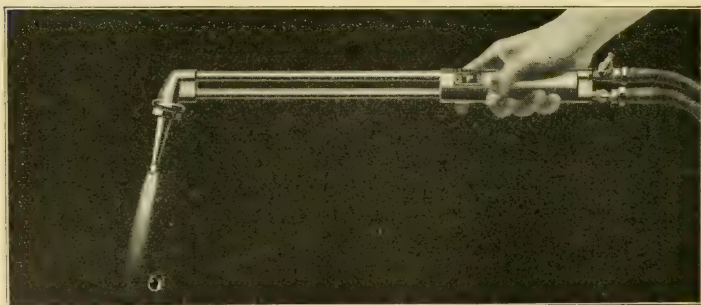
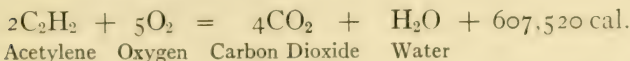


Fig. 124. — Oxy-acetylene torch and flame

334. The oxy-acetylene flame. — A mixture of acetylene and considerable oxygen burns with an intensely hot flame; a temperature of nearly 3000° C. can be reached

if the right mixture of acetylene and oxygen is burned in a special blowpipe called an oxy-acetylene torch (Fig. 124).

The thermochemical equation is:—



Ordinary tools cut hard metal slowly, but the tip of the oxy-acetylene flame when passed slowly across the metal melts ("cuts") it quickly. Metal structures, such as fences, bridges, frames of buildings, "scrapped" warships, etc., are speedily dismantled by this flame. The fire department of large cities is equipped with an oxy-acetylene outfit for cutting a passage through steel doors of vaults or effecting an entrance into parts of a fireproof building. The oxy-acetylene flame is also extensively used for welding metals (Figs. 28 and 125).



Fig. 125. — Welding with an acetylene torch. A cracked cylinder of a locomotive is being welded just inside the opening in the temporary brick wall

335. Non-luminous flames. — Some flames are non-luminous, *i.e.* they are colorless, or if colored, the flames do not give enough light for use as an illuminant. Thus, the ordinary hydrogen flame is almost invisible. The flames of carbon monoxide and methane are faint blue. The most common non-luminous flame is the Bunsen flame.

336. The Bunsen burner and its flame. — When illuminating gas is mixed with air before burning, and the mix-

ture burned in a suitable burner, a flame is produced which is non-luminous and hot, and deposits no carbon. Such a flame is called the **Bunsen flame**. It was first produced in a burner devised by the German chemist Bunsen. This burner is used in laboratories as a source of heat. The parts of a typical burner are shown in Fig. 126.

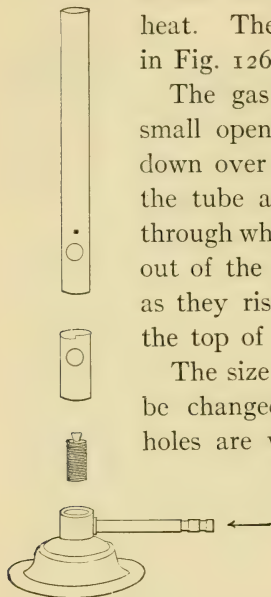


Fig. 126. — Parts of a typical Bunsen burner

The gas enters the base and flows from a small opening into the long tube, which screws down over this opening. At the lower end of the tube and above the inlet are two holes, through which air is drawn by the gas as it rushes out of the small opening. The gas and air mix as they rise in the tube, and the gas burns at the top of the long tube.

The size of the air holes at the bottom can be changed by a movable ring. When the holes are wide open, the typical non-luminous Bunsen flame is formed ; this flame

is free from soot, and apparatus heated by it is not blackened. When the holes are closed, the gas burns with a luminous flame and deposits carbon.

The gas burns at the top of the tube and not inside, because the proper mixture of gas and air rushes out more quickly than the flame can travel back through the tube to the small inlet. If the gas supply is slowly decreased, the flame becomes smaller, disappears with a slight explosion ("strikes back"), and burns at the small gas inlet inside the tube. A sudden draft of air, too much air admitted through the holes at the lower end of the tube, or too low gas pressure may cause the flame to "strike back."

This modified flame, which has a pale color, a disagreeable odor,

and deposits soot, should be extinguished and the proper flame produced before further use.

The Bunsen flame (Fig. 127) has a bluish color and consists essentially of two cones, which may often be distinguished by the different tints. The lower and inner cone consists of air and unburned gas. It is bluish, but becomes green when too much air is admitted (best seen in an imperfect flame). The upper and outer cone is the flame proper and consists of burning gases. It is faint blue and hot (about 1500°C.). The color is due to the burning mixture of carbon monoxide (blue flame) and hydrogen (colorless flame).

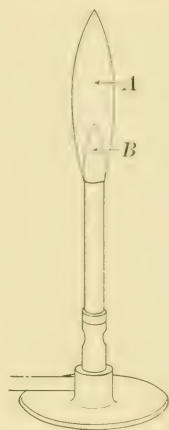


Fig. 127. — Sketch of a Bunsen flame

The fact that the *inner* cone consists of unburned gases can be shown by putting one end of a small bore glass tube into the cone; gas will rise through the tube and can be ignited at the upper end (Fig. 128, left). If a sulphur match is supported by a pin across the top of an unlighted burner, it will not be

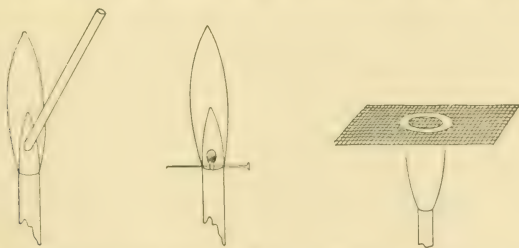


Fig. 128. — The cones of a Bunsen flame. Drawing unburned gases from the inner cone (left). A match does not ignite in the inner cone (center). The inner cone produces a dark disk and the outer cone a luminous ring (right)

come ignited until some time after the gas is first lighted (Fig. 128, center).

We can readily show that the *outer* cone consists of burning gases. A match held near the side of the flame ignites quickly, while a match laid for an instant across the top of the tube is charred only at the two points where it touches the outer cone. Finally, a wire gauze, if pressed down upon the flame, shows a dark disk surrounded by a luminous ring due to the inner and outer cones respectively (Fig. 128, right).

337. Oxidizing and reducing flames. — The outer portion of the Bunsen flame is called the **oxidizing flame**. Here oxygen from the air is abundant.

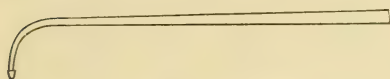


Fig. 129. — Blowpipe

The inner and lower portion is called the **reducing flame**. Here the excess of unburned hydrocarbons withdraws oxygen. A sketch of the general relation of these flames is shown in Fig. 127. *A* is the most effective part of the oxidizing flame, and *B* of the reducing flame. At *A* metals are oxidized, and at *B* oxygen compounds are reduced.

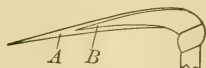


Fig. 130. — Blowpipe flame. *A* is the oxidizing part, and *B* the reducing part

Sometimes a tapering tube with a small opening at the bent end, called a blowpipe (Fig. 129), is used to produce these flames. A special tube with a flattened top is put inside the burner tube to produce a luminous flame. The tip of the blowpipe rests in or near this flame, and if air is gently and continuously blown through the blowpipe, a long slender flame is produced, called a blowpipe flame (Fig. 130). It is like the Bunsen flame as far as its oxidizing and reducing properties are concerned.

338. The Welsbach light. — The Bunsen flame is used in producing the Welsbach light. A conical shaped mantle consisting of a firm network of thorium oxide (99 per cent) and cerium oxide (1 per cent) is suspended over a Bunsen flame. The heat of the flame makes the mantle glow and

give a brilliant light. With equal volumes of gas, the Welsbach mantle gives about four times as much light as an ordinary gas burner. There are several kinds of mantles (Fig. 131).

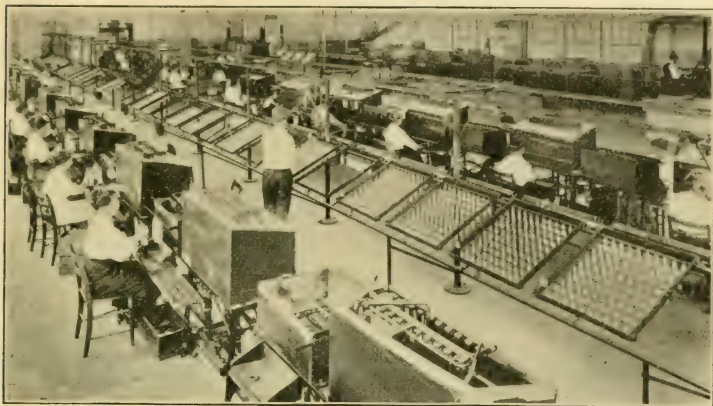


Fig. 131. — Making inverted mantles for the Welsbach light

EXERCISES

1. Name five fuels and three illuminants.
2. How is the heat value of fuels (*a*) measured and (*b*) stated?
3. What is the heat value of (*a*) hard coal, (*b*) fuel, oil, (*c*) wood, (*d*) coke?
4. Define and illustrate a thermal equation.
5. Prepare a summary of (*a*) burning coal, (*b*) manufacturing coal gas, (*c*) producer gas, (*d*) water gas, (*e*) fuel oil.
6. Explain the use of gasoline in an automobile.
7. Topics for home study: (*a*) Hydrocarbons. (*b*) Natural gas. (*c*) Construction of a gas range burner. (*d*) A gas flame. (*e*) Manufacture of candles. (*f*) Acetylene in metal working.
8. What is the formula of methane, ethylene, hexane, acetylene? What is the weight of a mole of each gas?
9. Complete: (*a*) $C + \text{---} = CO$; (*b*) $CO + \text{---} = CO_2$; (*c*) $CO_2 + \text{---} = CO$; (*d*) $CH_4 + \text{---} = CO_2 + \text{---}$; (*e*) $CaC_2 + \text{---} = \text{---} + Ca(OH)_2$.
10. Draw a diagram of the apparatus for manufacturing (*a*) coal gas, (*b*) water gas, (*c*) calcium carbide.

11. Essay topics: (a) The by-products of coal gas manufacture. (b) Manufacture of Welsbach mantles. (c) Illumination in light-houses. (See *National Geographic Magazine*, January, 1913.) (d) The petroleum industry. (e) Fuel oil.

12. Draw from actual observation a diagram of the parts of (a) a candle flame, (b) an illuminating gas flame, (c) a Bunsen flame (showing the oxidizing and reducing parts).

13. Describe a Welsbach burner and light. What is the mantle? What is its relation to the light?

14. Home exercises: (a) Examine a Welsbach burner from which the mantle has been removed and compare with a Bunsen burner. (b) Examine the burner and flame of a gas cooking range. Compare both with a Bunsen burner and flame. (c) Examine a kerosene lamp and sketch the burner. (d) Test illuminating gas for sulphur compounds. (*Suggestion.* Hold a paper moistened with lead nitrate solution in the escaping gas.)

PROBLEMS

1. A candle weighing 50 gm. consists of wax composed of 88 per cent carbon and 12 per cent hydrogen. What weight of carbon dioxide and of water will be formed by burning half the candle?

2. How many liters of hydrogen and of carbon monoxide at 10° C. and 750 mm. will be formed by passing 100 gm. of steam over incandescent carbon?

3. An acetylene gas plant consumes 100 cubic feet an hour. How much calcium carbide would be used in a month of 30 days, if the gas is burned an average of 5 hours a day?

4. What volume of air (containing 21 per cent of oxygen by volume) will be required for the combustion of 100 tons of coal, assuming that the coal is 80 per cent pure carbon and burns to carbon dioxide?

5. Ten tons of coke were burned and only 35 tons of carbon dioxide were produced. Calculate the per cent of carbon in the coke.

6. Calculate the B.t.u. liberated by burning the following: (a) 1 ton of coke, (b) 1000 lb. of fuel oil, (c) 10,000 cu. ft. of natural gas, (d) 2000 cu. ft. of producer gas, (e) the number of cubic feet of illuminating gas burned in your home for a month (assume 550 B.t.u. per cu.ft.), (f) apply (e) to the school building.

CHAPTER XXIII

OTHER CARBON COMPOUNDS

339. What are organic compounds?—Carbon is an essential element in a large number of compounds. Besides carbon, other elements are hydrogen, oxygen, and nitrogen; sulphur and phosphorus are sometimes found. Many carbon compounds form series, just as the hydrocarbons do (**317**). Carbon compounds occur so frequently in plants and animals and are so closely associated with life processes, they are called organic compounds in contrast to inorganic or mineral compounds which are found chiefly in the earth. The branch of chemistry which deals exclusively with carbon compounds is called **Organic Chemistry**. In this chapter we shall study a few important organic compounds.

340. Carbohydrates are composed of carbon, hydrogen, and oxygen. Examples are sugar, starch, and cellulose (the essential part of wood fiber and cotton fiber).

341. Sugars.—There are many different sugars. The most important is ordinary sugar or **cane sugar**, which is also called **sucrose**. Other sugars are **dextrose**, **levulose**, **lactose**, and **maltose**.

342. Sucrose ($C_{12}H_{22}O_{11}$) is widely distributed. Sugar cane contains about 18 per cent and sugar beets from 12 to 15 per cent, and these are the main source of sucrose.

Sucrose is a white solid; rock candy is well crystallized sucrose. It is very soluble in water; one part of water dissolves about three times its weight of sugar at ordinary

temperatures. If sugar is carefully heated it melts. As the temperature is raised, the sugar begins to decompose; *water is given off* and a light brown substance called **caramel** is formed, which is used to color soups and gravies. By

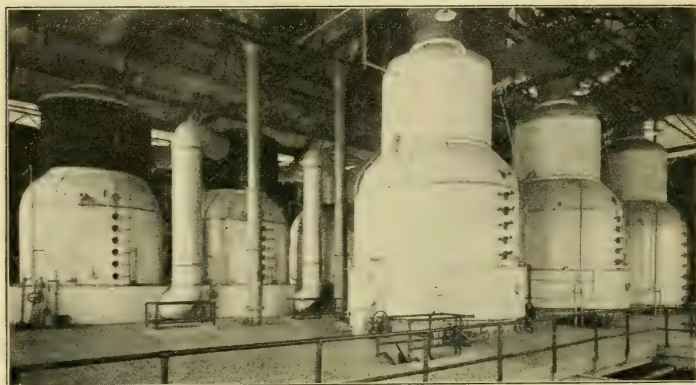


Fig. 132. — Vacuum pans and evaporator in a Cuban sugar mill

further heating, a black porous mass of **carbon** is finally obtained, often called sugar charcoal. Thus we see that sugar consists of carbon, hydrogen, and oxygen.

343. The manufacture of sugar from sugar cane and sugar beets involves two main operations.

(1) In the **preparation of raw sugar** from sugar cane the juice obtained by crushing the cane is first boiled with a weak calcium hydroxide solution to neutralize acids, remove impurities, and prevent fermentation; carbon dioxide is next added to remove the excess of lime; and the final solution is filtered through bone black. This purified juice is evaporated in vacuum pans until the sugar begins to crystallize from the cooled liquid (Fig. 132). The liquid is next allowed to stand several hours in crystallizing troughs (Fig. 133). And the crystals are separated finally from the brown liquid by a centrifugal machine (Fig. 134). The liquid left is **molasses**.

In the preparation of raw sugar from sugar beets the beets are

soaked in water, which dissolves the sugar. The solution is treated by processes much like those applied to cane sugar solutions.

(2) Raw sugar is dark colored, and must be **refined** before use.

(a) The raw sugar is dissolved in water, air is blown in to agitate

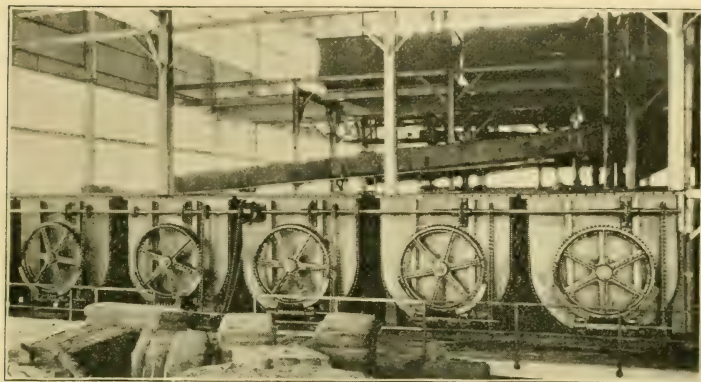


Fig. 133. — Crystallizing troughs

the heated solution, and lime and other substances are added to gather the impurities into a scum or clot. The colored liquid is filtered, first through cloth bags and then through animal charcoal. (b) The filtered sirup is treated as in (1). The crystals are dried in a heated tube, called a granulator, to form granulated sugar.

344. Dextrose ($C_6H_{12}O_6$) is a white solid about three fifths as sweet as sucrose. It is very soluble in water, but crystallizes from it with difficulty. Dextrose is found



Fig. 134. — Crystallizing troughs (upper row) and centrifugal machines (lower row)

in honey and in many fruits, especially grapes, and is sometimes called **grape sugar**. Another name for it is **glucose**.

The thick sirup called commercially by different names (*e.g.* "karo") contains about 20 per cent of glucose (besides 40 to 45 of maltose, and 30 to 35 of dextrine). It is manufactured by heating starch with dilute hydrochloric acid; if the process is carried far enough the product is a hard, wax-like solid known as commercial **grape sugar**, which is almost pure dextrose.

Glucose is an inexpensive substitute for sucrose, and is extensively used in making candy, jellies, sirups, and other sweet mixtures.

Levulose ($C_6H_{12}O_6$) is a sweet, white solid found in fruits and honey, and is often associated with dextrose. It is sometimes called **fructose** or **fruit sugar**.

345. Testing for dextrose. — Dextrose and levulose are reducing agents. An alkaline solution of dextrose is used to reduce a silver solution and deposit the silver as a bright film in making reflectors for automobiles, mirrors, Dewar flasks, and thermos bottles. Dextrose reduces a strong alkaline mixture of copper sulphate and sodium potassium tartrate, known as **Fehling's solution**. Thus, when this solution is boiled with dextrose (or a reducing sugar), a reddish copper compound (cuprous oxide, Cu_2O) is formed.

346. Isomerism. — The formula of both dextrose and levulose is $C_6H_{12}O_6$, yet their properties are very different. The difference is due to a different arrangement of the atoms in a molecule. Such compounds are called **isomers** and illustrate **isomerism**. There are many cases of isomerism among organic compounds.

347. Lactose ($C_{12}H_{22}O_{11}$) occurs in milk and is sometimes called **milk sugar**. It gives milk its sweet taste. Cow's milk contains from 3 to 5 per cent of lactose. Crystallized lactose is a rather hard, gritty solid, much like

sucrose, though not so sweet or soluble. A solution of lactose reduces Fehling's solution.

Lactose is not fermented by ordinary yeast, but a special ferment, called lactic ferment, converts it into alcohol and lactic acid. The lactic acid gives milk its sour taste and also assists in curdling the milk, *i.e.* in changing the casein into a clot or curd. Lactose is obtained from whey, which is the liquid left after the solids have been pressed from milk curdled by rennet in the manufacture of cheese. Lactose is used in preparing infant foods and certain medicines.

348. Maltose ($C_{12}H_{22}O_{11}$) is formed from starch by malt, hence the name maltose. The transformation is caused by **diastase**, which is formed in the malt by allowing moist barley to sprout in a warm place. Maltose is also formed from starch by the ptyalin in the saliva.

Maltose ferments readily with yeast, forming alcohol and carbon dioxide (see commercial production of alcohol (356)). Like lactose, maltose is a sweet solid, very soluble in water, from which it forms crystals; its solution reduces Fehling's solution.

349. Starch is the most widely distributed and abundant carbohydrate. It is found in wheat, corn, and all other grains, in potatoes, beans, peas, and similar vegetables, and also in rice, sago, tapioca, and nuts. Many parts of plants contain starch; *e.g.* the stalk, stem, leaves, and especially the root, seed, and fruit. The food value of vegetables depends largely on the starch they contain. Large quantities of starch are consumed as food; much is used in laundries, paper manufactories, and cotton cloth mills, and in the manufacture of glucose and adhesives.

Starch, as usually seen, is a white mass, but it really consists of minute grains which vary with the plant, as may be seen by examining starch with a microscope (Fig. 135).

Starch is extracted by a mechanical process from many plants — in the United States largely from corn and wheat and in Europe chiefly from potatoes, rice, and wheat.

Starch is only very slightly soluble in water because the granules are enveloped in an insoluble membrane of cellulose (352). But if boiled with water, the membrane

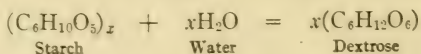


Fig. 135. — Starch grains (magnified) — wheat (left), rice (center), corn (right)

bursts, the grains swell, dissolve to some extent, and on cooling do not settle out but form a jelly-like mass — the familiar starch paste. With cold water, starch forms an ordinary suspension. Whereas with hot water, a colloidal solution is produced (86, 101).

Starch gives a blue colored substance when added to iodine solution, and its presence in many vegetables and foods can be readily shown by grinding the substance in a mortar with cold water and adding a drop of dilute iodine solution. It does not reduce Fehling's solution.

Starch is a complex carbohydrate and its composition corresponds to the formula $(C_6H_{10}O_5)_x$. Starch is readily transformed into other carbohydrates. Thus, it forms maltose and dextrin (348, 351); with dilute acids it forms maltose, dextrin, and dextrose (344). An equation for the change of starch into dextrose is: —



350. Making bread. — Wheat flour contains about 70 per cent of starch. The remainder is chiefly water and

gluten, though small quantities of mineral matter and fat are present. In **making bread**, the flour, water, and yeast are thoroughly mixed into dough, which is put in a warm place to rise. Fermentation begins at once. **Fermentation** is the conversion of an organic compound, like starch or some sugars, into simpler compounds by the action of catalytic substances called **enzymes**, *e.g.* diastase and ptyalin.

Enzymes from the yeast change starch into dextrose, or a similar fermentable substance, which undergoes fermentation, forming alcohol and carbon dioxide. The gases escape in part through the dough, which becomes light and porous. When the dough is baked, the heat stops the action of the enzymes; but the alcohol, carbon dioxide, and some water escape and puff up the mass still more. The heat, however, soon hardens the starch, gluten, etc., into a firm porous loaf.

351. Dextrin ($C_{31}H_{62}O_{31}$ probably) is a light brown, or white, sweetish solid formed by heating starch to 200° – 250° C. It dissolves in cold water and forms a sticky solution which is used as an adhesive, especially on postage stamps. It is also used in making mucilage, for thickening colors and sticking them to cloth in calico-printing, and as an ingredient of candy and beverages.

When starched clothes are ironed the hot iron changes some of the starch to dextrin, which gives a gloss to the fabric. Dextrin is also formed from starch when bread is baked or toasted.

352. Cellulose ($(C_6H_{10}O_5)_x$) is the substance of which the cell walls of plants consist, and is therefore very widely distributed. Wood contains cellulose and related compounds, while cotton, linen, and the best qualities of filter paper are nearly pure cellulose.

Pure cellulose is a white substance, insoluble in most liquids, but soluble in a mixture of ammonia and copper hydroxide. Sulphuric acid of a special strength, if quickly

and properly applied to paper, changes it into a tough form called **parchment paper**. The latter is often substituted for animal parchment (*e.g.* sheepskin).

353. Derivatives of cellulose. — With nitric acid cellulose forms **cellulose nitrates**. One of these is **gun cotton**. It looks like ordinary cotton, and may be spun, woven, and pressed into cakes. It burns quickly, if unconfined, but when ignited by a percussion cap or when burned in a confined space, gun cotton explodes violently. It is used in blasting and for torpedoes and submarine mines.

A mixture of gun cotton, ether, and alcohol soon becomes a plastic mass, which upon being rolled and carefully dried forms a transparent solid; this substance is called **smokeless powder**. When exploded, it forms carbon dioxide and monoxide, nitrogen, hydrogen and water vapor — all colorless *gases*.

A solution of certain cellulose nitrates in a mixture of alcohol and ether is called **collodion**. When collodion is poured or brushed upon

a glass plate or the skin, the solvent evaporates, leaving behind a thin film. It is used in preparing photographic films and as a coating for wounds.

A mixture of camphor and cellulose nitrates is called **celluloid**, which is widely used in making photographic films.

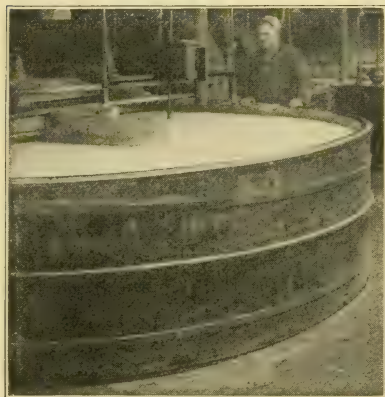


Fig. 136. — A beater full of pulp which is being separated and cut into fine particles

354. Paper consists chiefly of cellulose matted together. Most paper, especially that used for newspapers, is

made from wood. Considerable writing paper, however, is still made from cotton and linen rags.

In making paper from wood, the latter is first reduced to a pulp mechanically by grinding the wood upon a revolving stone or chemi-

cally by heating it under pressure with sodium hydroxide or calcium bisulphite (acid calcium sulphite). The pulp is carefully washed, bleached, and washed again. It goes next to the beater (Fig. 136) in which revolving knives separate and cut the fibers of cellulose into finer particles. Here the filler (clay), sizing (rosin), and coloring matter (if desired) are added and thoroughly mixed with the pulp. Sometimes this mixture is further treated in a refiner. The pulp is then suspended in a large volume of water (90 to 96 per cent) and the thin mixture is pumped to the Fourdrinier machine on which the sheet is made (Fig. 137). The pulp mixture flows on to a fine,

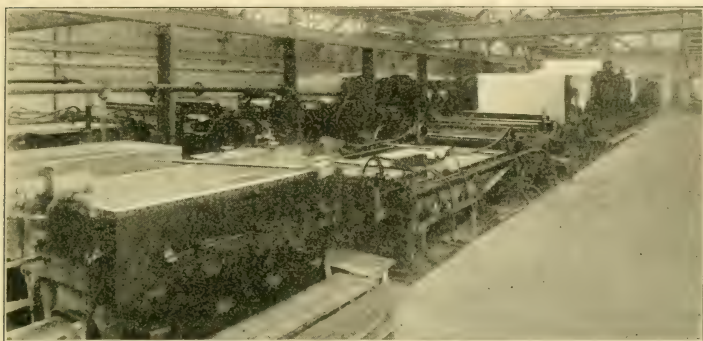


Fig. 137. — A Fourdrinier machine for making paper

wire cloth which moves slowly along; the water drains off and leaves the fibers on the wire as a thin moist layer, which is dried and pressed by rollers into a compact sheet. The sheet finally consists mainly of interlaced fibers of cellulose.

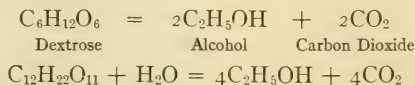
355. Alcohols consist of carbon, hydrogen, and oxygen. Some properties of methyl alcohol (CH_3OH) and ethyl alcohol ($\text{C}_2\text{H}_5\text{OH}$) have been described and their use as fuels has been stated (285, 314). Methyl and ethyl alcohols mix with water in all proportions. Ordinary commercial ethyl alcohol contains 4 to 5 per cent of water. **Absolute alcohol** is 100 per cent ethyl alcohol. **Denatured alcohol** is essentially a mixture of 100 parts ethyl alcohol,

10 parts methyl alcohol, and a small proportion of some poisonous, or unpalatable, substance, such as benzene, pyridine, or kerosene. (There are many legal formulas of denatured alcohol.) This mixture is impossible for use as a beverage, but is suitable for industrial processes.

Denatured alcohol and methyl alcohol are not taxed; ethyl alcohol is. Owing to this tax the price of ethyl alcohol is high. Hence its use as a fuel is very much restricted.

Ethyl alcohol is used in manufacturing varnishes, celluloid, collodion, artificial silk, extracts, perfumes, ether ($(C_2H_5)_2O$), chloroform ($CHCl_3$), iodoform (CHI_3), and numberless other organic compounds.

356. Manufacture of ethyl alcohol. — Ethyl alcohol is manufactured by the fermentation of certain sugars obtained from molasses or from starch. When yeast is added to a solution of dextrose, maltose obtained from starch by action of diastase (348), or any other fermentable sugar, complex chemical changes occur; the main products resulting from the action of the enzyme zymase (from the yeast) upon dextrose and maltose are alcohol and carbon dioxide, thus: —



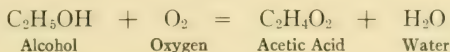
The alcohol, which constitutes about 15 per cent of the final mixture, is separated by fractional distillation.

357. Acetic acid ($C_2H_4O_2$ or $CH_3.COOH$) is the most common organic acid. It is manufactured on a large scale by the dry distillation of wood (285). The distillate, which is called pyroligneous acid, contains about 10 per cent of acetic acid, besides methyl alcohol, and acetone (367).

Very concentrated acetic acid is called **glacial acetic acid**. Commercial acetic acid contains about 30 per cent of pure acetic acid. It is a rather weak acid (247). Acetic

acid is used to prepare acetates, dyestuffs, medicines, and white lead. Some of its salts — the acetates — are useful compounds, *e.g.* lead acetate and Paris green.

358. Vinegar is dilute acetic acid, containing from 4 to 6 per cent of the acid. It is prepared by oxidizing dilute alcohol (by the action of bacteria); the essential chemical change is: —

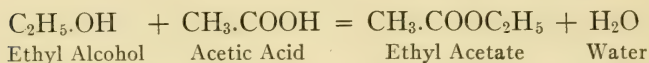


The alcohol is usually obtained from sugars. Substances containing starch or fermentable sugars, *e.g.* fruit juices, cider, and molasses, slowly ferment when exposed to the air (which always contains bacteria necessary for the chemical transformations), forming alcohol first and finally vinegar. Cider vinegar is made this way.

359. Other organic acids. — Rhubarb and sorrel contain a salt of **oxalic acid** ($\text{C}_2\text{H}_4\text{O}_2$). This acid is poisonous. The acid and some of its salts decompose iron rust and inks containing iron, and are often used to remove such stains from cloth. The acid is also an ingredient of mixtures used to clean metals and straw. **Lactic acid** ($\text{C}_3\text{H}_6\text{O}_3$) occurs in sour milk (**347**). When sour milk is used in cooking, the baking soda (HNaCO_3) and lactic acid interact, producing soluble sodium lactate and carbon dioxide gas; the gas puffs up the dough. **Malic acid** ($\text{C}_4\text{H}_6\text{O}_5$) is found free or as salts in apples, pears, cherries, currants, gooseberries, rhubarb, grapes, and berries of the mountain ash tree; also in the roots, leaves, and seeds of many vegetables. **Tartaric acid** ($\text{C}_4\text{H}_6\text{O}_6$) occurs as the potassium salt (acid potassium tartrate, $\text{HKC}_4\text{H}_4\text{O}_6$) in grapes and other fruits. During the fermentation of grape juice, the impure salt is deposited in the wine casks. From this **argol** or crude tartar the acid is prepared. Purified argol is called **cream of tartar**;

it is an ingredient of baking powder. **Citric acid** ($C_6H_8O_7$) occurs abundantly in lemons and oranges, and in small quantities in currants, gooseberries, raspberries, and other acid fruits. The acid is used in making lemonade. (For other organic acids, see **361**.)

360. Esters are compounds of carbon, hydrogen, and oxygen closely related to alcohols and organic acids. For example, ethyl alcohol and acetic acid form the ester called **ethyl acetate**, thus:—



Ethyl acetate has a pleasant, fruitlike odor. Its formation in this way is a simple **test for alcohol or acetic acid**. Ethyl acetate is analogous to sodium acetate, *i.e.* the organic salt contains the radical ethyl (C_2H_5), whereas the metallic salt contains sodium.

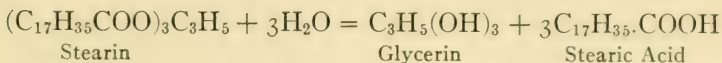
Organic acids form many important esters. Some occur in fruits and flowers, and in many cases give the fragrance and flavor. Others are manufactured, and used as the characteristic ingredient of flavoring extracts, perfumery, and beverages. **Ethyl butyrate** has the taste and odor of pineapples, **amyl acetate** of bananas, **amyl valerate** of apples, and **methyl salicylate** of wintergreen.

361. General relations of fats, glycerin, and soap.—Natural fats and oils are essentially mixtures of three esters, called glyceryl stearate, glyceryl palmitate, and glyceryl oleate. Their common names are stearin, palmitin, and olein. Stearin and palmitin are solids at ordinary temperatures; olein is a liquid. Hard fats are largely stearin and palmitin; soft or liquid fats and oils are largely olein.

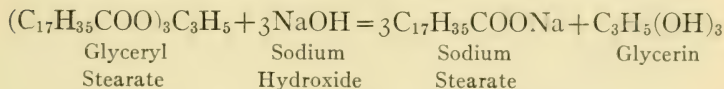
The organic acids corresponding to these esters are stearic acid ($C_{18}H_{36}O_2$), palmitic acid ($C_{16}H_{32}O_2$), and oleic acid

($C_{18}H_{34}O_2$). The corresponding alcohol is glycerin ($C_3H_5(OH)_3$). The radical of glycerin is glyceryl (C_3H_5). Hence the names glyceryl stearate, etc.

When fats are heated with very hot steam or with sulphuric acid, they are changed into glycerin and the corresponding acids. Thus, with stearin the change is:—



But if fats are boiled with sodium hydroxide or a similar alkali, glycerin and an alkaline salt of the corresponding acid are formed, thus (for stearin):—



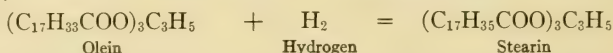
Soap is a mixture of such alkaline salts (**365**). In a few words, the general relations are these: (1) fats are esters; (2) treated with steam or acid, fats form glycerin and organic acids; (3) treated with alkalies, fats form glycerin and soap.

362. Natural fats and oils are often complex mixtures. The chief ingredients, however, are stearin, palmitin, and olein; small quantities of similar esters are usually present and often give certain fats characteristic properties. **Tallow** is about 66 per cent stearin and palmitin and 33 per cent olein; it is a solid fat obtained from the sheep and ox and is used in making soap and candles. **Lard** consists of olein, stearin, palmitin, and a little linolein; it is obtained from the fat of the hog and is used in cooking. **Olive oil**, which is obtained from the fruit of the olive tree, contains about 72 per cent of olein (and a similar fat) and about 28 per cent of stearin and palmitin, together with small quantities of other substances; the best qualities are used as salad oil, while cheap kinds are utilized in cooking, as a lubricant, and for making soap. **Cottonseed oil** is similar to olive

oil; it is obtained from the seeds of the cotton plant and is used extensively in cooking, as salad oil, and as a substitute for other oils.

Butter fat is 60 per cent olein, 30 per cent stearin and palmitin, and 5 per cent butyrin (glyceryl butyrate), together with small quantities of esters corresponding to capric, caprylic, and myristic acids. The pleasant flavor of butter is mainly due to the esters and some other substances that are present in small proportions. **Oleomargarine** and other substitutes for butter resemble real butter. They are made from different fats and oils (*e.g.* cocoanut oil).

363. Hydrogenation of oils. — Oils, such as cottonseed oil, when heated, mixed with finely divided nickel, and then treated with hydrogen under pressure, become solid fats. The chemical change consists in the addition of hydrogen. For example, olein becomes stearin, thus: —



The chemical change is called **hydrogenation**. The nickel acts as a catalyst, and is removed by filtering the melted fat. Substitutes for lard and other solid fats are made by this process, *e.g.* “crisco” from cottonseed oil. Fish oils are also converted into soap stock.

364. Glycerin ($\text{C}_3\text{H}_8\text{O}_3$) or ($\text{C}_3\text{H}_5(\text{OH})_3$) is a thick, sweet, colorless liquid. It absorbs water from the air and is often added to substances to keep them moist, *e.g.* stamping ink. When heated, it decomposes and gives off irritating fumes, like those produced by burning fat. It is used to make nitroglycerin and printers’ ink rolls; it is also used as a sweetening ingredient of certain foods, tobacco, and candy; cosmetics and lotions often contain glycerin.

Glycerin is often called **glycerol**. It is an alcohol, and when treated with a mixture of concentrated nitric and sulphuric acids, it forms an ester commonly known as **nitroglycerin** ($\text{C}_3\text{H}_5(\text{ONO}_2)_3$). This is a slightly yellow, heavy, oily liquid. It is the well-known explosive. When kindled by a flame, it burns without explosion; but if subjected to a shock or heated suddenly by a percussion cap, it explodes violently. Nitroglycerin is used in blasting; but since it is dangerous to handle and transport, it is usually mixed with some

porous substance, such as infusorial earth, fine sand, clay, or even sawdust. In this form, it is called **dynamite**. Other explosives contain nitroglycerin, *e.g.* blasting gelatin and cordite.

365. Manufacture of soap. — Soap is made by boiling fats with sodium hydroxide solution. This process is called **saponification**. Sodium hydroxide produces hard soap, consisting chiefly of sodium palmitate, sodium stearate, and sodium oleate.

Most soaps are made by boiling the fat and alkali in a huge kettle (Fig. 138). This operation produces a thick, frothy mixture of soap,

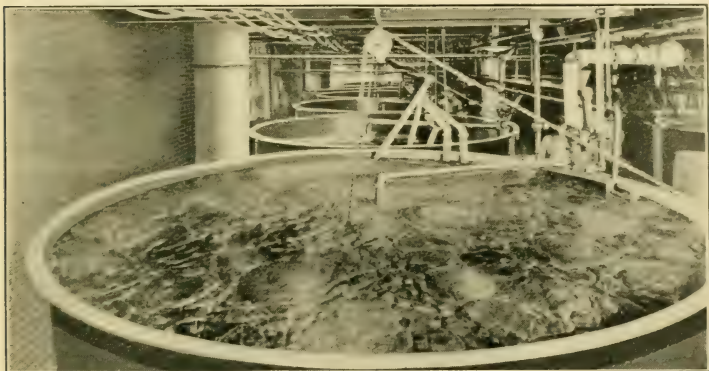


Fig. 138. — Soap kettle filled with a boiling mixture of fat and sodium hydroxide

glycerin, and alkali. At the proper time salt is added, thereby causing the soap to separate and rise to the top. The liquid beneath is drawn off, and from it glycerin is extracted.

Some soaps are boiled again with rosin or cocoanut oil, and then mixed (if desired) with perfume, coloring matter, or filling material (such as sodium silicate, sand, or borax). Floating soaps are made by forcing air into the semi-solid mass before cooling. The best soaps are prepared so that the finished product will not contain any unchanged fat or "free alkali," *i.e.* sodium hydroxide.

The cleansing action of soap is ascribed to two causes: (1) Soap hydrolyzes, *i.e.* interacts, with water — especially hot water — and

the liberated alkali (sodium hydroxide) acts upon the grease and oil that is usually mixed with the dirt. (2) Soap causes fat and grease to form an emulsion (86); the microscopic globules remain suspended in water and can be readily washed off with the dirt. The second cause is the more efficient.

366. Formaldehyde (CH_2O) is a gas with an irritating odor. The gas dissolves in water. The commercial solution sold as **formalin** contains 40 per cent of formaldehyde. It hardens tissue and is used as a preservative in museums. It is a convenient and efficient disinfectant and antiseptic. When so used, the solution is vaporized in a special apparatus and the vapors conducted into the infected room. A solid called para-formaldehyde is sometimes used to disinfect. When heated, it decomposes into formaldehyde. Para-formaldehyde candles are often used in place of sulphur candles (Fig. 95).

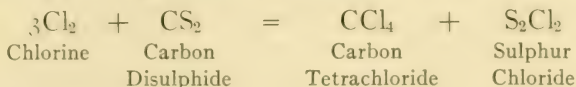
367. Acetone ($\text{C}_3\text{H}_6\text{O}$) is a colorless liquid which has an ethereal odor. It boils at about 56°C . It is used as a solvent for fats, oils, and waxes, and in the preparation of cordite and various smokeless powders and certain organic compounds (e.g. chloroform). Acetone is one of the products obtained by the distillation of wood (285).

368. Ethyl ether (ordinary ether, $(\text{C}_2\text{H}_5)_2\text{O}$) is a colorless, volatile liquid, with a peculiar, pleasing taste and odor. It boils at 35°C ., and the vapor is very inflammable. *The liquid should never be brought near a flame.* It is a good solvent for waxes, fats, oils, and other organic compounds. Its chief use is as an anæsthetic to produce unconsciousness in surgical operations. Ether is manufactured by heating a mixture of ethyl alcohol and sulphuric acid.

369. Chloroform (CHCl_3) is a heavy liquid made from alcohol (or acetone) and bleaching powder. It is used as an anæsthetic in special cases.

370. Iodoform (CHI_3) is a yellow solid made from iodine, alcohol (or acetone), and an alkali. It is widely used as an antiseptic for dressing wounds.

371. Carbon tetrachloride (CCl_4) is a heavy liquid. It is made by passing chlorine into carbon disulphide, thus: —



It is used to extract fats, grease, and gums from seeds, bones, and wool. Certain mixtures (*e.g.* “carbona”) used for cleansing fabrics contain carbon tetrachloride. When heated it forms a heavy non-combustible vapor, and is used in small hand fire extinguishers (*e.g.* “pyrene,” Fig. 66); it is especially useful in extinguishing fires due to gasoline.

372. Coal tar (326) yields important compounds by distillation. **Benzene** (C_6H_6) and **toluene** (C_7H_8) are liquids; **naphthalene** (C_{10}H_8) and **anthracene** ($\text{C}_{14}\text{H}_{10}$) are solids. These hydrocarbons are indispensable, being the parent substances of dyes, medicines, and explosives. Naphthalene is called moth balls and is used as a substitute for camphor. **Phenol** ($\text{C}_6\text{H}_5\text{OH}$) or carbolic acid is a white solid obtained from coal tar. It is used extensively as a disinfectant, especially in the form of a weak solution.

EXERCISES

1. How would you show in the laboratory that carbon is a constituent of (a) carbohydrates and (b) alcohol?
2. Discuss the distribution of sucrose. State its properties. Does cane sugar differ from beet sugar?
3. Compare dextrose and levulose. How are these sugars related to sucrose?
4. What is the test for dextrose and similar sugars?
5. Describe the manufacture of raw sugar. How is raw sugar refined?
6. What is (a) lactose and (b) maltose? Why is each so named?

7. What is (a) methanol, (b) absolute alcohol, (c) denatured alcohol?

8. Define and illustrate by means of sugars (a) hydrolysis and (b) fermentation.

9. How would you show that a leaf contains starch?

10. Topics for home study: (a) Dextrin. (b) Cellulose — its properties and derivatives. (c) The chemistry of bread-making. (d) The manufacture of paper. (e) Flour. (f) Alcohol. (g) Enzymes. (h) Glucose. (i) Manufacture of soap.

11. State the general relations of fats to glycerin.

12. Name several fats. What is (a) lard, (b) olive oil, (c) butter?

13. Discuss fully the chemistry of soap.

14. What is (a) ethyl acetate, (b) formaldehyde, (c) acetone, (d) iodoform, (e) ether, (f) phenol, (g) carbon tetrachloride? State a specific use of each.

15. Name five organic acids and state the source of each.

CHAPTER XXIV

FOOD AND NUTRITION

373. What are the functions of food? — The different kinds of food we eat perform two main functions. First, they **supply materials** needed for the growth, maintenance, and repair of the body. Second, they **provide energy** necessary to keep the body at the proper temperature, as well as to enable us to move about and perform our work. These functions are sometimes condensed by saying food supplies the body with building material and fuel.

374. What are nutrients? — The parts of the food that nourish the body are called **nutrients**. And the complex process by which the nutrients become of use is called **nutrition**. Nutrients are chiefly derived from three groups of organic compounds, viz. carbohydrates, fats, and proteins. Water and inorganic substances, *i.e.* mineral matter, though not nutrients are vitally connected with nutrition.

375. Uses of nutrients. — Carbohydrates and fats undergo chemical changes in the body and thereby provide energy. They are **fuel foods**. Both may also become transformed to some extent into a reserve supply. For example, carbohydrates may be stored in the liver in the form of glycogen and fats are often deposited in the form of protective tissue.

On the other hand proteins are **body builders**, *i.e.* they furnish material to replace worn-out muscle and nerve

tissue. They differ from carbohydrates and fats in being composed partly of nitrogen. Foods which contain protein are lean meat, eggs, milk, cheese, peas, beans, and grains like wheat (the cereals).

376. Function of water and mineral matter. — Water and mineral matter do not build tissue or furnish energy. Nevertheless both are indispensable for life processes. **Water** makes up about 70 per cent of the weight of the body. It keeps the tissues soft and pliable, dissolves juices and digested food, and assists in eliminating poisonous matter from the body.

Whereas **mineral matter** makes up only about 4 per cent of the weight of the body and consists of compounds of the following elements (in order of abundance): Calcium, phosphorus, potassium, sulphur, sodium, chlorine, magnesium, iron (and minute quantities of iodine, fluorine, and silicon). (Compare 11.) These elements supply the materials for the rigid parts of the body, *e.g.* bones and teeth. They furnish acids, bases, salts, and organo-metallic compounds, which give many fluids and juices of the body vital properties. Hydrochloric acid of the gastric juice and the hematin of the red blood corpuscles are examples of necessary mineral matter.

Mineral matter is obtained from seasoning added to food and from vegetables and fruits.

377. Composition of foods. — The proportion of carbohydrates, fats, proteins, and mineral matter varies greatly

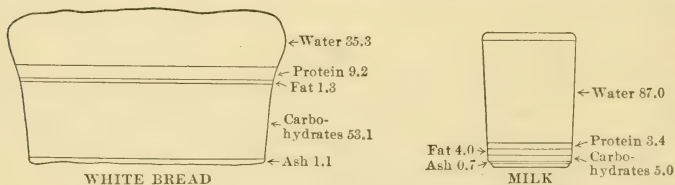


Fig. 139. — Composition of bread and milk

in different foods. The average composition (in per cent) of the edible portion of some common foods is shown in the accompanying Table of Composition of Foods, and also in Fig. 139.

TABLE OF COMPOSITION OF FOODS (IN PER CENT)¹

FOODS	WATER	CARBO- HYDRATE	FAT	PROTEIN	MINERAL MATTER
Apples	84.6	14.2	0.5	0.4	0.3
Bacon	20.2	—	64.8	9.9	5.1
Beans (dried)	12.6	59.6	1.8	22.5	3.5
Beefsteak (sirloin)	61.9	—	18.5	18.6	1.0
Butter	11.0	—	85.0	1.0	3.0
Cheese (cream)	34.2	2.4	33.7	25.9	3.8
Codfish (fresh)	82.5	—	0.3	16.3	0.9
Corn (green)	75.4	19.7	1.1	3.1	0.7
Eggs	73.7	—	10.5	14.8	1.0
Grapes	77.4	19.2	1.6	1.3	0.5
Ham (smoked)	40.3	—	38.8	16.1	4.8
Mutton (forequarter)	52.9	—	30.9	15.3	0.9
Oatmeal	7.3	67.5	7.2	16.1	1.9
Peanuts	9.2	24.4	38.6	25.8	2.0
Potatoes	78.3	18.4	0.1	2.2	1.0
Rice	12.3	79.0	0.3	8.0	0.4
Tomatoes	94.3	3.9	0.4	0.0	0.5
Walnuts (English)	2.5	16.1	63.4	16.6	1.4

378. Food as a source of energy. — The food we eat undergoes complex chemical changes in the body. These changes take place at first in the digestive organs and constitute the process called **digestion**. The digested food, which is in a liquid or dissolved form, is absorbed and transported to the various parts of the body, where it is built up into the tissue of which the various organs consist.

Sooner or later the tissue undergoes oxidation or some related process. Oxygen for this purpose comes from the air we breathe into the lungs; here the oxygen is taken up by the blood and distributed to the organs and

¹ A fuller table can be found in Bulletin 28 (Revised) or Farmers' Bulletin 142, United States Department of Agriculture, Office of Experiment Stations.

muscles of the body. The tissue is slowly transformed by the oxygen into carbon dioxide and water (27).

Heat is liberated by these chemical changes. New tissue is, of course, built up from the digested food. We might call food a fuel, because its digested products are oxidized, just as fuels are oxidized when they burn. The heat producing power of food is called its **fuel value**. And just as different fuels differ in the amount of heat liberated per pound, so various foods differ in their fuel value.

379. Fuel value of food. — The heat value, *i.e.* fuel value, of food is determined in the same way as the heat value of fuels, *viz.*, by burning a weighed quantity of the food in a bomb calorimeter and measuring the amount of heat liberated (301, 302). The unit used in measuring the fuel value of food is the **Calorie**. This is the amount of heat that will raise the temperature of 1 kilogram of water 1° C.

The food we eat, however, is not all digested nor is the nutritive portion completely transformed in the body. So the heat values of uneaten food obtained by the bomb calorimeter must be changed a little to account for these losses. These corrected fuel values are called **physiological fuel values**. They are the fuel values of the part of the food that is actually transformed into energy in the body — the real fuel value of the food digested and transformed. The physiological fuel values are the ones usually meant when the term *fuel value* is used.

The fuel value of food is often stated in Calories per pound, *i.e.* the number of Calories furnished by one pound of food. The fuel values of the foods tabulated in 377 are shown in the Table of Fuel Value of Foods.

TABLE OF FUEL VALUE OF FOODS (CALORIES PER POUND)

Apples 290	Codfish 325	Oatmeal 1860
Bacon 2840	Corn 470	Peanuts 2560
Beans 1605	Eggs 720	Potatoes 385
Beefsteak 1130	Grapes 450	Rice 1630
Butter 3401	Ham 1940	Tomatoes 105
Cheese 1050	Mutton 1505	Walnuts 3285

380. How much food do we need? — The amount of food needed varies with many factors, *e.g.* weight, work, age, and sex. A growing boy needs more than his father, a football player more than one who watches the game, and a hard laborer more than one who has a sedentary occupation. An adult who does moderate muscular work needs enough food to yield from 2500 to 3000 Calories a day. A satisfactory division would be: —

Carbohydrate	400–500 gm., or 1600–2000 Cal.
Fat	70–85 gm., or 630–765 Cal.
Protein	75–80 gm., or 300–320 Cal.

The fuel value of food is only part of the story. Sugar or butter would furnish enough heat, but a diet consisting largely of carbohydrates or fats would not repair worn-out tissue. We should eat food containing protein, as well as carbohydrates and fat. Authorities agree that an adult who does moderate muscular work needs 75–80 grams (3 ounces) of protein per day. If more is eaten, it is partly consumed as fuel and partly rejected by the body.

381. How to select an adequate diet. — The usual tables of composition and fuel value do not enable us to select the prepared food that is needed for an adequate diet. By means of the accompanying Table of Servings of Food it

is easy to arrange several sets of daily menus which will include the approximate amount of protein and furnish sufficient fuel value. By learning the protein content and fuel value of the important items, or those used frequently, you can readily tell if your diet is adequate.

TABLE OF SERVINGS OF FOOD

FOOD	WEIGHT IN GRAMS				TOTAL CALORIES
	Average Serving	Protein	Fat	Carbo- hydrate	
Apple, baked	135	1	1	26	117
Apple, raw	150	0.5	0.5	16	70
Apple sauce (3 heaping Tbs.)	125	0.25	1	47	198
Banana, raw	194	1.5	0.8	28	125
Beans, baked	185	19	9	47	345
Beans, lima	75	5	—	20	100
Beets (4 heaping Tbs.) . .	200	5	—	15	80
Biscuit (3 baking powder) .	90	8	11	45	311
Bread, white (2 slices) . . .	76	6.5	1.5	40	200
Butter	15	0.2	13	—	118
Cheese (1 cu. in.)	20	6	7	—	87
Chicken, creamed (on toast) .	125	17	13	22	273
Cocoa, 1 cup	230	5	6	12	122
Codfish cakes (2)	132	19	3	17	171
Corn chowder (1.5 cups) . .	333	10	10	39	286
Cream of wheat	250	5	1	33	161
Cream toast (1 slice)	148	11	11	49	339
Currant jelly (1 h. Tbs.) . .	37	0.5	—	28	114
Custard (2 heaping Tbs.) . .	134	7	8	19	176
Doughnut (1)	37	2.5	8	20	162
Dressing, French (2 ts.) . . .	9	—	7	—	63
Egg (1)	50	6.5	6	—	80
Figs (5)	100	4	0.3	73	309
Fish chowder (1 cup)	284	38	10	30	362
Fish, stuffed and baked . . .	152	33	4	7	196
Gingerbread (2.5 cakes) . . .	100	6	7	69	363
Hominy (1 cup)	245	3	—	32	140
Ice cream (2 heaping Tbs.) .	100	5	10	18	182
Lamb, roast (1 slice)	90	20	27	—	323
Lettuce, 4 leaves	50	1	—	1	8
Macaroni and cheese (1 cup)	200	10	14	32	294

FOOD	WEIGHT IN GRAMS				TOTAL CALORIES
	Average Serving	Protein	Fat	Carbo- hydrate	
Maple sugar (1 cake) . . .	100	—	—	83	332
Milk and sugar for cereal . .	73	2	2	15	86
Milk, glass	220	7	9	11	153
Onions, boiled	85	2	—	10	48
Orange	250	1.5	0.3	21	93
Orange ice (2 heaping Tbs.) .	100	1	0.3	75	307
Pie, apple ($\frac{1}{8}$)	126	4	12	54	340
Potato, baked	130	4	—	32	144
Potato, boiled	150	4	—	31	140
Potato, sweet	100	3	2	42	200
Pot roast	150	41	12	—	272
Prunes (5)	50	1	—	63	250
Pudding, chocolate farina . .	141	7	7	33	223
Pudding, cottage	144	6	10	77	422
Pudding, rice	133	6	7	34	223
Rice, steamed (1 cup) . . .	200	4	—	40	176
Salad, fruit	262	2	1	46	201
Salad, potato	150	4	—	31	140
Salad, vegetable	157	3	1	16	85
Sandwich, chicken	70	9	4	22	160
Sandwich, ham	70	7	10	27	226
Shredded wheat (1)	20	3	0.5	23	108
Snow pudding (2 heaping Tbs.)	80	4.5	—	12	66
Soup, cream of celery (1 cup)	125	3	9	5	113
Soup, cream of tomato (1 cup)	125	3	9.5	6.5	123
Spinach (1 heaping Tbs.) . .	100	2	4	3	56
Steak, Hamburg (1 cake) . .	50	16	8	—	130
Vegetable hash	140	9	8	30	252

382. We need an adequate diet. — To fulfill its functions our food should be carefully chosen. The carbohydrates and fats must be in the right quantity for fuel value and the protein in the proper proportion for tissue building. Moreover, we ought to select the three classes of nutrients from a wide variety of foods in order to provide a mixed diet, obtain the right kind of protein, and secure indispensable mineral matter. We should drink water freely —

at least six glasses a day. We should eat regularly an abundance of vegetables and cereals, which furnish bulky ingredients and assist the elimination of waste matter; they also yield mineral matter. Certain foods should always form a part of our diet, *e.g.* leaf vegetables, milk, whole wheat, unpolished rice, and fruit juices because they provide minute quantities of certain substances called **vitamins**, which are essential to growth and good health.

Finally, we ought not to forget that properly selected food must be well digested and assimilated by the body. Nutrition is a complex process. If we wish to have strong, healthy bodies, we must not only choose our food carefully, but masticate it well, and rest during the first part of the digestive process; we must also exercise regularly and establish early in life good habits of body and mind.

EXERCISES

1. Prepare a summary of this chapter.
2. Define the terms *food*, *nutrition*, and *nutrients*.
3. Name the three groups of nutrients. Give three examples of each.
4. Learn the composition and fuel value of (a) bread, (b) butter, (c) potatoes, (d) eggs, (e) milk.
5. Select from the table in **377** foods rich in (a) protein, (b) carbohydrate, and (c) fat.
6. Topics for home study: (a) Digestion. (b) Water and nutrition. (c) Enzymes and digestion. (d) Mineral matter in the body. (e) Respiration. (f) The blood. (g) Cost and fuel value of food. (h) Bomb calorimeter.
7. Discuss the topics: (a) Food is a source of energy. (b) The body resembles a steam engine.
8. Assuming that one square inch represents 1000 Calories, draw diagrams of the fuel value of five foods from the table in **379**.
9. Use the table in **381** for the following: (a) Make out a menu for breakfast, dinner, and supper which contains 75-80 gm. of protein and furnishes 2500-3000 Cal. (b) As in (a) for 100 gm. of protein and about 3500 Cal. (c) As in (a) for 100 gm. of fat, 85 of protein, and about 4000 Cal.

10. Use the table in **381** to keep a record (or make an estimate) of the approximate amount of carbohydrate, fat, and protein you eat in (a) one day, (b) three days, (c) one week, (d) one lunch.

PROBLEMS

1. By means of the table in **379** and prices obtained from your grocer compute (a) the number of Calories of 10 of the items that may be bought for 20 cents. (b) As in (a), compute the cost of 100 Cal. of the same items.

2. Calculate the weight of (a) mineral matter in 1 lb. of cheese, (b) water in 1 lb. of potatoes, (c) fat in 1 lb. of beefsteak, (d) protein in 1 lb. of beans, (e) water in 1 lb. of butter, (f) carbohydrate in 1 lb. of oatmeal.

3. (a) What weight of bacon is needed to furnish as much fat as 1 lb. of butter? (b) Of tomatoes to provide the carbohydrate in 1 lb. of potatoes? (c) Of oatmeal to equal the protein in 1 lb. of beans?

CHAPTER XXV

SILICA — SILICATES — GLASS — SILICON — CARBORUNDUM

383. Occurrence of silica. — The element silicon does not occur free in nature, but its compounds are very abundant and widespread, especially silica and the silicates. Sand is chiefly silica, while clay and most rocks consist of one or more silicates. Ordinary soil contains more or less silica. Silicon (through its compounds) makes up about one fourth of the earth's crust (11), being next to oxygen in abundance.

Silica is the most abundant and important compound of silicon. It is also called **silicon dioxide** (SiO_2). Sand, gravel, sandstone, quartzite, and the numerous varieties of quartz are almost wholly silicon dioxide; many rocks, *e.g.* granite and gneiss, contain silica as an essential ingredient.

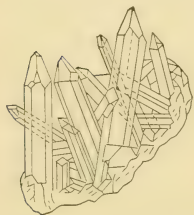


Fig. 140. — Quartz crystals

Quartz is the commonest form of silicon dioxide. Pure quartz is colorless and transparent, and is called rock crystal. It is crystalline and is frequently found as single crystals which have a six-sided pyramid at one or both ends; the crystals are sometimes distorted (Fig. 140).

There are many varieties of quartz, which differ in color and structure. Among the crystalline varieties are the clear, colorless rock crystal, the purple amethyst, and the rose, yellow, glassy, milky, and smoky forms. Varieties imperfectly crystalline are the waxlike

chalcedony, the various forms of agate having different colored layers, the reddish brown carnelian, the black and white onyx, the red or brown jasper, the brown or black flint.

Opal is a beautiful variety of silica containing varying per cents of combined water. Petrified or silicified wood is the remnant of wood in which the fiber has been replaced by silica. There is a petrified forest in Arizona. Infusorial or diatomaceous earth (also called Tripoli powder) is largely silica and consists of the skeletons of minute organisms called diatoms, many being of delicate and beautiful structure (Fig. 141).



Fig. 141. — Diatom shells (enlarged)

384. Properties of silica. — Most varieties of silica are hard and brittle, and melt only at a high temperature. *E.g.* quartz is harder than other common substances, breaks into fragments with sharp edges, and melts in the oxy-hydrogen flame or the electric furnace. If pure silica is fused with certain precautions, the viscous mass can be

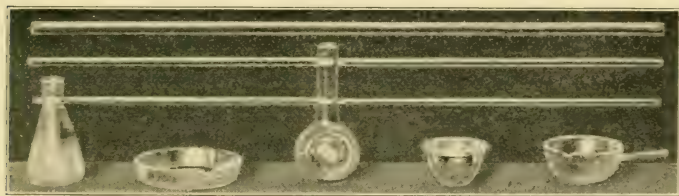


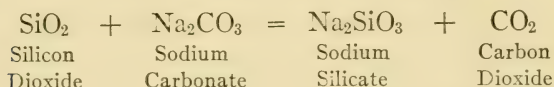
Fig. 142. — Apparatus made from fused silica for use in the laboratory

drawn into elastic threads, which are used to suspend delicate parts of electric instruments; it can also be shaped into tubes, flasks, crucibles (Fig. 142), and even large pieces of apparatus used in industrial processes.

Apparatus of fused silica has a low coefficient of expansion, *i.e.* it expands or contracts only a very little within

a wide range of temperature. Thus, a silica crucible, unlike a porcelain one, will not crack if heated and plunged into cold water. It also resists the action of many chemicals. These properties make silica apparatus very useful in the laboratory and chemical manufactories.

The different forms of silica do not dissolve in water. Nor are they attacked by acids, except hydrofluoric acid, which transforms them into a volatile fluoride (silicon tetrafluoride, SiF_4). They are converted into soluble silicates when boiled in water containing alkaline substances or when fused with the hydroxide or carbonates of sodium and potassium. Thus, when fine sand is fused with sodium carbonate the equation for the reaction is:—



335. Uses of silica.— Sandstone and quartzite are used as building stones, and some varieties of sandstone are shaped into grindstones and whetstones. Immense quantities of sand are used to make glass, porcelain, cement, and mortar. Different grades of sand are used as grinding and polishing material in making sandpaper. Glass is polished by rubbing it with fine wet sand; it is also roughened and cut by blowing or “blasting” fine sand against it. Glass stoppers for bottles used in the laboratory are “ground” with sand. Many of the varieties of quartz are cut and polished into ornaments and gems.

Infusorial earth (383) is used as a polishing powder for metals (“electro-silicon” being the commercial name of one kind), and in making scouring soaps, cement, soluble glass, and refractory brick; owing to the hollow structure of its minute particles, considerable is used as an

absorbent of nitroglycerin in the manufacture of dynamite.

386. Silicates are salts of silicic acid. There are several silicic acids, but only two are well known and easily prepared, viz. metasilicic acid (H_2SiO_3) and orthosilicic acid (H_4SiO_4). The salts of these and other silicic acids are among the most common substances in the earth's crust.

Most rocks consist wholly or largely of silicates of the metals aluminium, iron, calcium, potassium, sodium, and magnesium. Some common silicates are slate, asbestos ($\text{Mg}_3\text{Ca}(\text{SiO}_3)_4$), feldspar (KAlSi_3O_8), mica, hornblende, clay ($\text{H}_2\text{Al}_2(\text{SiO}_4)_2 \cdot 2\text{H}_2\text{O}$), beryl, garnet, serpentine ($\text{Mg}_3\text{Si}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$), and talc ($\text{H}_2\text{Mg}_3(\text{SiO}_3)_4$). The lava ejected by volcanoes consists largely of fused silicates.

Naturally occurring silicates are insoluble in water. But they decompose very slowly through the joint action of water and carbon dioxide. Even the moist carbon dioxide in the air slowly decomposes silicates. As a result of this gradual but very extensive chemical change, hard rocks like granite disintegrate. The more soluble products (*e.g.* sodium and potassium carbonates) are washed away and the less soluble ones such as clay, sand, and iron compounds, are left behind. This transformation, which is called **weathering**, is assisted by the mechanical action of water, especially alternate freezing and thawing.

The decomposition of silicates by the joint action of carbon dioxide and water (*i.e.* by carbonic acid (H_2CO_3)) is due to the fact that silicic acid is a weak acid. This property is strikingly shown by the formation of basins and terraces of silica in Yellowstone National Park. The hot waters of some of the springs in the Park contain dissolved alkaline silicates (*e.g.* Na_2SiO_3) which are transformed to silicic acid by the moist carbon dioxide of the air. The silicic acid, which is left where the waters overflow, gradually loses water and builds up a deposit of silica, often very beautiful. Silica thus deposited is called **geyserite**.

387. Sodium silicate. — When fine sand and sodium carbonate are fused together, sodium silicate (Na_2SiO_3) is formed. (See equation at end of **384**.) Sodium silicate is a glassy solid, which under special conditions dissolves in water; hence this silicate is sometimes called **water glass**. Silicate of soda is the name given to commercial solutions of varying composition. These solutions have different properties adapted to special uses. Certain brands are used as the adhesive in making the cor-

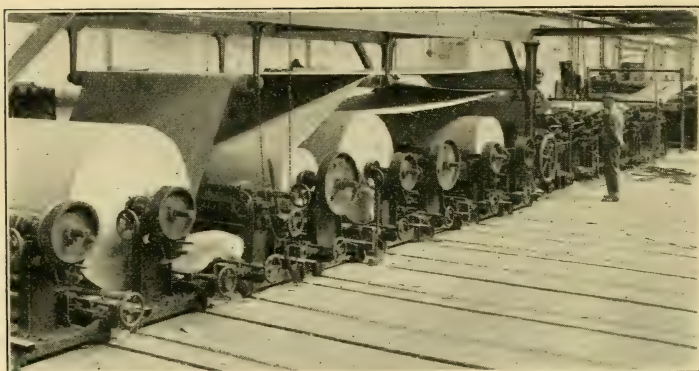
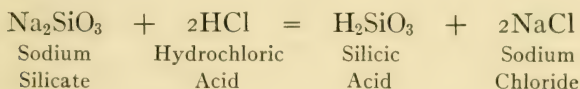


Fig. 143. — Making 4-ply paper board used for cartons, shipping containers, and wall board. The two center strips are coated on both sides with sodium silicate solution; the upper and lower strips on one side only. All four strips are united firmly together by pressure rolls. This machine is one of the largest in use and turns out over 200 feet of finished board per minute

rugated paper board, fiber board, and wall board which are made into cartons, tubes, trunks, and containers of various kinds (Fig. 143). Another brand is used as a binder in abrasive wheels, stove and furnace cements, and linings. Still another use is as a protective coating for wood, paper, and concrete, a fireproof coating or ingredient of wood and fabrics, and preservative coating

for eggs; the last use is due to the fact that the deposit of silicate in the pores of the shells keeps out the air and thus prevents the eggs from spoiling. Finally, considerable is used in many chemical processes, *e.g.* the manufacture of certain laundry soaps, sizing of paper, refining of oil, and removing paint.

388. Silicic acids. — When hydrochloric acid is added to sodium silicate solution, a white jelly-like precipitate called silicic acid is formed, thus: —



Under certain conditions probably the precipitate is a mixture of meta- and ortho-silicic acids (H_2SiO_3 and H_4SiO_4). These acids are closely related. The ortho-acid passes into the meta-acid upon drying, thus: —



And metasilicic acid when heated decomposes into silicon dioxide and water, thus: —

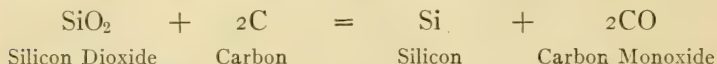


Silicon dioxide may be regarded as the anhydride of metasilicic acid, though contrary to the usual rule this acid cannot be formed from the anhydride (SiO_2) and water (**262**).

389. Colloidal acid. — Sodium silicate and hydrochloric acid do not always interact as described in **388**. If the sodium silicate solution is dilute, or the hydrochloric acid is concentrated or in excess, or the mixing is done quickly, then the silicic acid which is formed remains in solution. This solution, however, is not a solution of the gelatinous

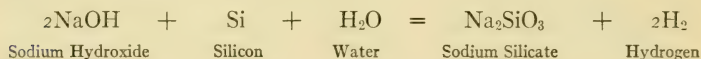
silicic acid described above, for the latter is insoluble in water. The silicic acid in the solution is in the colloidal state. It cannot be filtered out through paper in the usual way. (86, 101, 349.)

390. Silicon. — Silicon is manufactured by heating sand with coke in an electric furnace, thus: —



Thus prepared, silicon is a brittle, gray-black, lustrous, metallic looking solid. It melts at about 1400°C . The specific gravity is about 2.37. It is hard enough to produce scratches on glass, being almost as hard as quartz.

Silicon at high temperatures combines with oxygen, though not readily, to form silicon dioxide (SiO_2). With other elements it forms compounds often called silicides, *e.g.* carbon silicide (CSi). Chlorine and elements related to it, especially fluorine, combine with silicon to form volatile compounds. Sodium hydroxide and potassium hydroxide interact with silicon, thus: —



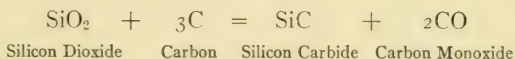
Most acids produce little or no effect upon silicon, hydrofluoric acid being the main exception.

391. Uses of silicon. — Silicon is made into vessels and parts of apparatus designed to withstand the action of acids and other liquids. Some is used in the steel industry to remove the gases (*e.g.* oxygen) that cause small holes. An alloy of silicon and iron called **ferro-silicon** is also used for the same purpose. An alloy of iron and silicon (14–15 per cent), called **duriron**, is hard and brittle; it resists the corrosive action of acids, especially nitric acid, and is extensively used in acid plants.

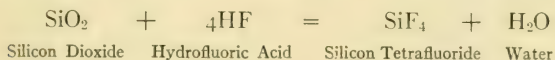
392. Silicon carbide or carborundum (SiC). — This carbide is a crystallized solid, which varies in color from white to brownish-green or black. It is extremely hard,

being nearly as hard as diamond. It is very resistant. Acids do not affect it, but potassium hydroxide and some other alkalis do. The extreme hardness of carborundum has led to its extensive application as an abrasive, and large quantities are made into a great variety of grinding wheels, whetstones, and polishing cloths.

Carborundum is manufactured by fusing a mixture of sand (silicon dioxide, SiO_2) and coke (carbon, C) in an electric furnace similar in form to that used in the manufacture of graphite (Fig. 100) and silicon. The mixture of sand and coke (to which salt and sawdust are added to contribute to the fusion and porosity) is packed around the core of granulated coke. The heat generated by the resistance of the carbon core to the passage of the powerful current of electricity produces a chemical change essentially as follows: —



393. Other silicon compounds. — When hydrofluoric acid interacts with silicon dioxide, silicates, or silicon, **silicon tetrafluoride** (SiF_4) is formed. With silicon dioxide the equation is: —



Silicon tetrafluoride is a colorless gas which fumes in moist air owing to interaction with water. The equation for the reaction is: —



The **hydrofluosilicic acid** (sometimes called fluosilicic acid) remains in solution, while the (ortho)silicic acid is precipitated. The formation of the white gelatinous silicic acid when the gases from the interaction of hydrofluoric acid and a compound of silicon are led into water is often used as a **test for silicon**.

394. Glass is essentially a mixture of silicates and silica. Ordinary glass, such as that used for bottles and window-panes, is made by heating sand, calcium carbonate, and

sodium carbonate to a high temperature. The product is a mixture of calcium silicate (CaSiO_3), sodium silicate (Na_2SiO_3), and silica (SiO_2). The composition might be represented as Na_2O , CaO , 6SiO_2 . Sodium-calcium glass is called **soft glass** because it softens readily when heated.

Other varieties can be made by substituting other substances, wholly or partly, for the calcium and sodium compounds. Thus, potassium carbonate (with calcium carbonate) produces a **hard glass** which melts at a much higher temperature than ordinary sodium glass.

If a lead compound is used in place of calcium carbonate, **flint glass** is produced which refracts light to a high degree; it is used to make lenses for optical instruments, and shades for gas and electric lights. On account of its brilliancy this glass is made into cut glass vessels for ornaments and table use. The design is traced on the glass, cut out by a revolving wheel, and the vessel is then polished with a very fine abrasive.

Another kind of glass, used extensively for chemical apparatus and certain cooking utensils, contains a large excess of silica together with boron oxide (B_2O_3) and aluminium oxide (Al_2O_3). It is made by heating together sand, borax ($\text{Na}_2\text{B}_4\text{O}_7$), and aluminium oxide. This glass is tough and has a much lower coefficient of expansion than ordinary glass; hence it does not break readily with sudden changes of temperature. Its trade name is "pyrex."

Besides the fundamental ingredients, mentioned above, carbon, sodium sulphate (Na_2SO_4), sodium nitrate (NaNO_3), arsenic trioxide (As_2O_3), and manganese dioxide (MnO_2) are used to accomplish specific results. For example, manganese dioxide is added to neutralize the green color due to iron compounds (present as an impurity usually in the sand). Cheap glass bottles and jars are green because the impurities are not removed. Selenium produces the red glass used in railroad and steamship lanterns and in automobile tail lights.

White glass is made by adding fluorspar (CaF_2), cryolite (Na_3AlF_6), stannic oxide (SnO_2), or calcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$).

395. Manufacture of glass. — The ingredients needed for the different varieties of glass (394) are mixed in the proper proportions and heated in a furnace or in large clay vessels to a high temperature. The substances interact and form a heavy, viscous semi-fluid. It is plastic over a considerable range of temperature, and can be poured into molds, rolled into sheets, and fashioned into various shapes by blowing, pulling, pressing, or stamping.

Bottles and jars of all kinds are blown by complicated machines. Special or ornamental objects are blown into a mold. A skilled workman gathers a mass of the plastic glass on the end of a long tube, called a glass blowpipe, blows the glass into a preliminary shape, lowers it into a mold, and blows until the mold is filled. In Fig. 144 a workman is shown about to lift an electric light bowl from a mold.

Window glass and other kinds of flat glass are made by machinery. In one process the glass is blown into a long cylinder (Fig. 145, upper) which is allowed to cool; the ends are then cut off, the cylinder is slit lengthwise, heated until it softens and opens, and then rolled out flat. In another process the mixture of the raw materials is put into one end of a furnace, melted,



Fig. 144. — The last stage (opening the mold) in blowing an electric light bowl

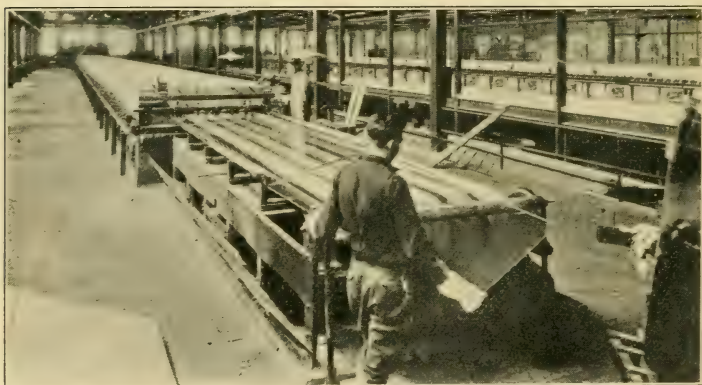
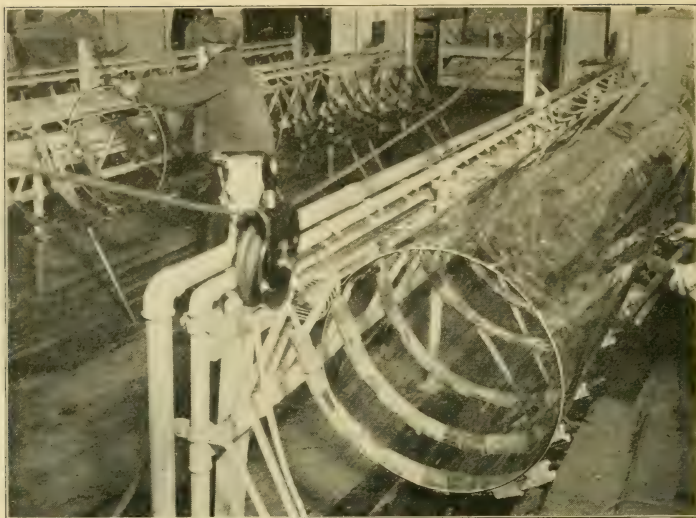


Fig. 145. — Making flat glass. Upper — a huge cylinder of glass on a frame about to be slit open lengthwise
Lower — removing a sheet of glass from an automatic sheet glass machine. The raw materials enter at one end and the sheets of glass are cut off at the other

and transformed into glass. The viscous mass is passed along (in the same machine) to a device which sticks to it, pulls it forward between rolls, through a cooling chamber, and finally out upon a table where the glass is automatically cut into sheets. In Fig. 145 (lower), a workman is shown taking off a sheet of glass.

Plate glass, which is used for windows and wind shields, is made by pouring the molten glass upon a large table, rolling it with a hot iron, and finally grinding and polishing the cooled sheet on a rotating table until the surfaces are parallel.

Glass must be cooled slowly, otherwise it will crack or crumble to pieces when jarred or scratched. This slow cooling is called

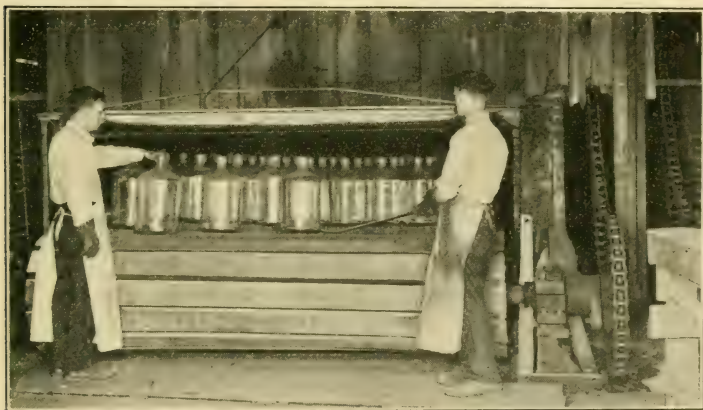


Fig. 146. — Bottles just coming from an annealing chamber

annealing. It is accomplished by passing the objects on a slowly moving frame through a chamber in which the temperature is gradually lowered (Fig. 146).

EXERCISES

1. In what compounds is silicon found in nature? What proportion of the earth's crust is silicon? Compare with other elements.

2. Summarize the properties of silica.
3. Describe the formation, state the uses, and enumerate the properties of water glass.
4. Starting with silicon, how would you prepare successively silicon dioxide, sodium silicate, silicic acid, silicon dioxide, silicon?
5. Topics for essays and discussion: (a) Diatoms, their formation, deposition, and uses. (b) Manufacture of glass. (c) Quartz. (d) Silicon dioxide as an abrasive. (e) Wire glass.
6. State the preparation, properties, and uses of carborundum.
7. Why is sand usually found at the sea shore? Why is sand often used to extinguish a small fire?

PROBLEMS

1. Calculate the per cent of silicon in (a) orthosilicic acid, (b) metasilicic acid, (c) potassium feldspar (KAlSi_3O_8).
2. How much sodium silicate can be made from 1000 kg. of sand?
3. Write the formula of (a) silicon chloride, (b) silicon bromide, (c) cupric silicide, (d) cuprous silicide, (e) sodium metasilicate, (f) sodium orthosilicate, (g) magnesium metasilicate, (h) magnesium orthosilicate, (i) aluminium metasilicate, (j) ferrous orthosilicate. Calculate the per cent of silicon in any three of these compounds.
4. Scheele found that 0.6738 gm. of silicon tetrachloride gave 2.277 gm. of silver chloride. Calculate the atomic weight of silicon. (Equation is $\text{SiCl}_4 + 4\text{AgNO}_3 + 2\text{H}_2\text{O} = \text{SiO}_2 + 4\text{AgCl} + 4\text{HNO}_3$.)
5. Silicon hydride (SiH_4) burns in air. Write the equation.
6. How much silicon can be made (a) by reducing a ton of sand (90 per cent pure) with C; (b) from 119 gm. of potassium silico-fluoride? (Equation is $\text{K}_2\text{SiF}_6 + 4\text{K} = \text{Si} + 6\text{KF}$.)
7. How much carborundum could be made by using (a) a ton of carbon (98 per cent pure) and (b) a ton of sand (95 per cent pure)?
8. Calculate the simplest formulas corresponding to (a) $\text{Si} = 35.897$, $\text{H} = 2.564$, $\text{O} = 61.538$; (b) $\text{Si} = 29.166$, $\text{H} = 4.166$, $\text{O} = 66.666$. What is the name of each compound?

CHAPTER XXVI

CLASSIFICATION OF THE ELEMENTS — METALS AND NON-METALS — PERIODIC CLASSIFICATION

396. Classification of the elements. — In the preceding chapters emphasis was laid on different elements, *e.g.* oxygen, hydrogen, chlorine, nitrogen, carbon, and sulphur; others were mentioned, *e.g.* sodium, potassium, calcium. These elements differ from one another in many ways. But some of them are quite similar in their chemical behavior and can be put into the same class. The arrangement into classes helps us in studying chemistry.

397. Metals and non-metals. — The elements have long been divided into two classes called metals and non-metals. At first those elements were called metals which were hard, lustrous, heavy, and good conductors of heat, whereas the others were called non-metals. This classification has been retained, though it is not entirely correct. A few metals are not heavy. Moreover certain elements act as metals under some conditions and as non-metals under other conditions.

A better classification is based on the ionic theory. According to this theory, metallic elements form positive ions and non-metallic elements negative ions. The only exception is hydrogen; this element is classed as a non-metal although its ions are positive (H^+). In the accompanying Table of Important Metals and Non-metals the common elements are put in the usual class.

TABLE OF IMPORTANT METALS AND NON-METALS

Metals			Non-metals	
Sodium	Magnesium	—	Hydrogen	Oxygen
Potassium	Zinc	Chromium	—	Sulphur
—	Cadmium	—	Boron	—
Copper	Mercury	Manganese	—	Fluorine
Silver	—	—	Carbon	Chlorine
Gold	Aluminium	Iron	Silicon	Bromine
—	—	Cobalt	—	Iodine
Calcium	Tin	Nickel	Nitrogen	—
Strontium	Lead	—	Phosphorus	(Aluminium)
Barium	(Arsenic)	Platinum	Arsenic	—
	Antimony		(Antimony)	(Tin)
	Bismuth			(Chromium)
				(Manganese)

398. Periodic classification of the elements. — In 1869 the Russian chemist Mendelejeff (Fig. 147) published the periodic classification of the elements. It is based on a relation between the properties of the elements and their atomic weights.

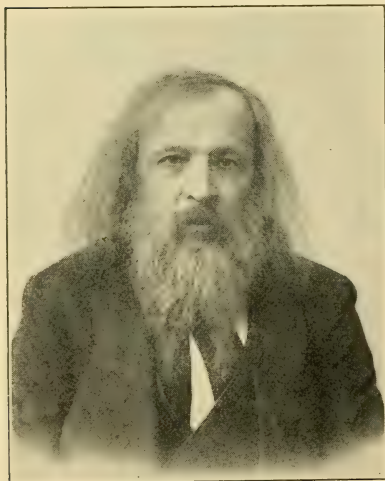


Fig. 147. — Mendelejeff (1834-1907)

The scheme of the classification is substantially as follows: If the elements beginning with helium are arranged in the order of their increasing atomic weights, a series results in which similar or closely related elements occur at intervals. That is, the series

PERIODIC CLASSIFICATION OF THE ELEMENTS

Periods	Group 0	Group I	Group II	Group III	Group IV	Group V	Group VI	Group VII	Group VIII
1	Helium He = 4	Hydrogen H = 1.008							
2	Neon Ne = 20.2	Lithium Li = 6.94	Beryllium Be = 9.1	Boron B = 10.9	Carbon C = 12	Nitrogen N = 14	Oxygen O = 16	Fluorine F = 19	—
3		Sodium Na = 23	Magnesium Mg = 24.32	Aluminium Al = 27.1	Silicon Si = 28.3	Phosphorus P = 31.04	Sulphur S = 32.06	Chlorine Cl = 35.46	—
4	Argon A = 39.9	Potassium K = 39.1	Calcium Ca = 40.07	Scandium Sc = 44.1	Titanium Ti = 48.1	Vanadium V = 51	Chromium Cr = 52	Manganese Mn = 54.93	Iron Fe = 55.84 Cobalt Co = 58.97 Nickel Ni = 58.68
5	—	Copper Cu = 63.57	Zinc Zn = 65.37	Gallium Ga = 70	Germanium Ge = 72.5	Arsenic As = 74.96	Selenium Se = 79.2	Bromine Br = 79.92	—
6	Krypton Kr = 82.92	Rubidium Rb = 85.45	Strontium Sr = 87.63	Yttrium Y = 89.33	Zirconium Zr = 90.6	Columbium Cb = 93.1	Molybdenum Mo = 96	—	Ruthenium Ru = 101.7 Rhodium Rh = 102.9 Palladium Pd = 106.7
7	—	Silver Ag = 107.88	Cadmium Cd = 112.40	Indium In = 114.8	Tin Sn = 119	Antimony Sb = 120.2	Tellurium Te = 127.5	Iodine I = 126.92	—
8	Xenon Xe = 130.2	Cesium Cs = 132.81	Barium Ba = 137.37	Lanthanum La = 139	Cerium Ce = 140.25	—	—	—	—
9	—	—	—	—	—	—	—	—	—
10	—	—	—	Ytterbium Yb = 173.5	—	Tantalum Ta = 181.5	Tungsten W = 184	—	Osmium Os = 190.9
11	—	Gold Au = 197.2	Mercury Hg = 200.6	Thallium Tl = 201	Lead Pb = 207.2	Bismuth Bi = 208	—	—	Iridium Ir = 193.1 Platinum Pt = 195.2
12	Nitron Ni = 222.1	—	Radium Ra = 226	Thorium Th = 232.15	—	—	Uranium U = 238.9	—	—

breaks up into several periods, and the classification is called periodic.

If the series is divided into these periods and the periods are placed below each other, the accompanying table is obtained in which the elements can be viewed in three ways: first as a long consecutive series, second as groups, and third as periods. The groups are in the vertical columns and are designated by the numerals 0 to VIII; the groups (except Group 0) are subdivided into families. The periods are in horizontal rows and are numbered from 1 to 12.

399. Groups and families. — An examination of the elements in the groups shown in the vertical columns of the periodic table reveals two interesting facts. First, elements which resemble one another are found in the same group. Second, in a given group certain elements are more closely related than others, giving rise to sub-groups or families. In some of these families the similarity of the members is very marked, *e.g.* the sodium family (Li, Na, K, etc.) and the halogen family (F, Cl, Br, I).

For convenience, the elements described (or mentioned) in this book are arranged here as groups or families.

Group 0. Inert elements or **argon family** — helium, neon, argon, krypton, xenon, niton.

Group I. Alkali metals or **sodium family** — lithium, sodium, potassium.

Univalent heavy metals or **copper family** — copper, silver, gold.

Group II. Alkaline earth metals or **calcium family** — calcium, strontium, barium, radium.

Bivalent heavy metals or **zinc family** — magnesium, zinc, cadmium, mercury.

Group III. **Boron family** — boron.

Earth metals or **aluminium family** — aluminium.

Group IV. Quadrivalent non-metals or **carbon family** — carbon, silicon.

Quadrivalent metals or **tin family** — tin, lead.

Group V. Quinivalent non-metals and metals or **nitrogen family** — nitrogen, phosphorus, arsenic, antimony, bismuth.

Group VI. Hexavalent metals or **chromium family** — chromium, tungsten, uranium.

Hexavalent non-metals or **oxygen family** — oxygen, sulphur.

Group VII. **Manganese family** — manganese.

Halogen elements or **chlorine family** — fluorine, chlorine, bromine, iodine.

Group VIII. **Iron family** — iron, cobalt, nickel.

Platinum family — platinum.

This arrangement should be examined carefully and referred to constantly as the different elements are studied. By comparing the periodic table with the table of metals and non-metals we see that related elements have been grouped in the same way (397).

400. Periods, properties, and atomic weights. — The elements in the same horizontal row in the periodic table belong to the same period. The periodic variations of the properties of the same typical elements may be illustrated by periods 2 and 3. Ignoring the argon group (Group 0), which is somewhat anomalous, and beginning with lithium, the general chemical properties vary with increasing atomic weight.

Let us consider this point in detail. The metallic character typified by lithium gradually diminishes through beryllium and boron; while the feeble non-metallic character typified by carbon becomes more marked as we pass on through nitrogen and oxygen until it reaches a maximum in fluorine. The next element is sodium, in which metallic properties reappear; its place therefore is beneath lithium, at the beginning of period 3. Proceeding from sodium, the same decrease of metallic and increase of non-metallic properties is noticed until potassium is reached, and here

again a marked metallic element reappears and period 4 begins. Hence sodium comes under lithium, magnesium under beryllium, aluminium under boron, carbon under silicon, and so on through chlorine to potassium, which comes under its closely related element sodium.

There is no sudden change in properties until we pass from one period to the next. Thus, fluorine at the end of period 2 forms a strong acid, but sodium at the beginning of period 3 forms a strong base. Similarly, chlorine is strongly acidic, but potassium, which is the first metal in the next period, is markedly basic; chlorine is a typical non-metal, while potassium is a typical metal.

401. The periodic law. — Not all the periods are as typical as those just cited. Nevertheless a careful and comprehensive study of all the elements shows that in most cases their properties vary periodically with the atomic weight. Mendelejeff summarized these facts in the **periodic law**, thus: —

The properties of the elements are periodic functions of their atomic weights.

The term *function* as used here means the exhibition of some special relation, viz. that of properties to atomic weight. It is not believed now that the relation emphasized by Mendelejeff is sufficiently accurate to be called a law. Interpreted freely, the facts at the basis of the periodic classification mean: (1) properties and atomic weights are related; and (2) this relation is exhibited in very many instances at regular intervals.

402. Defects in the periodic classification. — Examination of the periodic table shows imperfections. For example, there are gaps. These probably correspond to elements not yet discovered. Three such gaps which were in the original table have been filled. When Mendelejeff proposed his arrangement, he predicted the discovery

of three elements having definite properties. These elements — gallium, scandium, and germanium — were soon discovered, and now occupy their predicted places in the table. Possibly other gaps will be filled by newly discovered elements as was done in the case of the zero group. Several elements are out of place, *e.g.* argon, iodine, and tellurium. Hydrogen also lacks an acceptable place.

403. How can we use the periodic table? — The table is a little confusing unless we first **look for families of related elements**. For example, we have already studied the zero group (124–127). We shall study fluorine, chlorine, bromine, and iodine — the halogen family — in the next chapter. Similarly, we find the family containing nitrogen, phosphorus, arsenic, antimony, and bismuth. Nitrogen has already been studied, and we shall soon take up the others (Chapter XXVIII). Other families of related elements to be studied are sodium and potassium (Chapter XXIX), and copper, silver, and gold (Chapters XXXIII, XXXVI). So by studying the table we can find families of related elements.

Second, we should notice that **elements having similar properties are near each other**. The active metals are in Group I (the sodium family) and the less active in Group II. Whereas the active non-metals are in Group VII (the chlorine family) and the less active are in Group VI. Generally speaking the active metals and non-metals are at opposite ends of the table. This may be re-stated in another way, *viz.* the typical electropositive elements (those that form positive ions) are in Group I and the typical electronegative elements (those that form negative ions) are in Group VI — at opposite ends of the table.

Third, we can use the table in **learning atomic weights**. Since the elements are arranged in the table in the order of their increasing atomic weights, we can soon learn the

names of the light elements, heavy elements, and, in time, the atomic weight of the important intervening elements.

Fourth, the table is useful in **learning the valence of the elements**. Elements in the same group usually have the same valence. A comparison of the elements in typical periodic groups (I, II, VII) with the valence tables in 221 shows much agreement.

EXERCISES

1. State the general physical properties of metals and non-metals. What is the characteristic chemical behavior of a metallic element and a non-metallic element?
2. Memorize the names of the important metals and non-metals.
3. What metals are related to (a) sodium, (b) lead, (c) copper?
4. As in Exercise 3, what non-metals to (a) carbon, (b) chlorine, (c) nitrogen, (d) sulphur?
5. Classify the following metals and non-metals: aluminium, Zn, Na, silicon, Ca, Cu, bismuth, Pb, Ag, C, manganese, O, H, iron, K, Au, N, hydrogen, Cl, Br, boron, I, S, P.
6. What is meant by (a) period, (b) group, (c) family?
7. Illustrate the periodic classification by two periods.
8. Commit to memory the names of the elements in the following families: (a) Argon, (b) sodium, (c) copper, (d) calcium, (e) zinc, (f) nitrogen, (g) chlorine, (h) iron.
9. Topics for essays or discussion: (a) Mendeleeff. (b) Atomic weights and properties. (c) Review of valence.

PROBLEMS (Review)

1. Calculate the per cent of oxygen in (a) water, (b) potassium chlorate, (c) nitric acid, (d) lime, (e) silica.
2. A candle in burning forms 13.21 gm. of carbon dioxide and 5.58 gm. of water. How much weight did the candle lose? What volume of oxygen at 0° C. and 760 mm. was required?
3. What volume of air (free from carbon dioxide and water vapor) contains 1 gm. of nitrogen?
4. What weight of sulphur is contained in 500 cc. of SO_2 ?
5. Suppose 50 l. of nitrous oxide are decomposed into nitrogen and oxygen. How many volumes of the products are formed?
6. A compound has the composition C = 39.9, H = 6.7, O = 53.4, and the vapor density is 1.906. What is the molecular formula?

CHAPTER XXVII

FLUORINE — BROMINE — IODINE

404. The halogen family. — Fluorine, bromine, and iodine, together with chlorine (see Chapter XI), constitute a family of related elements often called the halogens. The elements and their analogous compounds have similar properties, differing mainly in degree (400, 418).

405. Occurrence of fluorine. — Fluorine is the most active of these elements, and is never found free in nature. It occurs abundantly in combination with calcium as calcium fluoride (fluor spar, fluorite, CaF_2). Other native compounds are cryolite (Na_3AlF_6) and apatite ($\text{Ca}_5\text{F}(\text{PO}_4)_3$).

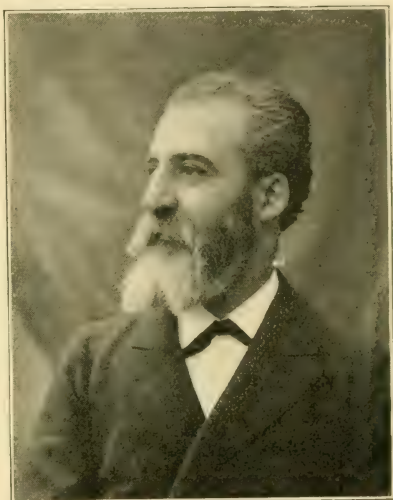


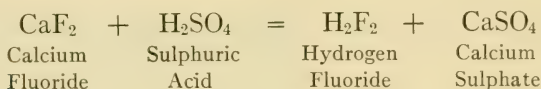
Fig. 148. — Moissan (1852-1907)

406. Preparation of fluorine. — Fluorine was first isolated in 1886 by the French chemist Moissan (Fig. 148) by the electrolysis of hydrofluoric acid in a solution of acid potassium fluoride (HKF_2). The experiment was difficult and dangerous owing to the corrosive properties of both acid and element.

407. Properties of fluorine. — Fluorine is a greenish yellow gas, though lighter and more yellow than chlorine. Chemically, fluorine

is intensely active. Most elements unite with it readily, the combining being accompanied by much heat and light. The compounds formed are fluorides. It does not combine with oxygen or nitrogen, while some metals, *e.g.* gold, platinum, and copper, are not readily (or only slightly) attacked by it.

408. Hydrogen fluoride is prepared by the interaction of concentrated sulphuric acid and calcium fluoride. The experiment is performed in a lead dish. The equation for the reaction is: —

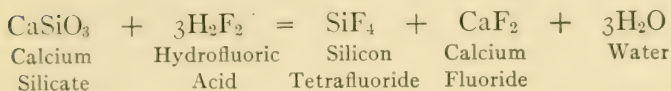
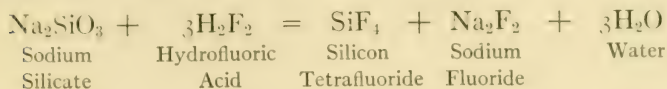


Hydrogen fluoride is gas, which can be readily condensed to a colorless liquid boiling at about 19°C . The gas forms fumes in moist air and dissolves readily in water. (Compare **155**.) The solution is **hydrofluoric acid**. Hydrogen fluoride in the form of gas, liquid, or solution is a dangerous substance. The gas is extremely poisonous, and the liquid, if dropped on the skin, produces terrible sores. Owing to its corrosive properties, hydrofluoric acid is kept in hard rubber or wax bottles.

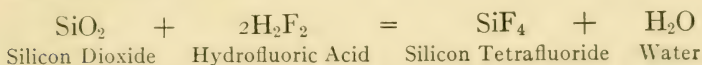
Hydrofluoric acid behaves chemically like hydrochloric acid. Thus, it interacts with metals, forming fluorides, and it neutralizes bases, forming salts and water. Unlike hydrochloric acid, it forms both normal and acid fluorides, *e.g.* potassium fluoride (K_2F_2) and acid potassium fluoride (HKF_2).

409. Etching with hydrofluoric acid. — The acid and moist gas attack glass, and are used extensively in etching. Glass, as we have seen, is essentially a mixture of silicates and silica (**394**). Hydrofluoric acid interacts with these compounds and forms among other substances a volatile compound called silicon tetrafluoride (SiF_4). Thus the

acid disintegrates the glass — literally “eats” or etches it. Typical equations for the reactions in case of ordinary sodium glass are: —



When hydrofluoric acid interacts with silicon dioxide, the equation for the reaction is: —



In etching with hydrofluoric acid, the glass is thinly coated with wax, and the design or marks to be etched are scratched through the wax. The glass is then exposed to the gas or liquid, which attacks the unprotected places. When the wax is removed, a permanent etching is left. Sometimes the design or marking is made more conspicuous by filling the etched cavity with an insoluble white or black substance. Hydrofluoric acid is utilized in marking the scales on thermometers, tubes, and other graduated glass instruments, and also in etching designs on glassware (Fig. 149).

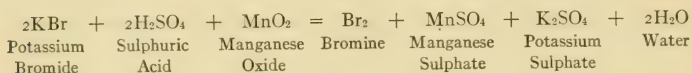
410. Occurrence and preparation of bromine. — Bromine is never found free, but bromides are widely distributed, especially magnesium and sodium bromides. The salt springs and wells of Ohio, West Virginia, Pennsylvania, and Michigan contain bromides; large quantities are found in the salt deposits at Stassfurt (462).

Bromine is prepared in the laboratory by

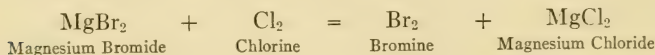


Fig. 149. — Etching on glass tumbler. (Designed and executed by a high school pupil)

heating potassium bromide with manganese dioxide and sulphuric acid. If an apparatus like that shown in Fig. 150 is used, part of the bromine vapor escapes and part condenses to a liquid, which collects in the U-bend. The complete equation for the reaction, which takes place in several stages, is :—



Another method consists in warming a bromide solution with chlorine water; an equation for this method is :—



Bromine is obtained industrially from the concentrated solution of bromides, called *bittern*, which is left after sodium chloride has been removed by crystallization from the brine of salt wells. Just enough chlorine is added to the solution to liberate the bromine; steam is then introduced, and the bromine distills over.

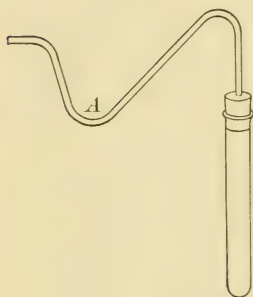


Fig. 150.—Apparatus for preparing bromine in the laboratory

It is interesting to note that the French chemist Balard, who discovered bromine in 1826, obtained it from *bittern*.

411. Properties of bromine.—

Bromine is a reddish brown liquid which is about three times as heavy as water. It is a volatile liquid, boiling at about 59°C . The vapor has a disagreeable odor. This property suggested the name bromine (from a Greek word meaning stench). The vapor irritates the mucous membrane of the eyes, nose, and throat; a bottle of bromine should

not be opened unless it is in the hood. Bromine is somewhat soluble in water. The solution, called **bromine water**, has a reddish brown color. Bromine dissolves in carbon disulphide and carbon tetrachloride; the solution is reddish yellow.

Liquid bromine burns the flesh frightfully, and care should be used in preparing or working with it.

The chemical behavior of bromine is similar to that of chlorine, though bromine is less active. Thus, it combines with metals and other elements; it also bleaches.

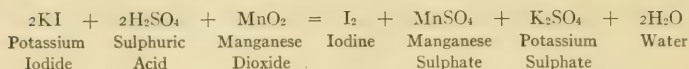
412. Compounds of bromine are similar to those of chlorine. **Hydrogen bromide** (HBr) is a colorless, pungent gas, which fumes in the air and dissolves freely in water. This solution is called **hydrobromic acid**; it is much like hydrochloric acid. Bromides are salts of hydrobromic acid, though many are formed by direct combination with bromine. **Potassium bromide** (KBr) is a white solid, made by decomposing iron bromide with potassium carbonate; it is used as a medicine. **Silver bromide** (AgBr) is used extensively in making photographic films and plates.

413. Occurrence of iodine. — Iodine, like chlorine and bromine, is found in nature only in compounds. Tobacco, water cress, cod-liver oil, oysters, and sponges contain minute quantities. Sea water contains a very small proportion of combined iodine. This is assimilated by certain seaweeds. Much iodine was formerly extracted from the ash of certain seaweeds. The French chemist Courtois, who discovered iodine in 1812, prepared it from seaweed.

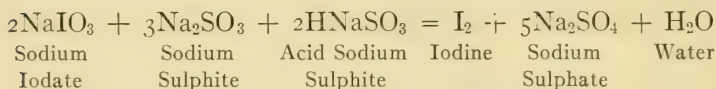
Iodine compounds, chiefly sodium iodate (NaIO_3), occur in the deposits of saltpeter (sodium nitrate) in Chile, and most of the iodine is now obtained from this source.

414. Preparation of iodine. — Iodine is prepared in the laboratory by a method similar to that used for bromine. Potassium (or sodium) iodide, manganese dioxide, and

sulphuric acid are heated together. The iodine is evolved as a violet colored vapor. The equation is :—



Iodine is prepared in a commercial scale from crude Chile salt-peter. Sodium sulphites are added to the liquid left after sodium nitrate (NaNO_3) has been removed by crystallization from a solution of the crude salt-peter, thus :—



In extracting iodine from the seaweed, the ash is treated with sulphuric acid and manganese dioxide or with chlorine.

415. Properties of iodine.—Iodine is a dark grayish crystalline solid, which is nearly five times as heavy as water. It is volatile at ordinary temperatures, and when gently heated changes into a beautiful violet colored vapor, which readily solidifies on a cold surface, often in the upper part of the vessel in which the iodine is heated.

This property of iodine, viz. ready transformation from solid into vapor and back directly into solid, is utilized in purifying iodine. The crude substance is heated gently and the vapor condensed; the non-volatile impurities remain behind. This process is called **sublimation** and is frequently used to purify substances (180).

The striking color of the vapor suggested the name iodine (from a Greek word meaning violetlike), which was given to the element by the English chemist Davy, who studied the substance soon after its discovery. The vapor is nearly nine times as heavy as air, and has an odor resembling dilute chlorine, though less irritating. Iodine melts at about 114°C . and boils at about 185°C .

Iodine dissolves slightly in water but freely in alcohol, chloroform, carbon disulphide, ether, or potassium iodide solution. The chloroform and carbon disulphide solutions are violet, but the others are brown, or even black. Iodine and its solutions turn the skin brown.

Iodine turns cold starch solution blue. A minute trace of iodine may thus be detected. The nature of this blue substance is unknown. The presence of starch in many vegetable substances can thus be shown (349).

In chemical conduct iodine resembles chlorine and bromine, but iodine is less active. Bromine and chlorine displace iodine from many of its compounds.

416. Uses of iodine. — A solution of iodine in alcohol (or in alcohol and potassium iodide), called **tincture of iodine**, or merely “iodine,” is applied to the skin to harden it, to prevent the spread of eruptions, or to reduce swellings. Iodine is used to make iodoform (CHI_3), which is used as an antiseptic for wounds. Large quantities of iodine are made into iodides, drugs, and dyes.

417. Compounds of iodine. — **Hydrogen iodide** and **hydriodic acid** (HI) are much like the corresponding compounds of chlorine and bromine, though unlike them in being reducing agents. **Iodides** are salts of hydriodic acid. In general behavior they are similar to bromides and chlorides. The best known salt is **potassium iodide** (KI). **Silver iodide** (AgI), like silver bromide, is used in photography.

418. The halogen elements and the periodic classification. — The halogen elements illustrate typically the periodic classification. These elements, as arranged in the periodic table, increase in atomic weight from fluorine (19.0) through chlorine (35.46) and bromine (79.92) to iodine (126.92), and many of their properties are graded in this order. Thus, as we pass from fluorine to iodine

the specific gravity increases, the color grows deeper, the volatility decreases, and the melting points of the solidified elements increase. The intensity of the chemical action decreases as we pass from fluorine to iodine.

EXERCISES

1. Review topics: (a) Chlorine. (b) Compounds of fluorine and silicon. (c) Periodic classification of the elements.
2. Summarize the chief properties of fluorine and hydrogen fluoride.
3. Describe the process of etching glass. Write the equations.
4. Write the equations for the preparation of (a) hydrogen fluoride, (b) bromine, (c) iodine, (d) silver bromide. Write (d) in ionic form.
5. Questions for home study: (1) Why did Moissan use acid potassium fluoride in the electrolysis of hydrofluoric acid? (2) Hydriodic acid and iodine compounds often turn dark on standing. Why? (3) What gas resembles bromine vapor in color? (4) How does bromine differ from all other elements previously studied (in this book)? (5) How would you identify by experiment (a) sand, (b) tincture of iodine, (c) calcium fluoride, (d) potassium bromide, (e) silver iodide?
6. Compare fluorine, chlorine, bromine, and iodine.
7. Essay topics: (a) Discovery of the halogen elements. (b) Iodine industry in Chile. (c) Etching with hydrofluoric acid. (d) Uses of iodine.

PROBLEMS

1. Calculate the per cent of fluorine in (a) hydrogen fluoride (H_2F_2), (b) silicon tetrafluoride, (c) apatite, (d) calcium fluoride.
2. Calculate the per cent of bromine or iodine in (a) sodium bromide, (b) hydrogen bromide, (c) calcium iodide, (d) sodium iodate.
3. How much (a) calcium sulphate and (b) hydrogen fluoride are formed by heating 60 gm. of fluor spar with sulphuric acid?
4. How much iron iodide (Fe_3I_8) can be made by the interaction of iron and 300 gm. of iodine?
5. How much potassium bromide (75 per cent pure) is necessary to prepare 47 gm. of bromine?
6. How much potassium iodide (80 per cent pure) is necessary to prepare 47 gm. of iodine?
7. Write the formulas of the fluoride, bromide, and iodide of Al, ammonium, Ba, Ca, copper (ous and ic), Fe^{II} , Fe^{III} , Pb, magnesium, Sb^{III} , Si, Hg (ous and ic), Sn^{II} , Sn^{IV} , zinc.

8. Calculate the atomic weight of fluorine, bromine, or iodine from the following: (a) 1 gm. of CaF_2 gives 1.745 gm. of CaSO_4 ; (b) 3.946 gm. of Ag (dissolved in HNO_3) require 4.353 gm. of KBr for precipitation; (c) 6.3835 gm. of silver iodide give 3.8965 gm. of silver chloride.

9. Calculate the simplest formula corresponding to (a) $\text{F} = 48.72$, $\text{Ca} = 51.28$; (b) $\text{Br} = 67.22$, $\text{K} = 32.77$; (c) $\text{I} = 76.5$, $\text{K} = 23.49$.

CHAPTER XXVIII

PHOSPHORUS — PHOSPHATES AND FERTILIZER — ARSENIC — ANTIMONY — BISMUTH

419. Introduction. — These elements together with nitrogen belong to Group V of the periodic classification.

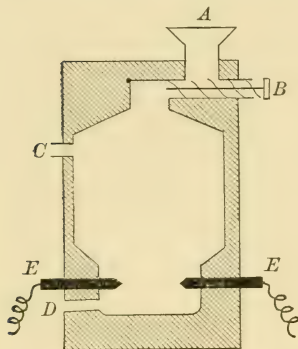


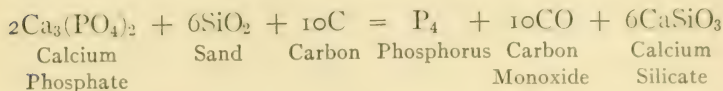
Fig. 151. — Electric furnace for the manufacture of phosphorus

420. Occurrence of phosphorus. — Free phosphorus is not found in nature, but phosphates are numerous and abundant. The most common phosphate is calcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$), which is the chief ingredient of “phosphate rock” and bones; about 80 per cent of bones is calcium phosphate. Small amounts of phosphates occur in fertile soils and some iron ores. Complex organic phosphorus compounds are found

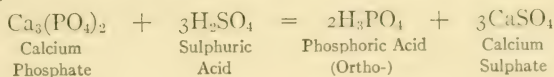
in the germs of seeds and the nerves, brains, and muscles of animals.

421. Phosphorus is manufactured from calcium phosphate. — In the new process phosphorus is manufactured in an electric furnace (Fig. 151). The mixture of calcium phosphate, carbon, and sand is introduced at *A* and fed into the furnace by the screw *B*. An electric current passed between the electrodes *EE* produces the intense heat needed for the chemical change. The phosphorus vapor

escapes through *C* into a condenser; the liquid residue, which is essentially calcium silicate, is drawn off as slag at *D*. The equation for the chemical change is:—



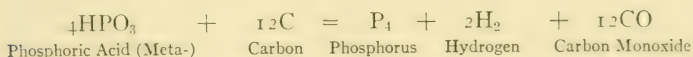
In the older process (not used now to any extent) the finely ground material is heated with enough sulphuric acid to produce the following change:—



The phosphoric acid is mixed with sawdust, coke, or charcoal, and dried, being changed thus:—



The dried mass is heated to a high temperature in clay retorts, the change being substantially:—



The phosphorus distils as a vapor through a pipe into a trough of water where it condenses to a heavy liquid.

The phosphorus obtained by either process is purified, melted under water, and cast in molds into small sticks.

422. Properties of phosphorus.—The phosphorus prepared by the methods just described is the white or ordinary form. It is a colorless, or slightly yellow, translucent solid. The color deepens by exposure to light. At ordinary temperatures it is soft like wax, and can be cut with a knife. At low temperatures it is brittle. It melts at 44°C ., but it should always be melted under water. When exposed to air it oxidizes quickly and gives off white fumes. At about 35°C . it takes fire and burns with a brilliant flame.

Since white phosphorus oxidizes so rapidly at lower temperatures, it is apt to take fire almost spontaneously. Hence it is kept beneath water and should not be handled unless it is wet; indeed it is better not to touch it at all, but to use wet forceps when it is necessary to transfer it or to hold it while it is being cut under water. Moreover unusual care should be taken not to leave bits of phosphorus in deflagrating spoons or lying about the laboratory.

In moist air white phosphorus is slightly luminous, as may be easily seen by rubbing the head of a phosphorus-tipped match in a dark room. This property gave the element its name (from a Greek word meaning light bringer).

White phosphorus has a faint odor. It is very poisonous, and the fumes cause a dreadful disease, which rots the bones, especially the jaw bones. It is practically insoluble in water, but dissolves readily in carbon disulphide.

423. Red phosphorus is made by heating white phosphorus to 250° – 300° C. in a closed vessel freed from air. Red phosphorus is a reddish brown powder. It is opaque and odorless, does not glow in the air, nor does it ignite until heated to about 250° C. It is not poisonous, and does not dissolve in carbon disulphide. Its specific gravity varies from 2.1 to 2.3, that of the white form being 1.83. It does not combine with oxygen at ordinary temperatures and being less dangerous than yellow phosphorus can be handled safely.

424. The formula of phosphorus. — The weight of 22.4 liters of each kind of phosphorus vapor (up to about 1500° C.) is approximately 128 grams. Hence a molecule must contain four atoms, and the molecular formula of the vapor is P_4 (207).

425. Matches. — On account of its ready inflammability phosphorus until recently was used in the manu-

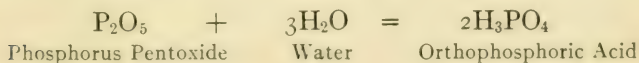
facture of matches. Phosphorus sulphide (P_4S_3) is now used in the United States as a substitute for the element. This change was made on account of a prohibitive tax (two cents per hundred matches) upon phosphorus matches, levied mainly to protect the workmen from the disease caused by breathing phosphorus fumes. The sulphide is not poisonous and is as suitable for match heads as phosphorus itself.

Ordinary matches are made by dipping one end of the match sticks first into melted paraffin and then into the "phosphorus mixture." The latter consists usually of different proportions of phosphorus sulphide, manganese dioxide or another oxidizing substance, and glue or some other binding material mixed with a little coloring matter. These matches are the ordinary friction kind. By rubbing them on a rough surface the friction generates enough heat to ignite the phosphorus compound, which continues to burn owing to the oxygen supplied (mainly) by the oxidizing agent, and the heat thereby produced sets fire to the paraffin, and this in turn kindles the wood.

In safety matches the head is usually a colored mixture of antimony sulphide, potassium chlorate, and glue, while the surface on the box upon which the match must be rubbed to ignite is a mixture of red phosphorus, glue, and powdered glass.

426. Phosphoric acid and phosphates. — When phosphorus burns freely in air, a white, snowlike solid is formed called **phosphorus pentoxide** (P_2O_5). It is very deliquescent, quickly withdrawing moisture from air and combining vigorously with water with a hissing noise. It is often used in the laboratory to dry gases, being much more effective than calcium chloride and sulphuric acid, which are similarly employed (90).

With hot water, phosphorus pentoxide forms **phosphoric acid**, thus:—



Phosphorus pentoxide is therefore called phosphoric anhydride. (Compare 262.)

Phosphoric acid (sometimes called orthophosphoric acid) is tribasic and forms three series of salts (phosphates), depending on the number of hydrogen atoms replaced by a metal. Orthophosphates — usually called simply **phosphates** — have several names based on the replacement of the hydrogen. Thus, Na_3PO_4 is **normal or trisodium phosphate**; HNa_2PO_4 is **acid or disodium phosphate**; and H_2NaPO_4 is **acid or monosodium phosphate**. Disodium phosphate (HNa_2PO_4) is the commercial “sodium phosphate.” Similarly, we have normal calcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$), and acid calcium phosphates, *e.g.* $\text{H}_2\text{Ca}_2(\text{PO}_4)_2$ and $\text{H}_4\text{Ca}(\text{PO}_4)_2$.

The “acid phosphate” sold as a beverage is a solution of one or more acid calcium phosphates. In phosphate baking powder the acid is a calcium phosphate.

With silver nitrate, phosphoric acid and soluble phosphates precipitate yellowish silver phosphate (Ag_3PO_4); they also precipitate yellow ammonium phosphomolybdate from an excess of a nitric acid solution of ammonium molybdate. These reactions serve as **tests for phosphoric acid** and its salts.

Phosphoric acid forms several kinds of ions besides hydrogen ions (H^+), *viz.* H_2PO_4^- , HPO_4^{--} , and PO_4^{---} . It is a weaker acid than the common acids.

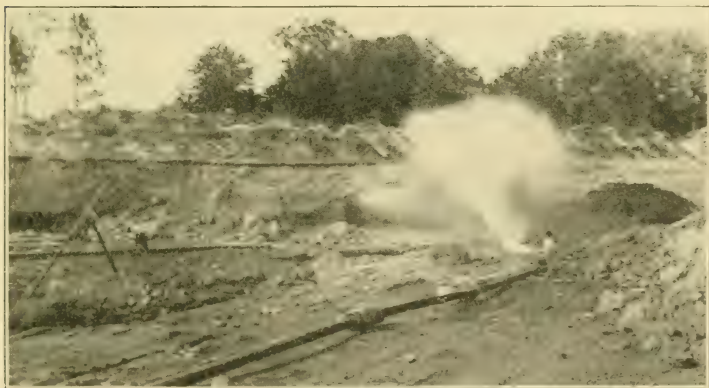
427. Relation of phosphorus to life. — Phosphorus is essential to the growth of plants and animals. Plants take phosphates from the soil and store up the phosphorus compounds, especially in their seeds. Animals eat this vegetable matter, assimilate the phosphorus compounds, and deposit them in the bones, brain, and nerve tissue. Most of these phosphorus compounds are complex. Bones,

however, as already stated, consist of about 80 per cent of calcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$).

The complex phosphorus compounds in the food consumed by animals are transformed by vital processes into phosphates which are eliminated to a large extent, and thus often find their way back into the soil. Here they are taken up again by plants, converted into complex compounds, stored up in the tissues and seeds, which are in turn eaten by animals. And so the process goes on — a phosphorus cycle analogous to the carbon cycle (29, 391 end), Fig. 17).

428. Phosphate fertilizers. — In order to furnish plants with phosphorus, various phosphorus-bearing substances are added to the soil in the form of fertilizers.

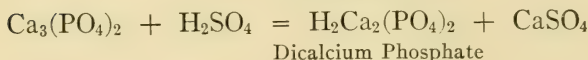
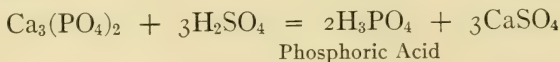
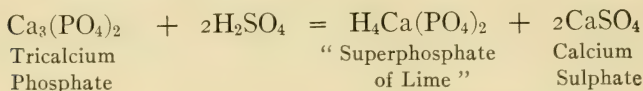
Artificial fertilizers are made from phosphate rock. This occurs in large beds in North and South Carolina, Tennessee, and Florida (Fig. 152). It consists of the hardened



Courtesy American Agricultural Chemical Company

Fig. 152. — Mining phosphate rock in Florida. The powerful stream of water washes the phosphate rock down into a pit from which both water and rock are pumped to washers, where sand is removed and low grade rock rejected. When dried, the phosphate rock is ready for manufacture into fertilizer

remains of land and marine animals, and is mainly tricalcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$). It is insoluble in water, and must be changed into the soluble monocalcium salt ($\text{H}_4\text{Ca}(\text{PO}_4)_2$), so that it can be evenly distributed through the soil and easily taken up by plants. This soluble salt is called "superphosphate of lime." When phosphate rock is treated with sulphuric acid, the changes involved may be written thus:—



The mixture of superphosphate and calcium sulphate, when ground and dried, is ready for use as a phosphate fertilizer. Usually "superphosphate" is mixed with compounds of nitrogen (116) and of potassium (463, 469) to form a **complete fertilizer**.

The law requires the dealer to state the analysis of the fertilizer on the bag or label. The per cent of phosphorus is usually stated as per cent of P_2O_5 , which is popularly called "phosphoric acid" (426).

The beneficial results of adding (complete) fertilizer to the soil are strikingly shown in Fig. 153. In the wheat field (top), the left was fertilized and the right was unfertilized; the left yielded $17\frac{3}{4}$ bushels per acre but the right only 5. The contrast is more conspicuous in the sorghum field (bottom) where the unfertilized part (left) yielded only 66 gallons of sirup per acre, whereas the right yielded 140. From the cotton field (middle) about 1350 pounds of seed cotton were obtained from the heavily fertilized



Fig. 153. — Contrast of fertilized and unfertilized fields

part and about 700 pounds from the scantily fertilized part.

429. Occurrence of arsenic. — Arsenic occurs combined with sulphur or a metal, or with both, *e.g.* as realgar (As_2S_2), orpiment (As_2S_3), arsenopyrite or mispickel (FeSAs). Many sulphide ores (*e.g.* copper ores) contain arsenic.

430. Properties and uses of arsenic. — Arsenic is a brittle, steel-gray solid having a metallic luster. Heated in the air, it volatilizes without melting, and the vapor has an odor like garlic. At about 180°C . it burns in the air with a bluish flame, forming arsenious oxide (As_2O_3). Arsenic is used to harden the lead made into shot.

The molecules of arsenic vapor at about 650°C . contain four atoms, hence the molecular formula As_4 . (Compare **424**.)

431. Arsenic trioxide (As_2O_3) is the most important compound of arsenic. It is often called “white arsenic,” or simply “arsenic.” It is obtained as a by-product in roasting ores that contain arsenic. It is odorless, has a slight taste, and dissolves slightly in cold water.

It is converted readily by hot hydrochloric acid into soluble arsenic trichloride (AsCl_3), which is a convenient solution to use in the laboratory.

Arsenic trioxide is used to a limited extent in making pigments for green paints, as the poisonous ingredient of fly and rat poison, in the manufacture of glass (especially plate glass), in making arsenic compounds (*e.g.* insecticides (**432**)), for destroying weeds, and in preserving skins in museums.

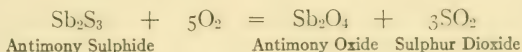
Arsenic trioxide is an active poison. The antidote for arsenic poisoning is fresh ferric hydroxide, which is made by adding ammonium hydroxide to a ferric salt, *e.g.* ferric chloride, which forms an insoluble substance with the arsenic compound.

432. Other arsenic compounds. — The native mineral **orpiment** (As_2S_3) is used in making a yellow paint, and **realgar** (As_2S_2) a red paint. **Paris green** ($\text{Cu}_3(\text{AsO}_3)_2 \cdot \text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$) and **lead arsenate** ($\text{Pb}_3(\text{AsO}_4)_2$) are effective insecticides and are used extensively to exterminate potato bugs and other insect pests.

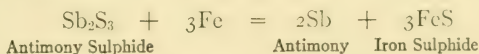
433. Test for arsenic. — The formation of yellow arsenious sulphide (As_2S_3) by passing hydrogen sulphide into an arsenic solution containing hydrochloric acid is the usual **test for arsenic**.

434. Occurrence and preparation of antimony. — Small quantities of free antimony are found. The most common native compound is the sulphide (stibnite, Sb_2S_3).

Antimony is prepared by roasting the sulphide and reducing the oxide with charcoal, thus: —



In another method the sulphide is heated with iron, thus: —

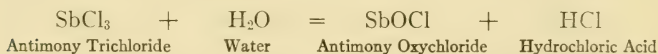


435. Properties of antimony. — Antimony is a silver-white, crystalline, brittle solid. It melts at about 630°C . At ordinary temperatures it does not tarnish in the air, but when heated it burns with a bluish flame, forming white, powdery antimony trioxide (Sb_2O_3). Nitric acid oxidizes it to antimonic acid (H_3SbO_4) and *aqua regia* transforms it into soluble antimony trichloride, which is a convenient solution of antimony for use in the laboratory.

436. Antimony is used to make certain alloys. When antimony is melted with some metals, especially lead and tin, the metals dissolve one another. Such a metallic solution upon solidifying forms an **alloy**. Alloys have different, often very different, properties from the original

metals. Thus, an alloy of lead (70 to 80 per cent), antimony, and tin expands on cooling and is harder than lead. It is used as **type metal** because it makes the face of the type hard and reproduces sharply the dots and fine lines (of the mold). **Babbitt metal** contains antimony, tin, and copper. It is used for the bearings of machines to reduce friction. Other **anti-friction alloys** contain lead, tin, antimony, and a little copper. Another alloy containing an appreciable proportion of antimony is **Britannia metal**, which is used in making ornaments and tableware.

437. Compounds of antimony. — Antimony forms stibine (SbH_3), which is analogous to ammonia (NH_3), and to arsine (AsH_3). It also forms complex compounds in which the group SbO — called antimonyl — acts as a univalent radical, *e.g.* tartar emetic or potassium antimonyl tartrate ($\text{KSbOC}_4\text{H}_4\text{O}_6$), which is used as a medicine and as a mordant in dyeing cotton. **Antimony trisulphide** (Sb_2S_3) is obtained as an orange red precipitate by passing hydrogen sulphide gas into a solution of an antimony salt — the usual **test for antimony**. This sulphide is used in making the red rubber tubing and stoppers used in the laboratory. **Antimony trichloride** (SbCl_3) is formed by interaction of the metal and *aqua regia*. It hydrolizes readily, *i.e.* interacts with water, thus: —



Antimony oxychloride is a white solid insoluble in water, and its formation is sometimes used as a **test for antimony**.

438. Occurrence and preparation of bismuth. — Bismuth is found in the native state, though it is not abundant nor widely distributed. The oxide (bismite, Bi_2O_3) and the sulphide (bismuthinite, Bi_2S_3) are native compounds.

439. Bismuth is prepared from the native metal by melting it on an inclined plate and allowing it to drain away from the solid impurities. Sometimes the sulphide is roasted, and the resulting oxide is reduced with charcoal, as in the case of antimony.

440. Properties of bismuth. — Bismuth is a silvery metal with a reddish tinge. Like antimony, it is very brittle. When heated in air it burns with a bluish flame, forming the yellowish trioxide (Bi_2O_3). Hydrochloric acid does not readily attack it, but hot concentrated nitric acid converts it into a nitrate and hot sulphuric into a sulphate. With *aqua regia* it forms bismuth chloride (BiCl_3).

441. Bismuth is used in making alloys which have very low melting points. The metal itself melts at 269°C . But alloys of bismuth, lead, and tin melt at a much lower temperature. For example, Newton's metal melts at 94.5°C . and Rose's metal at 93.8°C .; while Wood's metal, which contains the metal cadmium also, melts at only 60.5°C .

These alloys are called **fusible metals**. They are used in making safety plugs for steam boilers, fuses for electrical apparatus, and as connecting links to hold in place automatic fireproof doors and to close the heads in the automatic sprinkling apparatus frequently installed in large buildings (Fig. 154 — fusible metal at A).

In case of fire, the heat soon melts the fusible metal in the sprinkler heads, thereby providing openings in the

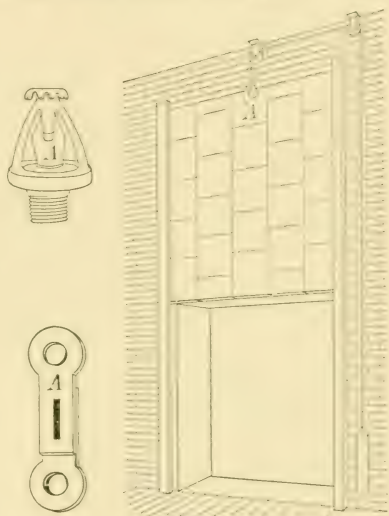


Fig. 154. — Sprinkler head, fusible link, and fireproof door (held in place by a link of fusible metal). Fusible metal is at A

pipes from which the water flows. The fireproof door is kept open by a weight until the heat melts the fusible metal and lets the door close automatically. (Study Fig. 154.)

442. Compounds of bismuth. — Bismuth sulphide (Bi_2S_3) is obtained as a black precipitate by passing hydrogen sulphide into a solution of a bismuth salt. The **trichloride** (BiCl_3) is formed by treating bismuth with *aqua regia*. With an excess of water the trichloride undergoes hydrolysis, forming **basic bismuth chloride** ($\text{Bi}(\text{OH})_2\text{Cl}$), which by loss of water becomes **bismuth oxychloride** (BiOCl). The latter is a pearl-white powder, insoluble in water, and its formation is the usual **test for bismuth**.

EXERCISES

1. Prepare a summary of phosphorus.
2. Describe the manufacture of phosphorus (*a*) from a phosphate and sulphuric acid and (*b*) by the electrothermic method.
3. Summarize the properties of (*a*) white phosphorus and (*b*) red phosphorus. Why is phosphorus so named?
4. What is the formula of (*a*) tricalcium phosphate, (*b*) "sodium phosphate," (*c*) monohydrogen calcium phosphate, (*d*) superphosphate of lime, (*e*) dihydrogen dicalcium phosphate?
5. Discuss the relation of phosphorus to life. Compare with nitrogen and carbon in this respect.
6. Describe the manufacture of phosphate fertilizer.
7. Suggest an experiment to show that bones contain calcium phosphate.
8. By what other names is arsenic trioxide known? What is the antidote for arsenic poisoning?
9. Describe a test for (*a*) arsenic, (*b*) antimony, and (*c*) bismuth.
10. State the uses of alloys of (*a*) antimony and (*b*) bismuth.
11. Topics for home study: (*a*) Fertilizers. (*b*) Matches. (*c*) Why does the soil need fertilizer? (*d*) Fireproof doors. (*e*) Sprinkler systems. (*f*) The nitrogen family and the periodic system.

PROBLEMS

1. Calculate the weight of phosphorus in 40 tons of calcium phosphate.
2. Calculate the percentage composition of (*a*) arsenic trioxide and arsenic pentoxide, and (*b*) antimony trichloride and antimony

pentachloride. Show that these two sets of substances illustrate the law of multiple proportions. (Use exact atomic weights.)

3. How many liters of air (containing 21 per cent of oxygen by volume) will be required to burn 5 gm. of phosphorus (standard conditions)?

4. How many gm. of phosphorus can be made by the electro-thermal process from a ton of calcium phosphate (70 per cent pure)?

5. How much "superphosphate" can be made from 2 tons of phosphate rock (75 per cent calcium phosphate)?

CHAPTER XXIX

SODIUM AND ITS COMPOUNDS — POTASSIUM

443. Metals. — The elements studied so far belong (with one or two exceptions) to the class of non-metals.

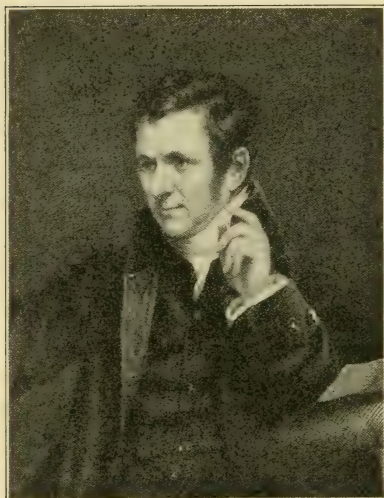


Fig. 155. — Davy (1778–1829)

Metals, *e.g.* sodium and calcium, have been discussed, and the properties of many compounds of metals have been quite fully treated, especially bases and salts. A table of the common metals and non-metals is given in **397**.

Sodium and potassium belong to a natural family of elements known as the **alkali metals** (**399**).

444. Sodium is manufactured on a large scale by the electrolysis of fused sodium hydroxide. This was the method by which the English chemist Davy isolated sodium in 1807 (Fig. 155). Figure 156 is a sketch of one form of apparatus used at Niagara Falls, where many electrical industries are located.

The body of the steel cylinder (*S*) rests within a heated flue. The cathode (*C*) is iron and the connected carbon rods (*AA*) constitute

the anode. The sodium hydroxide in the neck (*B*) is solid, but is kept melted in the main part. The melted sodium hydroxide conducts a current just as a solution does. As the electrolysis proceeds, sodium and hydrogen are liberated at the cathode, rise, and collect in the cylindrical pot (*P*). The hydrogen escapes to some extent through the cover, but enough always remains in the upper part of *P* to protect the sodium from the air. The molten sodium, which floats on the top of the fused sodium hydroxide, is ladled out at intervals. Oxygen is liberated at the anode and escapes through the pipe *O* without coming in contact with the sodium or hydrogen.

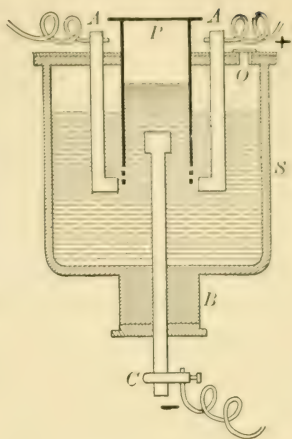


Fig. 156. — Sketch of the apparatus for the manufacture of sodium by the electrolysis of sodium hydroxide

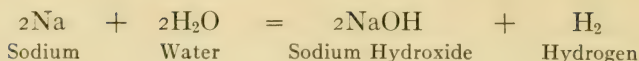
445. Properties of sodium. —

Sodium is a silver-white metal. It is so soft that it can be easily molded with the fingers and cut with a knife. It floats on water, since its specific gravity is only about 0.97. (Compare 396, 397.)

446. Chemical conduct of sodium. — Heated in air, sodium melts at 96° C., and at a higher temperature it volatilizes and burns with a brilliant yellow flame, forming sodium peroxide (Na_2O_2). This intense yellow color is characteristic of sodium and its compounds and is the usual **test for sodium** (free or combined).

In moist air the bright surface of sodium quickly tarnishes, and the metal as usually seen has a yellow or brownish coating (instead of a shiny surface). It is, therefore, kept under kerosene or a liquid free from water.

Sodium decomposes water at ordinary temperatures, forming hydrogen and sodium hydroxide, thus:—



If held in one place upon the water by filter paper, enough heat is generated to set fire to the hydrogen, which burns with a yellow flame, owing to the presence of volatilized sodium (49, 51). It combines vigorously with many non-metals, especially oxygen and chlorine.

447. Sodium chloride (NaCl) is the most important compound of sodium. It is familiar under the name of **salt** or **common salt**. The presence of salt in the ocean, in lakes and springs, and in the earth is mentioned in the oldest historical records. It is one of the most abundant substances, and is the chief of sodium compounds.

448. Preparation of common salt. — Salt is obtained from sea water, rock salt deposits, and brines. Sea water contains nearly 4 per cent of salts, and three fourths of this amount is sodium chloride. The water is evaporated, often by exposure to the sun, and the salt separates from the concentrated solution. Deposits of salt are found in many parts of the globe, the most important being in England, Austria-Hungary, and Germany. In these regions and some parts of the United States most of the salt is obtained from natural or artificial brines. These solutions of salt are evaporated in shallow basins by the sun's heat or in large kettles.

According to the standard established by the United States Department of Agriculture, dry table or dairy salt must not contain over 1.4 per cent of calcium sulphate, 0.5 per cent of calcium or magnesium chloride, and 0.1 per cent of matter insoluble in water. The dampness of salt is due to traces of magnesium and calcium chlorides which absorb moisture from the air (85). Pure salt does not absorb moisture.

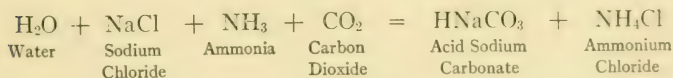
449. Properties and uses of salt. — Salt is rather uniformly soluble in water, 100 gm. of water dissolving about 36 gm. of salt at 20° C., and about 39 gm. at 100° C. (Fig. 43). It crystallizes in cubes, and does not contain

water of crystallization. The crystals, when heated, often snap open sharply (*i.e.* decrepitate), owing to the sudden evaporation of inclosed water. It melts at about 800° C.

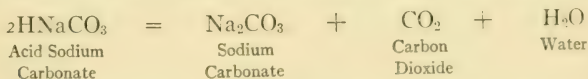
Salt is an essential ingredient of the food of man and animals. Besides its universal domestic use, enormous quantities are used in making sodium carbonate, sodium hydroxide, and hydrochloric acid.

450. Sodium carbonate (Na_2CO_3) is next to sodium chloride in importance. Formerly it was obtained from the ashes of marine plants, hence the old name **soda ash**; sodium chloride is now the source. The manufacture of sodium carbonate is one of the largest chemical industries. Two processes are used, the Solvay and the Leblanc.

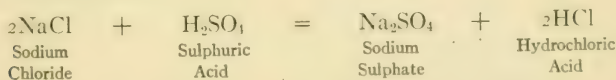
The **Solvay process**, which is operated very successfully in the United States, consists in saturating a cold concentrated solution of sodium chloride first with ammonia (gas) and then with carbon dioxide. The equation for the complete chemical change is:—



The acid sodium carbonate is sparingly soluble in cold ammonium chloride solution, and is precipitated. The acid sodium carbonate is changed into normal sodium carbonate by heating, thus:—

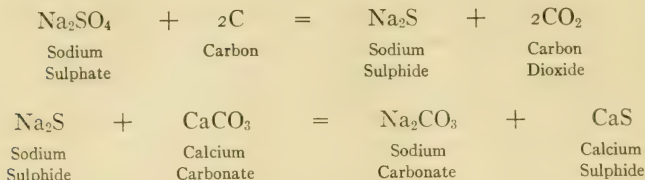


The **Leblanc process**, which is the older and is used chiefly in Europe involves three reactions. (1) Sodium chloride is changed into sodium sulphate, thus:—



(2) and (3) The sodium sulphate is changed into sodium carbonate by heating it with coal and calcium carbonate; the two main

changes, which are accomplished by one operation, are represented thus:—



From the dark mass, called black ash, the sodium carbonate is dissolved, and the solution evaporated to crystallization.

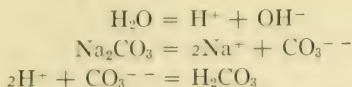
451. Properties and uses of sodium carbonate. — Crystallized sodium carbonate ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$) is often called **sal soda** or **washing soda**. It effloresces, *i.e.* slowly loses its water of crystallization when exposed to air (84). When heated, it first dissolves in its water of crystallization, and finally changes into the white anhydrous salt (Na_2CO_3) which is called **soda ash** or **calcined soda**.

It is soluble in water, and forms an alkaline solution which is widely used as a cleansing agent; hence the name washing soda. Besides its use as a cleansing agent, enormous quantities are consumed in the manufacture of glass, soap, sodium hydroxide (456, first paragraph), and many other useful substances.

452. Hydrolysis of sodium carbonate. — The alkalinity of sodium carbonate is due to hydrolysis and can be explained in terms of the ionic hypothesis. Hitherto water has been called a non-electrolyte, *i.e.* it does not ionize. As a matter of fact it does form the ions H^+ and OH^- , but to such a very slight extent that they have little or no effect in most cases. Under certain conditions, however, these ions participate in reactions, *e.g.* with sodium carbonate.

Sodium carbonate ionizes into 2Na^+ and CO_3^{--} , but the unstable CO_3 ions form HCO_3 ions with the H ions from the slightly dissociated water. This removal of H ions finally leaves in the solu-

tion sufficient OH ions to produce an alkaline reaction. Equations for these ionic reactions are: —



We may define **hydrolysis** as a chemical change in which water is a factor. A more restricted definition is the interaction of the ions of water with the ions of a dissolved salt. Salts of weak acids (*e.g.* H_2CO_3) and strong bases (*e.g.* NaOH) give alkaline solutions. On the other hand, salts of strong acids (*e.g.* HCl , H_2SO_4) and weak bases (*e.g.* $\text{Cu}(\text{OH})_2$, $\text{Fe}(\text{OH})_3$) give acid solutions. Salts of strong acids and strong bases give neutral solutions, *e.g.* NaCl , KNO_3 , Na_2SO_4 .

453. Sodium bicarbonate (HNaCO_3) is prepared by the Solvay process (see above), or by treating sodium carbonate solution with carbon dioxide.

It is a white powder, less soluble in water than the normal sodium carbonate. When heated alone or when mixed with an acid or an acid salt, sodium bicarbonate gives up carbon dioxide. This property early led to its use in cooking, and gave the names **cooking soda**, **baking soda**, or simply **soda**.

Sodium bicarbonate is sometimes called **acid sodium carbonate** (though it is nearly neutral to litmus) and hydrogen sodium carbonate. The neutral reaction of a solution of sodium bicarbonate is due to the fact that neither of its ions (Na^+ and HCO_3^-) affects litmus. It should be noted that the name "acid" sodium carbonate emphasizes the method of formation (from carbonic acid) not the properties of the salt (**292**, **293**).

454. Baking powders. — Sodium bicarbonate is an essential ingredient of baking powders and of the various mixtures (except yeast) used to raise bread, cake, and other food. The other ingredient is a substance which has a weak acid reaction, such as acid calcium phosphate (**426**),

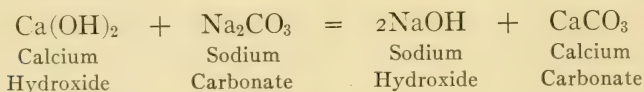
cream of tartar (acid potassium tartrate ($\text{HKC}_4\text{H}_4\text{O}_6$)), or alum.

If baking powder is mixed with water, carbon dioxide is slowly liberated. When pastry is raised with baking powder, or with a mixture of baking soda and cream of tartar, the escaping carbon dioxide puffs up the dough. Hence baking soda is often called **saleratus** — the salt that aerates (from the Latin words *sal*, salt, and *aer*, air).

455. Sodium hydroxide or caustic soda (NaOH) is a white, crystalline, brittle, corrosive solid. It absorbs water (85) and carbon dioxide rapidly from the air, and is thereby changed into sodium carbonate. It dissolves readily in water, with rise of temperature. The solution is strongly alkaline and disintegrates many substances; hence the term *caustic*. It is a strong base and its solution contains a high per cent of hydroxyl ions (247). It melts easily.

Immense quantities are used in making soap, paper pulp, phenol ($\text{C}_6\text{H}_5\text{OH}$), and dyestuffs, and in refining petroleum.

456. Manufacture of sodium hydroxide. — The **chemical process** consists in boiling a dilute solution of sodium carbonate with calcium hydroxide; the main change is represented thus: —



The solution of sodium hydroxide is filtered from the insoluble calcium carbonate, evaporated, and the molten mass allowed to solidify in small cylindrical molds about the diameter of a lead pencil or in large iron barrels called drums; some is made into flakes.

In the **electrolytic process**, which is operated on a large scale at Niagara Falls, and elsewhere, a solution of sodium chloride is used. When an electric current is passed through such a solution, sodium hydroxide and hydrogen

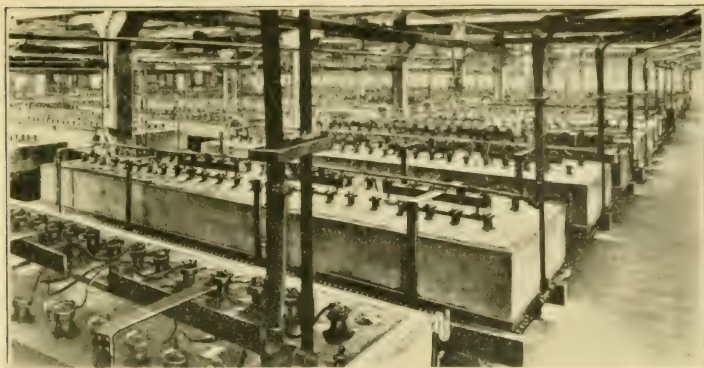


Fig. 157. — The cell room of a plant for making sodium hydroxide by electrolysis

are produced at the cathode and chlorine at the anode. The cells are constructed to prevent secondary action between the sodium hydroxide and chlorine. A view of the cell room in an electrolytic alkali plant is shown in Fig. 157. The **porous diaphragm type** of cell is now largely used.

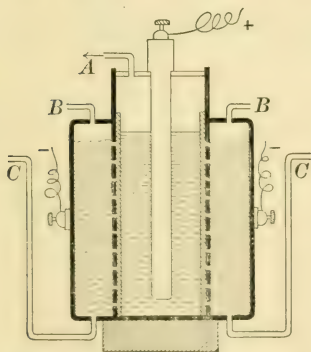
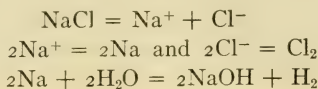


Fig. 158. — Sketch of the diaphragm type of apparatus for the manufacture of sodium hydroxide by the electrolysis of sodium chloride solution

An example of the porous diaphragm type is shown in Fig. 158. The liquid can penetrate the porous diaphragm. Hence the diaphragm does not interfere with the flow of the electric current, but it does prevent the mixing of the two solutions. The diaphragm is a sheet of asbestos (mixed with iron oxide), which is supported on the perforated iron cathode. The graphite anode dips into the sodium chloride solution in the middle compartment; here the solution is kept at a certain level by regulation of the inflow. The outer compartment contains kerosene.

When the current is passing, the sodium ions (Na^+) migrate to the cathode, lose their charges and become sodium atoms (Na), which interact with the water and form sodium hydroxide and hydrogen. The sodium hydroxide drops through the kerosene to the bottom of the outer compartment, and is drawn off through *C*; the hydrogen escapes through *B*. Similarly, chlorine ions (Cl^-) migrate to the anode, lose their charges, and become chlorine atoms (Cl) which unite and escape as chlorine gas (Cl_2) through *A*. The equations may be written thus:—



In the **non-diaphragm** cells the solutions are kept apart by partitions which extend nearly to the bottom of the cell and dip into a layer of mercury.

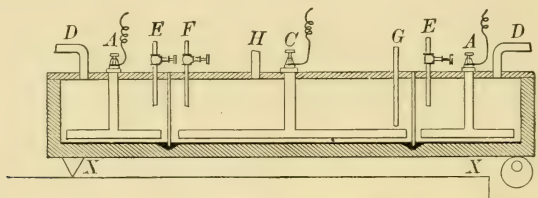


Fig. 159. — Sketch of the non-diaphragm type of apparatus for the manufacture of sodium hydroxide by electrolysis of sodium chloride solution

An example of this type is shown in Fig. 159. The cell is a slate box divided into one cathode and two anode compartments. The T-shaped anodes (*A, A*) of graphite and the cathode (*C*) of iron reach nearly to the mercury (shown in black). The anode compartments contain sodium chloride solution, while the cathode compartment contains sodium hydroxide solution; sodium chloride of the right concentration flows slowly and continuously into the anode compartments by means of the pipes *E, E*.

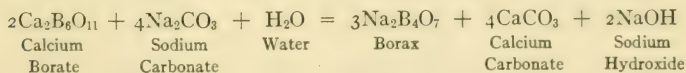
During the electrolysis the chlorine ions (Cl^-) ultimately become chlorine gas (Cl_2) and escape through the pipes *D, D*. The sodium ions (Na^+) move toward the cathode, meet the mercury, are liberated

on this intermediate cathode in the anode compartments and form an amalgam with it. When in operation the cell is slowly rocked on the device *X*, *X* and the sodium amalgam, *but not the solutions*, flows beneath the partitions from the anode compartments into the cathode compartment and back again. Once in the cathode compartment, the sodium is liberated at the cathode, and reacts with the water, forming hydrogen (H_2) and sodium hydroxide. The hydrogen escapes through the pipe *H*. The sodium hydroxide solution is drawn off (through *G*) and replaced by water (through *F*).

The sodium hydroxide solution is treated as described above (second paragraph, this section). The chlorine is stored or compressed into steel cylinders (Figs. 35, 63). In some industries, *e.g.* paper pulp plants, both sodium hydroxide and chlorine are used. In that case, the chlorine is made into bleaching mixtures.

457. Sodium sulphate (Na_2SO_4) is a white solid. It dissolves readily in water, and when a strong solution made at 30° C. is cooled, large transparent, bitter crystals separate ($Na_2SO_4 \cdot 10H_2O$), called Glauber's salt. Large quantities are obtained as a by-product in making hydrochloric acid (154). It is used in the glass and other industries.

458. Sodium tetraborate or borax ($Na_2B_4O_7$) is made from calcium borate (colemanite, $Ca_2B_6O_{11} \cdot 5H_2O$) by boiling it with sodium carbonate and separating the borax by crystallization. The equation for the reaction is:—



Borax is a white crystalline solid, having five or ten molecules of water of crystallization; a common household form is the powdered crystals. The crystals readily effloresce and crumble in the air. When heated, crystallized borax loses its water of crystallization and swells into a white porous mass, which finally melts into a glass-like

solid. This glassy borax dissolves metallic oxides and is colored by them.

If borax is melted on the end of a looped wire, the transparent globule is called a **borax bead**. These beads usually assume different colors after being heated in an oxidizing or a reducing flame, and the colors are characteristic of the metals (Fig. 160). Thus, a copper

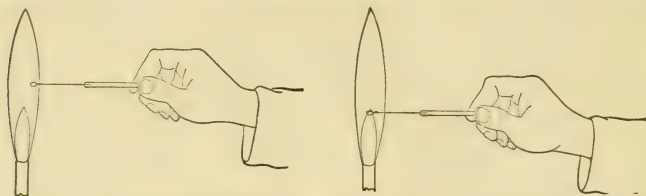


Fig. 160. — Testing with a borax bead in the oxidizing flame (left) and reducing flame (right)

bead is made blue-green by an oxidizing flame and red by a reducing flame. Borax beads are used in testing small quantities of minerals.

Borax is chiefly used in the manufacture of enamels for coating iron ware. The so-called “granite” or “agate” ware and “porcelain-lined” vessels are made of iron coated with an easily fused glass called enamel. Some is used for preserving meat, fish, cheese, and other foods, because it prevents the growth of certain bacteria.

A solution of borax has a slight alkaline reaction owing to hydrolysis (452); hence it is sometimes used instead of soap as a cleansing agent. Some soaps contain borax.

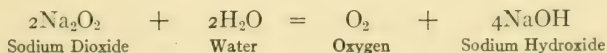
Its power to dissolve oxides adapts borax for use in soldering and welding metals. Solder adheres only to clean metals, so a little borax is used to dissolve the film of oxide on the surfaces to be joined. Considerable is consumed as an ingredient of ointments, lotions, and toilet powders.

459. Sodium nitrate (NaNO_3) is found abundantly in Chile and is often called **Chile saltpeter**. It is a white or

brownish solid, which becomes moist in the air. Large quantities are used as a fertilizer, either alone or mixed with compounds of potassium and of phosphorus (428, and compare 116). It is used in making nitric (184) and sulphuric acids, and potassium nitrate.

The deposits of sodium nitrate are in a dry region near the coast and cover a large area. Chile controls the industry and exports annually over a million tons. The crude salt, which is called caliche, looks like rock salt. The commercial salt is extracted from caliche by treating with water, settling, and evaporating the solution of the nitrate to crystallization. The final mother liquor is a source of iodine (413, 414).

460. Sodium peroxide (Na_2O_2) is a yellowish solid. It is used to bleach straw and delicate fabrics. With water it liberates oxygen, thus:—



461. Other sodium compounds.—**Sodium cyanide** (NaCN) is a white, deliquescent solid. It forms an alkaline solution (by hydrolysis—452). It is used in gold and silver plating and in the cyanide process of extracting gold. This compound is the sodium salt of **hydrocyanic**, or **prussic**, acid (HCN). It is a violent poison and great care must be taken in working with it. **Sodium phosphate** (426), **sodium thiosulphate** (276), **acid sodium sulphite** (263), and **sodium silicate** (387) have been described.

462. Potassium.—Potassium and its compounds are much like sodium and the corresponding compounds. Minerals and many rocks contain potassium compounds. The minerals mica and feldspar are silicates containing potassium. By the decay of these, soluble potassium compounds find their way into the soil and are taken up by plants.

Potassium salts are found in wood ashes and in the deposits in wine casks. Sea water and mineral waters contain potassium salts, particularly potassium chloride and

potassium sulphate. Extensive beds of potassium salts are found in Germany, especially at Stassfurt.

The most important Stassfurt potassium minerals are : —

Sylvite — KCl	Carnallite — KCl, MgCl ₂ .6H ₂ O
Kainite — KCl, MgSO ₄ .3H ₂ O	Picromerite — K ₂ SO ₄ , MgSO ₄ .6H ₂ O

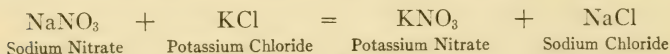
Potassium is **prepared** from potassium hydroxide by electrolysis.

Potassium is a soft, silver-white metal with a bluish tinge. It floats on water, the specific gravity being about 0.86. Its brilliant luster soon disappears in air, owing to rapid oxidation. Potassium as ordinarily seen is, therefore, covered with a grayish coating, and, like sodium, must be kept under mineral oil. It melts at 62.5° C., and at a higher temperature burns with a violet-colored flame. This color is characteristic of burning potassium, and is a **test for the metal and its compounds**. It is more active chemically than sodium.

463. Potassium chloride (KCl) resembles sodium chloride, and is used chiefly to prepare other potassium salts and as an ingredient of fertilizers (**428**).

464. Potassium nitrate (KNO₃), also called **niter** and **salt-peter**, is formed in the soil of many warm countries by the decomposition of nitrogenous organic matter.

It is manufactured by mixing hot, concentrated solutions of sodium nitrate and potassium chloride. The equation for the reaction is : —



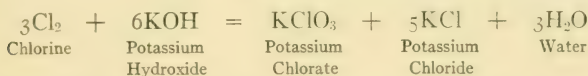
The sodium chloride, being much less soluble than the potassium nitrate, separates and is removed by filtration. By evaporating the filtrate, crystals of potassium nitrate separate and are further purified by recrystallization. The solubility of these salts is shown in Fig. 43.

Potassium nitrate melts at 333° C., and on further heating changes into **potassium nitrite** (KNO₂) and oxygen. At a high temperature, potassium nitrate gives up oxygen readily, especially to charcoal, sulphur, and organic matter.

This oxidizing power leads to its extensive use in making gunpowder, fireworks, matches, explosives, and in many chemical operations.

Gunpowder is a mixture of potassium nitrate, charcoal, and sulphur. The proportions differ with the use of the powder. A common variety contains 75 per cent of potassium nitrate, 15 of charcoal, and 10 of sulphur. When gunpowder burns in a closed space, hot gases are suddenly formed. The pressure exerted by these gases forces the bullet from a gun and tears rocks to pieces. The chemical changes attending the explosion of gunpowder in a closed space are complex.

465. Potassium chlorate (KClO_3) is used to prepare oxygen, and in the manufacture of matches and fireworks. It is manufactured by the electrolysis of potassium chloride in a special apparatus which allows the two products — chlorine and potassium hydroxide — to mix and interact. The equation for the reaction is: —



466. Potassium carbonate (K_2CO_3) is very soluble in water, and the solution, like that of sodium carbonate, has a strong alkaline reaction owing to hydrolysis (**452**).

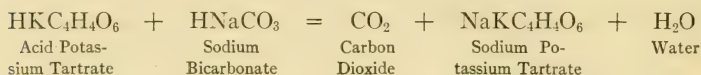
It was formerly obtained by treating wood ashes with water and evaporating the solution to dryness. The crude salt thus obtained has long been called **potash**, and a purer product is known as **pearlash**. The name of the element was suggested by the word potash; the symbol, K, comes from the Latin word *kalium*. It is now made from potassium chloride by the Leblanc or other processes. It is used extensively in the manufacture of hard glass, soft soap, caustic potash (potassium hydroxide), and other potassium compounds.

467. Potassium hydroxide (KOH) resembles sodium hydroxide in properties. It is prepared from potassium chloride by the methods used for sodium chloride. Like sodium hydroxide, it dissolves readily in water with evolution of heat, forming a strongly alkaline solution. Its

solutions corrode and disintegrate animal and vegetable matter and many mineral substances; hence the term *caustic potash*.

468. Other potassium compounds. — Potassium cyanide (KCN) and potassium sulphate (K_2SO_4) resemble the corresponding sodium compounds.

Purified acid potassium tartrate ($HKC_4H_4O_6$) is commonly known as **cream of tartar**. It is extensively used in the manufacture of tartrate baking powders. These are mixtures of cream of tartar and sodium bicarbonate ($HNaCO_3$), together with a small proportion of starch (**454**). When dissolved in water or moistened by the water in a food mixture, the two ingredients interact and liberate carbon dioxide as the main product, thus: —



469. Relation of potassium to life. — Potassium, like nitrogen and phosphorus, is essential to the life of plants and animals. The ash of many common grains, vegetables, and fruits contains potassium carbonate, which is formed from the complex organic potassium compounds in them. Potassium salts are taken from the soil by plants and must be returned if the soil is to be productive. Sometimes wood ashes, or the sulphate and chloride, are applied to the soil. Usually the potassium salts are supplied in the form of fertilizer. Experiments show that many soils need potassium salts as plant food (Fig. 160). (Compare **116**, **427**, **428**.)

EXERCISES

1. Describe the manufacture of sodium.
2. Summarize the physical properties and chemical conduct of sodium.
3. Give an outline of the manufacture of sodium carbonate by (a) the Leblanc process, and (b) the Solvay process. Write the es-

sential equations for each process.

4. What is (a) soda, (b) soda ash, (c) sodium carbonate, (d) soda crystals, (e) sal soda, (f) washing soda, (g) "alkali," (h) acid sodium carbonate, (i) saleratus, (j) baking powder, (k) baking soda, (l) caustic soda?

5. Describe the manufacture of sodium hydroxide by (a) the chemical process and (b) the electrolytic process.

6. What is a simple test for (a) sodium, and (b) potassium?

7. How is potassium nitrate manufactured?

8. Why does sodium carbonate form an alkaline solution?

9. Topics for home study: (a) Davy. (b) Baking powders. (c) Gunpowder. (d) Salt. (e) Food contains potassium compounds.



Fig. 161. — Result of an experiment with buckwheat. The pot on the left received a complete fertilizer, while the pot on the right differed only in receiving a fertilizer without potassium salts

PROBLEMS

1. Calculate the weight of sodium in (a) 20 gm. of NaOH, and (b) 22 gm. of acid sodium sulphate.

2. Calculate the weight of potassium in (a) 15 gm. of KCl, and (b) 45 gm. of potassium carbonate.

3. Write the formulas of the sodium and potassium salts of the following acids: chloric, phosphoric (ortho), sulphurous, hydrofluoric, carbonic, acetic, hydrobromic, dichromic, permanganic, manganic.

4. Give the name and formula of the ions in dilute solutions of (a) sodium hydroxide, (b) potassium nitrate, (c) sodium chloride, and (d) potassium sulphate.

CHAPTER XXX

CALCIUM CARBONATE — LIME — CEMENT— CALCIUM SULPHATE

470. Occurrence of calcium compounds. — Calcium is never found free. Combined calcium makes up about 3.5 per cent of the earth's crust (**11**). The most abundant compound is calcium carbonate (CaCO_3). Many rocks are complex silicates of calcium and other metals (**383**, **386**). The extensive deposits of calcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$) have been mentioned (**420**, **428**). Calcium sulphate (CaSO_4) also occurs abundantly.

Calcium compounds are essential to the life of plants and animals, being found in the leaves of plants, and in the bones, teeth, and shells of animals. Many rivers and springs contain calcium salts, especially the acid carbonate ($\text{H}_2\text{Ca}(\text{CO}_3)_2$) and the sulphate.

471. Calcium carbonate (CaCO_3). — This is the most common calcium compound. The most abundant form is **limestone**; vast beds are found in many regions. Pure limestone is white or gray, but impurities, especially organic matter and iron compounds, produce many colored varieties. Much limestone contains silica, clay, iron and aluminium compounds, and the fossil remains of plants and animals. Hard, crystalline limestone which takes a good polish is called **marble**; it is extensively used as a building and an ornamental stone. **Calcite** is the purest form of crystallized calcium carbonate; a transparent variety called Iceland spar has the property of double refraction, *i.e.* of making objects appear double.

Different grades of calcium carbonate are used in making lime, cement, iron, glass, and sodium carbonate.

472. Deposition of calcium carbonate. — Calcium carbonate is practically insoluble in water. But if water contains carbon dioxide the carbonate dissolves, owing to its transformation into the soluble acid calcium carbonate ($\text{H}_2\text{Ca}(\text{CO}_3)_2$) (293).

Many underground waters contain carbon dioxide, and as this water works its way along in limestone regions, the limestone is dissolved and caves are often formed or enlarged. When the water enters a cave and drips from



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Fig. 162. — Interior of a limestone cave at Luray, Va., showing stalactites and stalagmites

the top, the water evaporates, or the gas escapes, or both, and calcium carbonate is redeposited, often forming stalactites and stalagmites. The **stalactites** hang from the roof like icicles, and are often exquisitely shaped; the **stalagmites**, which grow up from the floor, sometimes meet the stalactites and form a column (Fig. 162). Mexican onyx is a variety of stalagmite. Vast deposits of this beautiful mineral are found in Algeria and Mexico. It is translucent and delicately colored, and is used as an ornamental stone, especially for altars, table tops, mantles, soda fountains, and lamp standards. Travertine is another variety; it occurs near many springs in Italy. When fresh it is soft and porous, but it soon hardens and becomes a durable building stone in dry climates. A portion of the walls of the Colosseum and St. Peter's is travertine.

Calcium carbonate dissolved in the ocean is transformed by marine organisms into shells and bony skeletons. The hard parts of these animals accumulate in vast quantities on the ocean bottom, become

compact, often hardened and crystallized, and subsequently form a part of the land. **Chalk** is the remains of shells of minute anima's.

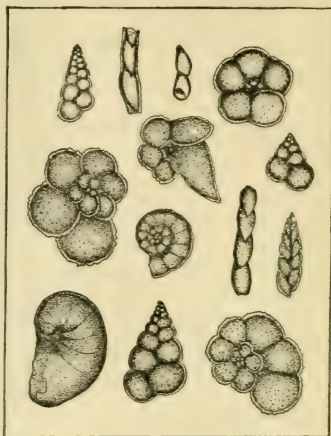
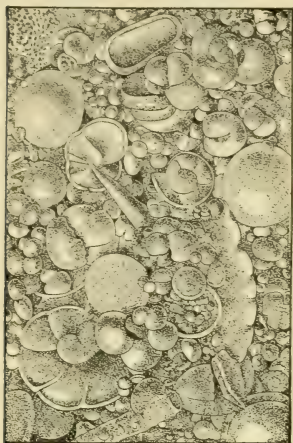


Fig. 163. — Ooze from the ocean bottom showing limestone shells (left), and the same kind of shells (magnified) from chalk deposits in Iowa (right)

When examined under a microscope, a good specimen is seen to consist almost entirely of tiny shells (Fig. 163).

Limestone often contains **fossils**, confirming the belief that limestone is the remains largely of the shells of animals (Fig. 164, left). On the coast of Florida, **coquina** or shell rock is found (Fig. 164, right).

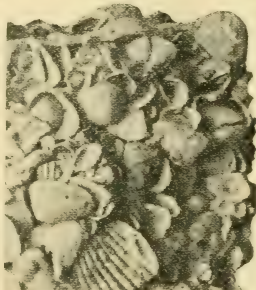
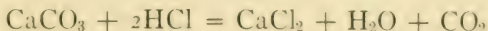


Fig. 164. — Limestone containing fossils (left). Coquina (right)

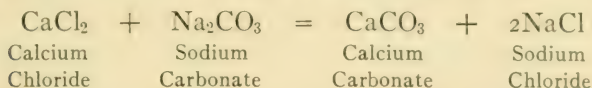
It is a mass of fragments of shells cemented by calcium carbonate, and in time will become compact limestone (164, right).

Coral is calcium carbonate, and the vast accumulations in the sea are the skeletons of the coral animals.

473. Chemical conduct of calcium carbonate. — Calcium carbonate is decomposed by heat into lime (CaO) and carbon dioxide (**475**). It interacts with acids, thus: —



Calcium carbonate itself is precipitated by the interaction of a soluble calcium salt and a soluble carbonate, thus: —

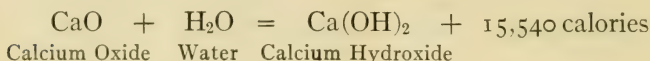


Purified calcium carbonate prepared this way is called **precipitated chalk**, and is used extensively as the polishing ingredient of tooth powder. An impure variety is called **whiting**: a mixture of whiting and linseed oil is **putty**.

474. Lime. — This familiar substance is **calcium oxide** (CaO). It is a hard, white solid. Pure lime is almost infusible, and when heated in the oxyhydrogen flame, it gives an intensely bright light, called the lime light (**57**). In the intense heat of the electric furnace it melts (at about 2750°C.) and at a higher temperature it boils.

Lime when exposed to the air becomes “air slaked,” *i.e.* it slowly absorbs water and carbon dioxide, swells considerably, and soon crumbles to a powder. This powder is a mixture of calcium hydroxide and calcium carbonate; such a mixture is not suitable for many of the uses of lime. (Compare hydrated lime, **476**.) Lime that is not air slaked is called **quicklime** or **caustic lime**. When just the right amount of water is slowly added, the product is **calcium hydroxide** or hydrated lime (**476**). If an excess of water is added quickly, lime and water combine readily and vigorously; considerable heat is liberated, as is seen when mor-

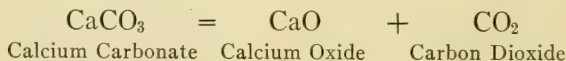
tar is being prepared. This operation is called **slaking**, and the product is **slaked lime**. The thermo-chemical equation is:—



Sometimes water leaks into barrels, cars, or buildings in which lime is stored, and the heat evolved causes a fire.

Lime has many indispensable **uses**. Immense quantities are consumed in preparing mortar, plaster, and cement. Many useful chemicals are made from lime, *e.g.* bleaching powder (**149**), calcium carbide (**295**), sodium hydroxide (**456**), calcium bisulphite (**263**), lime-sulphur mixtures (**248**), and calcium cyanamide (CaN_2C) (**484**). Much is used in such industrial operations as purifying illuminating gas, refining sugar, softening water, removing hair from hides, bleaching cotton cloth, extracting metals from ores. In agriculture it is added to soil to neutralize acids.

475. Manufacture of lime.—Lime is manufactured by heating limestone in a partly closed cavity or in a furnace. (Either one is called a **kiln**.) The decomposition takes place according to the equation:—



The carbon dioxide escapes; the lime is left in the kiln.

Limestone was formerly “burned” in a cavity on a hillside, and in some regions it is so prepared today. An arch of limestone is built across the cavity above the fire pit, and limestone is introduced until the kiln is full.

The arch kilns have been largely replaced by furnaces (Fig. 165). The heat is produced by burning gases (at *B*, *B*). The hot air and gaseous products of combustion pass up through the limestone (fed

in at *A*) and heat it to the proper temperature (about 750 to 900° C.). The rising gases sweep out the carbon dioxide, thus aiding the process. The solid sinks down through the furnace and is removed frequently (at *C*, *C*). The towers of modern kilns are 60 feet or more high (Fig. 166). They operate continuously and produce from 25 to 60 tons a day according to size. Several towers are often connected with a single gas producer.

476. Calcium hydroxide ($\text{Ca}(\text{OH})_2$) is a white solid. It is manufactured by adding carefully just enough water to calcium oxide to produce the hydroxide. This **hydrated lime**, as it is called, is a fine, white powder. If properly packed, it will keep indefinitely. Also, it can be stored without danger of causing fire. It is suitable for the same purposes as the lime slaked just before use.



Fig. 166. — A modern limekiln in operation

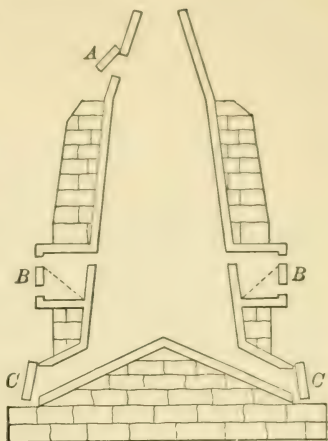


Fig. 165. — Sketch of a continuous limekiln

Calcium hydroxide is sparingly soluble in water, but more soluble in cold than in warm water (79). The solution has a bitter taste and a mild alkaline reaction; it is often called **limewater**. Exposed to the air, limewater becomes covered with a thin crust of calcium carbonate, owing to interaction with carbon dioxide. For the same reason, limewater be-

comes milky or cloudy when carbon dioxide is passed into it. The formation of calcium carbonate in this way is the **test for carbon dioxide** (1).

477. Limewater is prepared by carefully adding lime to considerable water, allowing the mixture to stand in a stoppered bottle until the solid has settled, and then removing the clear liquid. When considerable calcium hydroxide is suspended in the liquid, the mixture is called **milk of lime**. Ordinary **whitewash** is thin milk of lime.

478. Mortar is a thick paste formed by mixing lime, sand, and water. It slowly hardens or "sets" without much shrinking, owing to loss of water and to interaction with carbon dioxide. When placed between bricks or stones it holds them firmly in place, and is used to construct buildings, walls, foundations, etc.

The sand gives bulk and rigidity; it also makes the mass porous and thus facilitates the change of the hydroxide to the carbonate. We can readily prove that a carbonate is formed by adding hydrochloric acid to a lump of old mortar; the liberated gas is carbon dioxide. Hair is sometimes added to make the mortar stick better, especially when it is used as plaster for walls. Hair is not necessary, if cement (**479**) is mixed with the mortar.

479. Cement is a kind of strong, firm mortar. Like ordinary mortar, it hardens in the air; unlike mortar, however, it has the peculiar and useful property of hardening even under water.

The chemical changes which occur in the setting of cement are complex and not well understood. The products, whatever they are, set into a very hard mass.

Cement is next to iron and steel in importance as a building material. Immense quantities (about 100,000,000 barrels annually) are used in a great variety of structures — foundations, dams, bridges, fireproof buildings (*e.g.* garages), storage tanks, warehouses, floors, walks. A mixture of cement, sand, water, and crushed stone is known as

concrete, which is used, usually instead of cement alone, as construction material. Sometimes concrete is strengthened by imbedding rods of steel in it; it is then called **reinforced concrete**.

480. Manufacture of cement. — Cement is made from natural or, more commonly, artificial mixtures of limestone

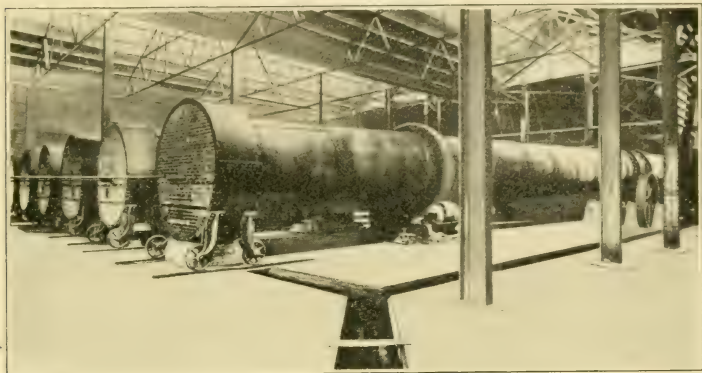


Fig. 167. — Rotary kilns for making cement

and clay. The raw materials must contain the proportions of the essential ingredients, viz. limestone, clay (aluminium silicate), and sand, which have been found by ex-

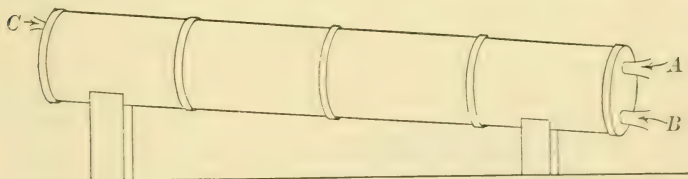


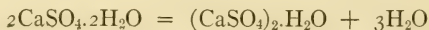
Fig. 168. — Sketch of a cement kiln

perience to give the best results. The materials are mixed, ground very fine, and fed into a long furnace made of steel and lined with fire-brick. The furnace is slightly inclined and rotates slowly (about once a minute); it is called a **rotary kiln** (Fig. 167).

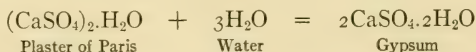
The process can be best understood by studying the simple sketch in Fig. 168. The mixture enters at the upper end (C). As it gradually works its way along through the slowly rotating kiln, it is heated by the flame and hot gases produced (inside the kiln) by burning oil or coal dust, which is forced in at A by a powerful air blast. The mixture forms a semifused, gray-black mass which drops out at B. The cooled lumps, called clinker, are mixed with about 2 per cent of gypsum (calcium sulphate, 481), and ground to a very fine powder. This powder, which is grayish, is cement; it is often called Portland cement.

481. Calcium sulphate (CaSO_4). — Extensive deposits of different forms of calcium sulphate are found in many localities; in the United States large quantities are obtained in New York, Michigan, and the Middle West. **Gypsum** is the commonest form; it occurs as white masses which have the composition $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. A translucent variety of gypsum is called **selenite**. The mineral **anhydrite** is anhydrous calcium sulphate (CaSO_4). Gypsum is used as an ingredient of some fertilizers and in making plaster of Paris, paper, white paint, and cement.

482. Plaster of Paris is a fine white powder made by heating gypsum to the proper temperature (about 145°C). The equation is: —



This powder has the composition $(\text{CaSO}_4)_2 \cdot \text{H}_2\text{O}$. If moistened with water, it swells and quickly sets or solidifies to a hard mass which consists of a network of very small crystals. The equation for the setting of plaster of Paris may be written: —



Plaster of Paris is used to coat plastered walls, to cement glass to metal, but more largely to make casts and reproductions of statues and small objects. **Stucco** is a mixture of glue and plaster of Paris.

483. Calcium compounds and hardness of water.—

Calcium sulphate is slightly soluble in water, and calcium carbonate, as we have already seen, is changed into soluble acid carbonate by water containing carbon dioxide. Water containing these salts is called **hard water**. And water from which they are absent is often called **soft water**.

Soap does not dissolve readily in hard water, but forms sticky, insoluble compounds with calcium (and magnesium) salts; hence a large quantity of soap must be used up before a lather will form.

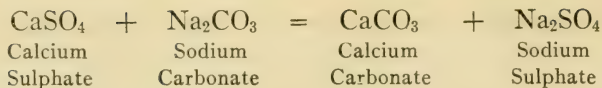
Hard water, if used in boilers, forms deposits on the inside of the boiler tubes, thus causing waste of heat (Fig. 169); in some cases acids (*e.g.* HCl) are liberated which corrode the boiler.

Hardness due to acid calcium carbonate (or acid magnesium carbonate) is called **temporary hardness**, because boiling removes it. Temporary hardness can also be removed by adding calcium oxide or hydroxide to change the soluble acid carbonate to the insoluble carbonate. After either method, the water must be filtered, or siphoned off, to get rid of the calcium carbonate.

Water containing calcium sulphate or chloride is said to have **permanent hardness**, because these salts cannot be removed by boiling. (Magnesium sulphate and chloride, like the corresponding calcium salts, produce permanent hardness.) Permanently hard water can be softened by adding sodium carbonate (*e.g.* ordinary washing soda), which converts the calcium (and magnesium) salts into insoluble carbonates, thus:—

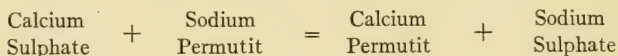


Fig. 169. — Section of a boiler tube showing the scale deposited by hard water

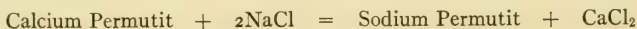


This process is used on a large scale to soften boiler water. In the home, borax or ammonia may be used.

Several processes are used to soften boiler water. A recent one utilizes the fact that substances called **permutit** (essentially an artificial sodium silico-aluminate) will interact with calcium (and magnesium) compounds, and thereby remove them from the water. The water filters through a porous layer of the permutit, and the calcium (and magnesium) replaces the sodium. A conventional equation might be written thus:—



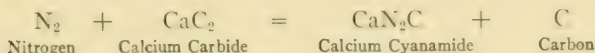
After a time, the calcium permutit accumulates to such an extent that the mixture no longer reacts. Water containing sodium chloride is then added and allowed to remain long enough to regenerate the sodium permutit, thus:—



The calcium chloride is removed, and the filter is ready for use again. This regenerative process can be repeated, thereby permitting the use of the original charge of permutit many years. Water softened by this process contains practically no calcium (or magnesium) salts.

484. Other calcium compounds.—Important calcium compounds already described are the fluoride, carbide, phosphates, and hypochlorite (bleaching powder). **Calcium chloride** (CaCl_2) is used to dry gases and liquids (85). It is a by-product in the manufacture of sodium carbonate by the Solvay process (450). A solution of calcium chloride is used as a brine in the manufacture of ice (177). **Calcium sulphide** (CaS) is formed by reducing calcium sulphate with carbon; like other sulphides, it stains silver brown (274). **Calcium oxalate** (CaC_2O_4) is a white solid formed by the interaction of ammonium oxalate and a dissolved calcium compound; it is insoluble in acetic acid but soluble in hydrochloric acid. Its formation and properties serve as a **test for calcium**. Another test for calcium is the orange-

red color imparted to the Bunsen flame. **Calcium nitrate** ($\text{Ca}(\text{NO}_3)_2$) and **calcium cyanamide** (CaN_2C) are made from the nitrogen of the air, and are used as fertilizers because they provide nitrogen in a form easily taken up by plants. The commercial substances are dark solids. For the nitrate see 196. The cyanamide is made by passing nitrogen over very hot calcium carbide, the equation being:—



485. Preparation and properties of metallic calcium. —

Metallic calcium is prepared by the electrolysis of melted calcium chloride (Fig. 170).

The anode is a graphite crucible (*A*) and the cathode is a rod of iron (*B*), which dips into the melted calcium chloride a short distance and is adjusted so that it can be elevated by a screw (*C*). The lower part of the crucible, which is kept cool by running water (*E, E*), contains solid calcium chloride. When the current passes, calcium is deposited on the cathode, which is slowly raised so that its end only is in contact with the surface of the melted chloride; the irregular rod of deposited calcium (*D*) thus becomes the end of the cathode.

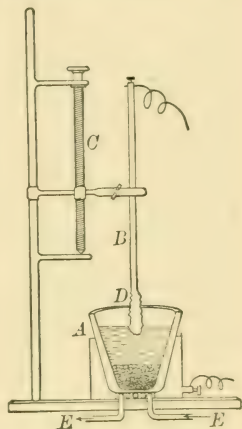
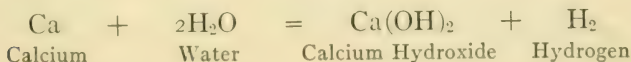
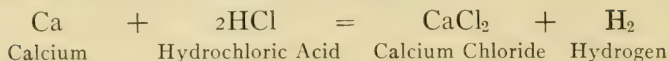


Fig. 170. — Apparatus for preparing calcium by electrolysis

Calcium is a silvery white metal. It tarnishes slowly in air. When heated, it combines with most non-metals. If burned in air, it forms both the oxide (CaO) and the nitride (Ca_3N_2). It interacts with water, slowly at ordinary temperatures, rapidly at high temperatures, thus:—



It also interacts readily with acids, thus: —



486. Compounds of strontium and barium. — Compounds of these elements resemble the corresponding ones of calcium. **Strontium nitrate** ($\text{Sr}(\text{NO}_3)_2$) and other salts of strontium color a flame crimson; the nitrate is used in making red signal lights and fireworks, especially **red fire**. The latter is essentially a mixture of potassium chlorate, shellac, and strontium nitrate. The production of the crimson colored flame is a **test for strontium**. **Another test** is the precipitation of white strontium sulphate by the addition of calcium sulphate solution to a strontium salt solution.

Barium chloride (BaCl_2) is used in testing for sulphuric acid and soluble sulphates, because it readily interacts with them and forms insoluble **barium sulphate** (BaSO_4); conversely, this serves as the **test for barium**.

Barium sulphate is a fine, white powder, and being cheap and heavy it is a common adulterant of ordinary white paint. Ground native barium sulphate, often called **barytes**, has a similar use. Barium sulphate is also used to increase the weight of paper and to give it gloss.

Barium salts color a flame green and **barium nitrate** ($\text{Ba}(\text{NO}_3)_2$) is used in making fireworks, especially **green fire**. The production of the green flame is a **test for barium**. **Barium chromate** (BaCrO_4) is a yellow precipitate formed by the interaction of potassium dichromate (or potassium chromate) and a soluble barium compound; its formation is sometimes used as a **test for barium**.

EXERCISES

1. Name several native compounds of calcium. What proportion of the earth's crust is calcium? Compare this proportion with that of other abundant elements (11).

2. Review topics: (a) The properties of normal and acid calcium carbonate. (b) Calcium compounds previously studied. (c) Compare the manufacture of calcium and sodium.

3. Topics for home study: (a) Does limestone "burn"? (b) Is the term *limewater* accurate? Why? (c) How should lime be stored? (d) Compare the setting of plaster of Paris and mortar. (e) Uses of cement. (f) Suggest experiments to show that lime is calcium oxide.

4. State the properties and uses of lime. How is it made?

5. Describe the manufacture of cement.

6. Starting with calcium, how would you prepare successively the oxide, hydroxide, carbonate, chloride, and metal?

7. What is plaster of Paris? Why so called? How is it prepared? What is its chief property? What are its uses? What is the chemical explanation of "setting"? What is stucco?

8. What is hard water? How does it act with soap? What is (a) temporary hardness and (b) permanent hardness? How can each be removed? What is soft water? Why is rain water often called soft water?

9. Essay topics: (a) Famous limestone caves. (b) The cement industry. (c) Colored fireworks. (d) Industrial uses of lime. (e) Chalk. (f) Coral. (g) Boiler scale.

10. Write equations for the reactions necessary to prepare (a) barium nitrate from barium carbonate, (b) barium hydroxide from barium chloride, (c) strontium carbonate from strontium hydroxide.

11. State the flame tests for (a) calcium, (b) strontium, and (c) barium.

PROBLEMS

1. How many grams of calcium can be obtained from (a) 150 gm. of calcium chloride, (b) 1 kg. of Iceland spar?

2. Calculate the percentage composition of the two oxides of barium (BaO and BaO_2) and show that they illustrate the law of multiple proportions. (Use exact atomic weights.)

3. Calculate the simplest formula from the following data: $\text{Ca} = 29.49$, $\text{O} = 46.92$, $\text{S} = 23.59$.

4. How many tons of lime can be made from 2000 tons of limestone (95 per cent pure)?

5. Write the formulas of the following compounds by applying the principle of valence: Calcium chlorate, calcium permanganate, calcium fluoride, calcium (meta-) silicate, calcium sulphide.

6. Calculate the atomic weight of calcium from 31.20762 gm. of CaCO_3 give 17.49526 gm. of CaO .

7. Express the following reactions by equations: (a) Carbon dioxide, water, and calcium carbonate form —; (b) barium hydroxide and carbon dioxide form — and water; (c) strontium carbonate forms — and carbon dioxide.

8. Express the following interactions in the form of complete ionic equations: (a) calcium chloride and sulphuric acid; (b) ammonium carbonate and strontium chloride; (c) barium chloride and potassium chromate.

CHAPTER XXXI

IRON AND STEEL — IRON COMPOUNDS

487. Introduction. — Iron is one of the oldest metals. It is also the most useful, and has been indispensable in the development of the human race. The different kinds of steel that are manufactured from iron have made the present times an age of steel.

488. Occurrence of iron. — In abundance iron ranks fourth among the elements and second among the metals (11). Uncombined iron is found in meteorites. Combined iron is found in most rocks, soils, and natural waters. It is assimilated by plants and animals and is essential to their life processes, being a constituent of chlorophyll (the green coloring matter of plants) and of hemoglobin (the red coloring matter of blood).

Metals usually occur as compounds, *e.g.* oxides, sulphides, or carbonates. A mineral or rock from which the metal can be more or less profitably prepared is called an **ore**. The important **ores of iron** are hematite (Fe_2O_3), limonite ($2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$), magnetite (Fe_3O_4), and siderite (FeCO_3). The most abundant ore and the chief source of iron and steel is **hematite**, which comes mainly from the Lake Superior region. Large quantities of iron ore are also mined in Alabama, Tennessee, and the Virginias.

Other abundant compounds of iron, not, however, used as a source of this metal, are iron pyrites (FeS_2), pyrrhotite (varying from Fe_9S_7 to $\text{Fe}_{11}\text{S}_{12}$), and the copper-iron sulphides (chalcopyrite, CuFeS_2 , and bornite, Cu_3FeS_3 , **526**, **527**).

489. How iron is obtained from its ores. — The science of extracting metals from their ores is called **metallurgy**. Iron is obtained by reducing its oxides with carbon. The

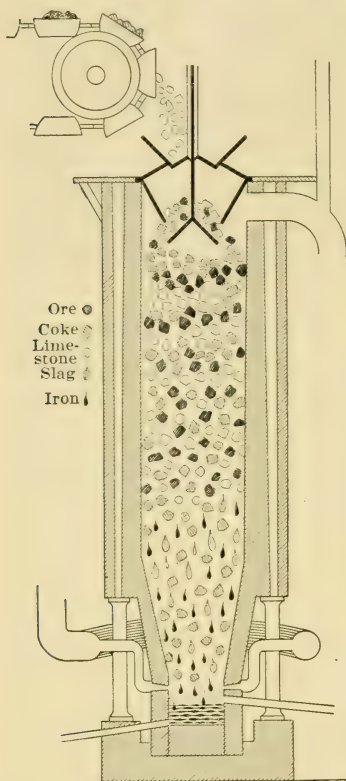


Fig. 171. — Sketch of a blast furnace and the process of smelting iron ore

ore is mixed with a flux (usually limestone) and carbon (usually in the form of coke) and heated in a furnace. This process is called **smelting**. The carbon together with carbon monoxide reduces the oxide to metallic iron. The flux converts the mineral impurities in the ore, called **gangue** (e.g. silicon and aluminium compounds), into fusible silicates called **slag**. The operation is carried out in a blast furnace (Figs. 171, 172).

The blast furnace, as shown in the sketch (Fig. 171), is a tower, about ninety feet high and twenty feet in diameter at the largest part; it is narrower at the top and bottom than in the middle. It is built of steel and lined with fire brick. Near the bottom are pipes, called tuyères, through which

large quantities of hot, dry air are forced into the furnace, thereby producing the high temperature required in the smelting. The air is heated, before it enters, by the stoves (the chimney-like towers between the furnaces shown in Fig. 172).

Another pipe at the top permits the escape of hot gaseous products,

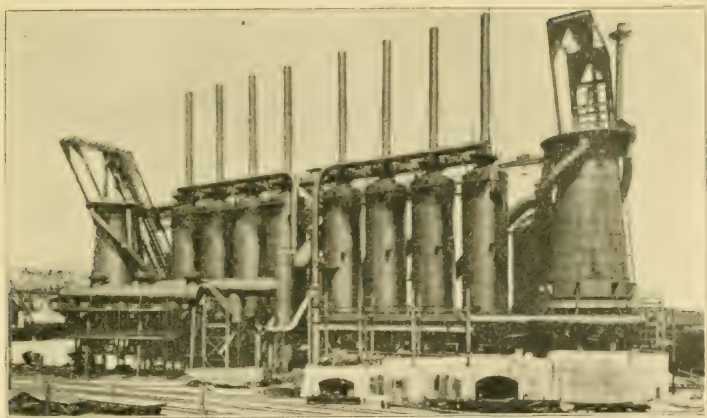
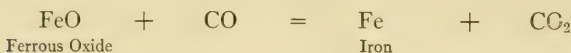
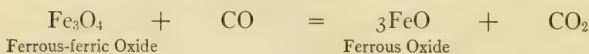
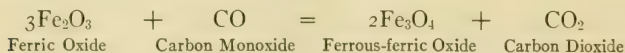


Fig. 172. — Blast furnaces and stoves

and also conducts them into a series of pipes which lead to different parts of the plant, where the hot gases are utilized to heat the air (in the stoves) blown through the tuyères, and also as fuel.

When the blast furnace is in operation, charges of the proper proportions of ore, coke, and flux are introduced at intervals by dumping them upon the cone-shaped cover. The latter is constructed and operated so that the smelting is not interrupted. The hot air which enters at the bottom, through the tuyères, changes most of the carbon in the lower part of the furnace into carbon dioxide and thereby generates intense heat. The carbon dioxide is largely reduced by the hot carbon above it to carbon monoxide, which rises through the furnace and reduces the iron oxide to iron. As the smelting proceeds, the reduction continues and the flux forms a slag (largely calcium silicate). Both iron and slag sink, the molten iron finally falling through the slag to the bottom of the furnace, where each is drawn off through separate openings at desired intervals (as shown in Fig. 171).

The chemical changes during the smelting vary in different zones. In the **top zone** the moisture in the charge is removed. In the **second zone**, where the temperature rises above 800°C ., carbon monoxide interacts with the iron ore and forms a mixture of iron and ferrous oxide (FeO). These reactions are expressed thus:—



At this stage the ore, though not wholly reduced, becomes soft and porous and sinks down into the **third zone**. The temperature here is about 1300°C . The reduction of the ferrous oxide is completed, hastened no doubt by the action of the hot carbon, thus:—



Here, too, certain impurities, present in small proportions in the ore, are changed to elements, *e.g.* manganese, silicon, phosphorus, and sulphur, which unite with the iron.



Fig. 173 — Tapping a blast furnace

the iron. In the **last zone**, where the temperature rises to 1500°C ., the iron fuses completely, takes up some carbon, and sinks down to the bottom of the furnace. In this zone, too, the reactions occur which complete the formation of slag, which is essentially a mixture of calcium silicate and calcium aluminate.

The molten slag, which floats on the molten

iron, is tapped off at intervals. The iron is tapped off into huge ladles (Fig. 173). Sometimes it is run from the furnace into molds of sand or iron (*i.e.* in a casting machine) and allowed to solidify; such iron is called **cast iron** or **pig iron**. In some plants the molten iron is run directly into huge vessels, called **converters**, and made into steel (493).

490. Cast iron. — The metal that comes from a blast furnace is impure iron. Besides iron, it contains from 3 to 5 per cent of carbon, 1 to 3 of silicon, about 0.7 each of manganese and phosphorus, and 0.02 to 0.05 of sulphur.

The **properties of cast iron** depend largely on the proportion of carbon and on the rate at which the molten iron cooled. If the cooling takes place rapidly (as in the casting machine), most of the carbon is combined with the iron as a carbide (Fe_3C), called **cementite**. This variety of cast iron is called **white cast iron**. But if the cooling occurs slowly (as in sand molds), much of the carbon remains uncombined as scales of graphite. This variety of cast iron is known as **gray cast iron**. It is softer and less brittle than the white variety, and melts at a lower temperature.

Cast iron has a crystalline structure and is brittle; it will withstand great pressure. It cannot be welded nor forged, that is, hot pieces cannot be united nor be shaped by hammering. But it can be cast, *i.e.* it can be formed into a desired shape by pouring the molten metal into a mold.

Cast iron is the variety used in an ordinary iron foundry. Here the iron, which melts at about 1200°C ., is heated in a furnace similar to a blast furnace, and when molten is poured into sand molds of the desired shape. Stoves, pipes, pillars, railings, radiators, parts of machines, and many other useful objects are made of cast iron. Considerable cast iron is made into steel (493).

Cast iron to which 5 to 20 per cent of manganese has been added is called *spiegel iron*, while *ferro-manganese* contains 20 or more per cent of manganese; both are used in making steel.

Cast iron is not attacked by alkalis and only slightly by concentrated acids. Concentrated sulphuric acid is transported in iron tank cars. Cast iron interacts readily, however, with dilute acids.

491. Wrought iron. — Wrought iron is made from cast iron by removing most of the impurities (carbon, silicon, phosphorus, and sulphur).

This can be done by heating the cast iron with iron oxide.

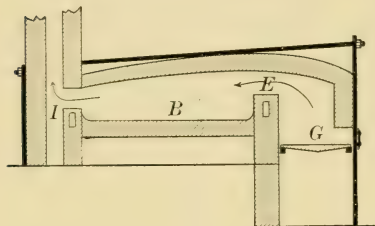


Fig. 174. — Reverberatory furnace.

The fire burns on the grate *G*, and the long flame which passes over the bridge *E*, is reflected down by the sloping roof upon the contents of the furnace. Gases escape through. The charge, which rests upon *B*, does not come in contact with the fuel

The process is conducted in a reverberatory furnace (Fig. 174). The hearth (*B*), of the furnace is covered with iron ore (ferric oxide, Fe_2O_3) and the charge of cast iron and flux is laid upon it. The intense heat that is reflected down upon the charge by the roof of the furnace melts the cast iron. The carbon in the cast iron unites with the oxygen of the iron oxide and escapes

as carbon monoxide. The silicon and phosphorus are oxidized and react with the flux to form a slag; the manganese and sulphur (in the form of ferrous sulphide) also become a part of the slag. The mixture is stirred or "puddled" with long rods, and as the impurities are removed, the mass becomes pasty owing to the rise of its melting point.

Large balls, called **blooms**, are removed and hammered, or, more often, rolled between ponderous rollers. The operation squeezes out most of the slag. If the rolling is repeated, the quality of the

iron is improved; the final rolling often leaves the iron in the desired commercial shape.

Wrought iron is the purest variety of commercial iron. It is practically pure iron, containing only 2 per cent (or less) of slag (Fig. 174, left). The iron itself seldom contains more than 0.5 per cent of carbon and sometimes only 0.06 per cent, the average being about 0.15 per cent; the other elements are present in mere traces.

If a specimen of wrought iron, or other metal, is polished and then etched with weak acid, the microscope reveals the crystalline or other

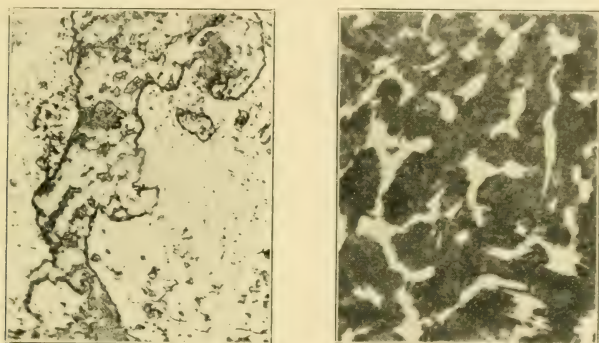


Fig. 175. — Photomicrographs of wrought iron (left) and cast iron (right). The slag can be seen in the wrought iron

formation and the presence of carbon, slag, carbides, etc. Photographs of a treated specimen of wrought iron and cast iron as seen under the microscope are shown in Fig. 175.

Wrought iron, unlike cast iron, is fibrous and can be bent. It melts at a higher temperature than cast iron (1600° to 2000° C). Since it softens at about 1000° C., wrought iron can be forged and welded. It is very malleable and ductile, can be readily rolled into plates and sheets and drawn into fine wire; in these forms the metal is very strong. Wrought iron is made into wire, sheets, rods, nails, spikes,

bolts, chains, anchors, horseshoes, tires, and agricultural implements. It is less important than formerly, since it is being replaced by soft steel (498).

Wrought iron rusts more rapidly than cast iron, and is also more vigorously attacked by acids and alkalis at a high temperature.

492. What is steel? — We have just seen that cast iron is hard and brittle, whereas wrought iron is soft and tough. Also, that cast iron can be easily melted and poured into molds, whereas wrought iron softens readily and can be welded. Moreover, cast iron contains a relatively high per cent of carbon (3 to 5), but in wrought iron the per cent of carbon is low (0.15). Between these extremes of composition come the different grades of **steel**.

The physical properties of the different grades of steel depend not only on the proportions of carbon, phosphorus, silicon, sulphur, etc., but also to a large extent on the method of manufacture and treatment.

493. Manufacture of steel. — Steel is made from cast iron. The aim in the manufacture is to prepare a product containing the desired proportion of carbon but little or no sulphur, phosphorus, and silicon. The steel must also

possess specific and known properties. This twofold aim is accomplished by several processes.

494. The Bessemer process is carried on in a converter (Fig. 176). This is a huge, pear-shaped vessel, supported on trunnions so it can be tipped into different

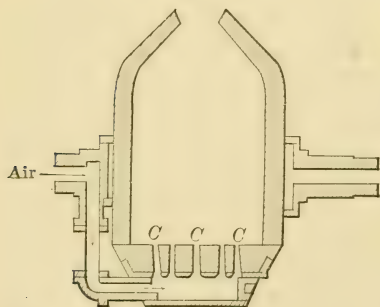


Fig. 176. — Sketch of a converter

positions; one trunnion is hollow, and at the bottom there are holes (*C, C, C*), through which a powerful blast of air can be blown. It is made of thick wrought-iron plates and is lined with an infusible mixture rich in silica.

The converter when in use is swung into a horizontal position, and fifteen to twenty tons of molten cast iron are run in, often directly from the blast furnace (Fig. 177, right). The air blast is turned on, and the converter is swung back to a vertical position. As the air is forced in fine jets through the molten metal, the temperature rises, and the carbon, silicon, and manganese, that are in the iron, are oxidized. The carbon forms carbon monoxide, which burns at the mouth of the converter in a large brilliant flame (Fig. 177, left), while the other oxides pass into the slag. This oxidation generates enough heat to keep the metal melted. In about fifteen minutes the diminished flame of burning carbon monoxide shows that the carbon has been oxidized and the other impurities removed. Then sufficient spiegel iron or ferro-manganese is added to the molten iron to furnish the proper amount of carbon and manganese. By adding certain metals, *e.g.* aluminium, gases are removed (by uniting with the metal), and a better quality of steel is produced.

After the completion of the whole operation the converter is tilted and the metal is poured into ladles, and then into molds to form blocks called **ingots** (Fig. 177, left foreground), which are subsequently shaped into rails or other objects (Figs. 183, 184, 185).

The process described in the preceding paragraph is called the **acid Bessemer process** because the converter is lined with silica, which is an acid anhydride (388). By this process the carbon and silicon can be removed but not all the sulphur and phosphorus. Both are objectionable. Sulphur makes steel brittle when hot, and phos-



Fig. 177. — Making steel by the Bessemer process. Charging a converter (right). Converter in operation (left).
Pouring molten steel into ingot molds (left foreground)

phorus, when cold. The acid Bessemer process is used in the United States because most domestic ores are low in phosphorus and sulphur.

In Europe the **Thomas-Gilchrist** or **basic process** is used. The converter in this modified process is lined with burned dolomite (*i.e.* practically a mixture of lime and magnesia, which are basic oxides), which removes the phosphorus and sulphur. This lining after use is known as Thomas slag. It is utilized as a fertilizer on account of its phosphorus content.

495. The open-hearth process. — This process is conducted in a special kind of furnace called an open-hearth furnace (Fig. 178). A vertical section of an open-hearth



Fig. 178. — General view of open-hearth furnaces in a steel plant

furnace is shown in Fig. 179. The hearth (*H*), on which the charge is put, is lined with burned dolomite. A sloping roof of fire brick covers the hearth. At the base of the furnace are duplicate chambers of checkerwork (*A*, *B* and *C*, *D*) arranged for alternate use. This arrangement is necessary in order to obtain continuously the high temperature needed in this process.

Fuel gas (or oil) is burned in a furnace and the hot gases are passed through *A*, *B* to the chimney, thus heating the checkerwork very hot. The fuel gas is then passed

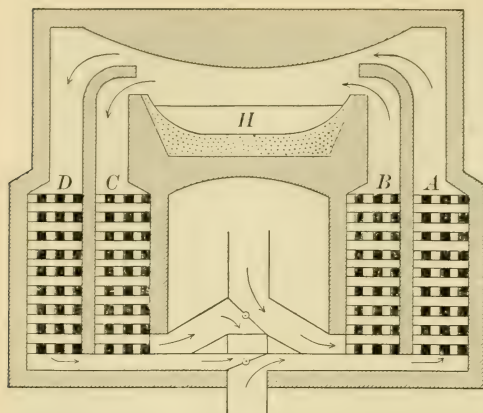


Fig. 179. — Sketch of an open-hearth furnace
(vertical section)

through *B* and air through *A* and the two brought together over the hearth. Here the gas burns and produces a high temperature on the hearth. Meanwhile the hot products of combustion and the unused gases,

instead of escaping immediately up the chimney, are directed by valves through the other two chambers of the checkerwork *C*, *D*, and heat them. That is, while *A*, *B* are cooling, *C*, *D* are heating. At the proper time the fuel gas and air are shifted (by valves) to *C*, *D* and made to pass through this checkerwork to the hearth and out over the other checkerwork (*A*, *B*) to the chimney.

By this plan the process is alternated, one checkerwork being cooled as the other is heated, and vice versa. It is only by this **regenerative process**, as it is called, that enough heat is ob-



Fig. 180. — Pouring molten cast iron
into an open-hearth furnace

tained continuously to keep the charge melted as it becomes purer and purer.

The charge consists of cast iron and some iron oxide (*e.g.* hematite); scrap iron, or steel, and lime are usually added (Fig. 180). The iron oxide furnishes oxygen which converts silicon, sulphur, and phosphorus into oxides (acid oxides),

which form a slag with the hearth lining (a basic oxide). The charge is heated from six to twelve hours. Samples are drawn out at intervals (Fig. 181) and tested by the chemist. When tests show that the metal contains

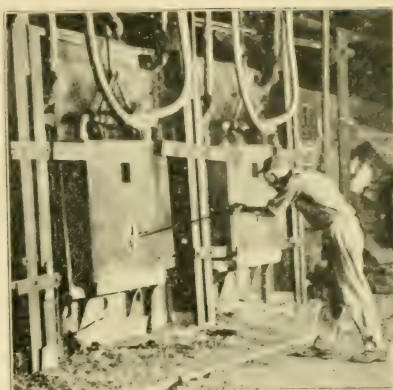


Fig. 181. — Drawing a sample of steel from an open-hearth furnace for a chemical test



Fig. 182. — Tapping an open-hearth furnace

the desired proportion of carbon and other constituents, the steel is tapped into ladles, and certain materials are added to improve the product, *e.g.* aluminium or silicon (or ferro-silicon), which removes oxygen, and ferro-manganese (Fig. 182). It is then quickly poured into

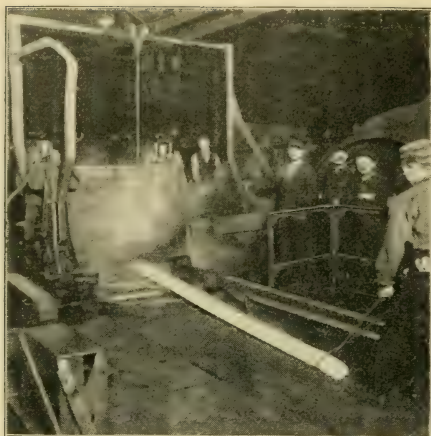


Fig. 183. — Making a steel rail — first stage

molds and allowed to cool into ingots (Fig. 177, middle). Subsequently the ingots are softened by reheating and rolled, pressed, or stamped into desired shapes (Figs. 183, 184, 185).

The open-hearth process is easily controlled and yields a tough, elastic steel, which is excellent for

bridges, rails, large machines, large guns, and gun carriages.

496. The crucible process consists in melting wrought iron, or low carbon steel, in crucibles made of graphite and clay. The charge varies with the product desired. For example, iron oxide may be added, or certain metals, such as chromium, vanadium, or molybdenum. The crucibles are covered and then heated to a high temperature from four to five hours. During the melting the iron is slowly changed into steel by absorbing the proper proportions of carbon. Crucible steel is very hard, and is used

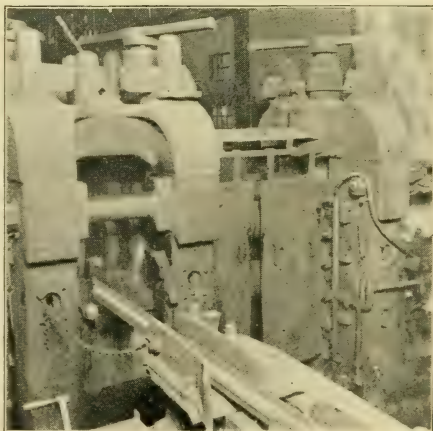


Fig. 184. — Making a steel rail — final stage

to make tools, springs, drills, dies, pens, and needles.

497. The electric process consists in heating a selected charge of cast iron, or steel made from inferior materials, in an electric furnace (Fig. 186). The heat is generated, usually, by the arc established between the carbon electrode and the melted charge. Very high temperatures are obtained. Moreover, the operation is conducted in a non-oxidizing atmosphere. Hence, the electric process is advantageously used in conjunction with the Bessemer and open-hearth processes to produce a superior steel free from gases and sulphur.



Fig. 185. — Steel plate passing through the last rolling machine

498. Properties of steel. — The properties are numerous because there are many kinds of steel. Thus, steel, using this term broadly, is fusible and malleable, and can be forged, welded, and cast. Varieties containing 0.2 per cent

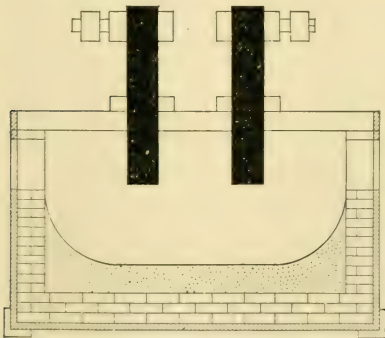


Fig. 186. — Sketch of an electric furnace for the manufacture of steel

of carbon are much like wrought iron and are called **soft or mild steel**. **Structural steel** contains more carbon (0.2 to 0.8 per cent) and is hard like cast iron, while **tool steel**, which contains upwards of 1.5 per cent of carbon, is very hard indeed.

The properties of steel

depend not only on the proportion of carbon (and other elements) but also on the special **heat treatment** which it receives. If steel is heated very hot and then suddenly cooled by plunging it into cold water or oil, it becomes brittle and very hard (Fig. 187). But if heated and cooled slowly, it becomes soft, tough, and elastic. All

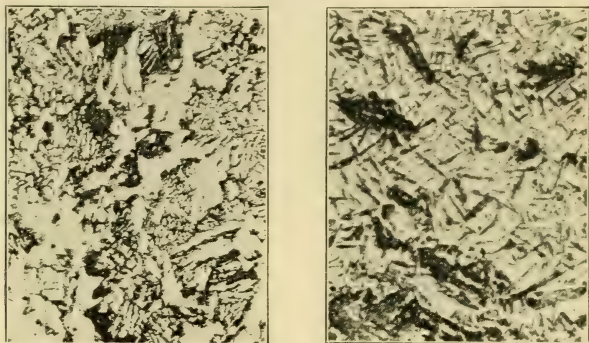


Fig. 187. — Photomicrographs of hard steel (right) and cast steel (left)
(Compare Fig. 175)

grades of hardness can be obtained between these two extremes. Thus, if hardened steel is reheated to a definite temperature, determined approximately by the color the oxidized metal assumes, and then properly cooled, a desired degree of hardness and elasticity is obtained. This last operation is called **tempering**.

499. Special steels, or steel alloys as they are sometimes called, are made by introducing certain metals, or their alloys with iron, into steel produced by the open-hearth or crucible process. These special steels have properties which adapt them to indispensable uses. **Nickel steel** up to 3.5 per cent nickel is hard and tough, and is used for armor plate, cables, drills, and marine engine parts. Steel containing 36 per cent of nickel expands so very slightly

with changes of temperature that it is made into surveyor's tapes, pendulums, and scientific apparatus. It is called **invar**. The alloy containing about 42 per cent of nickel expands and contracts to the same extent as platinum and glass. It is used in making wire glass and as the wire that connects the inner and outer parts of electric light bulbs. It is called **platinite** and is used instead of the scarce and expensive metal platinum.

Chromium steels, made by adding the alloy ferro-chrome to molten steel, seldom contain more than 2 per cent of chromium. They are very hard and are used for armor-piercing projectiles, safes, and crushing machinery. If small proportions of other metals are added, such as vanadium and manganese, the steels are tough, elastic, and hard; they resist shocks and strain, and are used in making automobile parts. **Tungsten steels** are hard, and if of the right composition, do not lose their hardness at a red heat. A typical one contains 18 per cent of tungsten, 3.5 per cent of chromium and a small fraction of a per cent of vanadium. They are called **high speed steel** and are used to make tools for cutting metals; the tools, unlike the usual tool, will cut when they are dull red from the heat produced by friction. Molybdenum sometimes replaces tungsten, and much less is needed to produce the same results as with tungsten. **Manganese steels**, containing about 13 per cent of manganese, are extremely hard without being brittle. They are used for making the jaws of rock-crushing machinery, dredger buckets, safes, parts of brakes, and rails.

Vanadium is often added in small amounts to special steels to increase certain desired properties.

500. Preparation and properties of pure iron. — Chemically pure iron, though uncommon in commerce, can be obtained as a powder by reducing the oxide with hydrogen ("iron by hydrogen") or

as irregular plates by the electrolysis of a solution of ferrous sulphate.

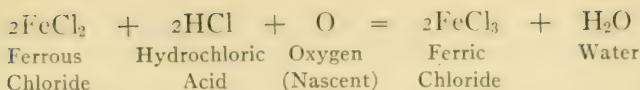
Pure iron is a silvery white, lustrous metal. It is ductile and malleable, and softer than ordinary iron, being about as soft as aluminum. The specific gravity is 7.86 and the melting point is 1520° C. It is attracted by a magnet, but soon loses its own magnetism.

Iron forms an oxide (Fe_3O_4), if heated to a high temperature in steam or burned in oxygen. Iron readily interacts with dilute acids, and as a rule hydrogen and ferrous compounds (e.g. ferrous sulphate, FeSO_4) are the products.

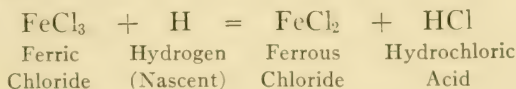
501. What is iron rust? — Dry air has no effect on iron, but moist air rusts it. Rusting is a complex process and is explained in different ways. A recent and acceptable interpretation based on the theory of ionization is as follows: The iron goes into solution as ferrous ions (Fe^{++}). Hydrogen ions (H^{+}) from the water lose their charges and become atoms; the atoms unite to form molecules which escape as hydrogen gas (H_2). The ferrous ions combine with the hydroxyl ions (OH^{-}) left in the water, thereby forming ferrous hydroxide ($\text{Fe}(\text{OH})_2$), which is subsequently converted into the complex substance called iron rust. Once begun, rusting proceeds rapidly, because the film of rust is not compact enough to protect the metal.

502. Two series of iron compounds. — Iron forms two series of compounds — ferrous and ferric. Corresponding members differ in properties. In each series the iron plays a different rôle. We sometimes distinguish the members of the two series by saying the valence of iron is two in ferrous compounds and three in ferric. We also distinguish the two series by saying ferrous salts in solution give ferrous ions (Fe^{++}) and ferric salts give ferric ions (Fe^{+++}).

Ferrous compounds pass readily into the corresponding ferric compounds by oxidation. For example, *ferrous* chloride in hydrochloric acid solution becomes *ferric* chloride in the presence of an oxidizing agent, such as nascent oxygen, hydrogen peroxide, nitric acid, or potassium permanganate. An equation is: —



Whereas *ferric* chloride becomes *ferrous* chloride by the action of a reducing agent, *e.g.* nascent hydrogen, hydrogen sulphide, sulphurous acid, or stannous chloride (SnCl_2). An equation is:—



In these two reactions it is unnecessary to use nascent oxygen or hydrogen. Thus, ferrous chloride becomes ferric chloride by action with chlorine, while ferric chloride becomes ferrous chloride by action with iron, thus:—



That is to say, the change from a ferrous to a ferric compound is the same as the change from sulphurous acid to sulphuric acid. It is an example of oxidation, while the reverse is reduction. To be sure, no oxygen is involved. Nevertheless, we often use the terms *oxidation* and *reduction* in a broader sense than mere addition and removal of the element oxygen (**23, 24, 43, 55**).

Let us interpret the broader meaning of these terms. Oxygen belongs to the class of negative elements. So does chlorine. Now if we add chlorine to ferrous chloride, we are doing chemically just what we do if we add oxygen to sulphurous acid, *viz.* oxidizing. In a broad sense, then, **oxidation** is the process of adding oxygen, chlorine, or another negative element. Conversely, **reduction** is the process of removing oxygen, chlorine, or another negative element.

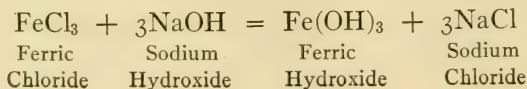
As stated above, the valence of iron is two in ferrous and three in ferric compounds. In passing from ferrous to ferric compounds the valence of the iron increases; and conversely, from ferric to

ferrous it decreases. From the standpoint of valence, **oxidation** is an increase in the valence of a positive element (*i.e.* a metal), whereas **reduction** is a decrease.

Furthermore, since dissolved iron salts pass readily from one series to the corresponding members of the other, **oxidation** is sometimes called adding positive electricity, *e.g.* Fe^{++} to Fe^{+++} ; whereas **reduction** is the removal, *e.g.* Fe^{+++} to Fe^{++} .

503. Three oxides of iron. — Iron forms three oxides. **Ferrous oxide** (FeO) is an unstable black powder — an unimportant compound. **Ferric oxide** (Fe_2O_3) occurs native as hematite. This oxide is manufactured by heating the ferric hydroxide ($\text{Fe}(\text{OH})_3$) obtained as a by-product in the cleaning of iron castings, rods, and sheets. One variety, called rouge or crocus, is used to polish glass and jewelry. Another variety, called Venetian red, is used to make red paint. **Ferrous-ferric** or **ferroso-ferric oxide** (magnetic oxide of iron, Fe_3O_4) occurs as magnetite; if magnetic, it is called loadstone. It is produced as a black film or scale by heating iron in the air; heaps of it are often seen beside the anvil in a blacksmith's shop. The firm coating of this oxide formed by exposing iron to steam protects the metal from further oxidation; iron thus coated is called Russia iron. Some authorities regard this oxide as iron ferrite ($\text{Fe}(\text{FeO}_2)_2$).

504. Iron hydroxides. — **Ferrous hydroxide** ($\text{Fe}(\text{OH})_2$) is a white solid formed by the interaction of a ferrous salt and an hydroxide. Exposed to the air, it soon turns green, and finally brown, owing to oxidation to ferric hydroxide. **Ferric hydroxide** ($\text{Fe}(\text{OH})_3$) is a reddish brown solid, formed by the interaction of a ferric salt and an hydroxide, thus: —



505. Ferrous sulphate (FeSO_4) is a green salt obtained by the interaction of iron (or of ferrous sulphide) and dilute sulphuric acid. It is manufactured by roasting (*i.e.* oxidizing iron pyrites (FeS_2), or by exposing pyrites to moist air; the mass is extracted with water containing scrap iron and a little sulphuric acid. The large light green crystals ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) are called **green vitriol** or **copperas**.

Exposed to air, ferrous sulphate effloresces and oxidizes. Hence the ferrous sulphate used to prepare a ferrous solution, *e.g.* in testing for nitric acid or a nitrate, **190**, should be thoroughly washed to remove the ferric salt.

Large quantities are used in dyeing silk and wool, as a disinfectant, and in manufacturing ink, bluing, and pigments. Much black writing **ink** is made essentially by mixing ferrous sulphate, nutgalls, gum, and water. A mixture of ferrous sulphate and lime is used to purify water and sewage by the settling process (**69**).

506. Iron sulphides. — Commercial **ferrous sulphide** (FeS) is a black, brittle, metallic-looking solid made on a large scale by fusing a mixture of iron and sulphur. It is also obtained as a black precipitate by the interaction of a dissolved ferrous salt and ammonium sulphide. It is used chiefly in preparing hydrogen sulphide (**255**).

One of the commonest minerals is **ferric sulphide** (iron disulphide, iron pyrites, pyrite, FeS_2). It is a lustrous, brass-yellow solid. Crystals of pyrites are often mistaken for gold — hence the name “fool’s gold.” It is valueless as an iron ore, but large quantities are used in making sulphuric acid.

507. Iron chlorides. — When iron interacts with hydrochloric acid, **ferrous chloride** (FeCl_2) is formed in solution. Heated in the air or with potassium chlorate or nitric acid, it is changed into ferric chloride. (For the equation see **502**, second paragraph.) **Ferric chloride** (FeCl_3) is a deliquescent solid. It is prepared by passing chlorine into ferrous chloride solution, or by the interaction of iron and *aqua regia*. With nascent hydrogen or another reducing agent,

ferric chloride becomes ferrous chloride. (See 502, second paragraph.) Ferric chloride solution is acid, owing to hydrolysis (452).

508. Ferrocyanides and ferricyanides. — The most important is **potassium ferrocyanide** ($K_4Fe(CN)_6$). It is a lemon-yellow, crystallized solid, containing three molecules of water of crystallization, and is sometimes called yellow prussiate of potash. Unlike the simple cyanogen compounds (*e.g.* HCN and KCN), it is not poisonous. It is manufactured by fusing iron filings with potassium carbonate and nitrogenous animal matter (such as horn, hair, blood, feathers, and leather). The mass is extracted with water, and the salt is separated by crystallization. Large quantities are used in dyeing and calico printing, and in making bluing and potassium-cyanogen compounds. **Potassium ferricyanide** ($K_3Fe(CN)_6$) is a dark red crystallized solid, containing no water of crystallization. It is often called red prussiate of potash. It is manufactured by oxidizing potassium ferrocyanide. In alkaline solution it is a vigorous oxidizing agent, and finds extensive use in dyeing.

509. Making a blue print. — Blue print paper is prepared by coating paper with a mixture of potassium ferricyanide and ammonium ferric citrate solutions, and drying in a dark place. In the sunlight the ferric salt is partly reduced and forms a bronze colored deposit by interaction with the potassium ferricyanide. .

If such prepared paper is covered with a photographic negative, or with transparent cloth marked with lines in black ink, and placed in the sunlight, the paper is acted upon only in the exposed places. Upon washing, the exposed parts become blue, and the covered parts white.

510. Tests for ferrous and ferric compounds. — Ferrous salts and potassium ferricyanide interact in solution and precipitate ferrous ferricyanide ($Fe_3(Fe(CN)_6)_2$). This is a dark blue solid, and is called **Turnbull's blue**. Ferric salts interact with potassium ferrocyanide and precipitate

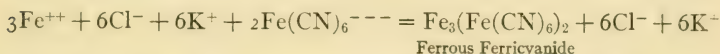
ferric ferrocyanide ($\text{Fe}_4(\text{Fe}(\text{CN})_6)_3$). This precipitate is likewise a dark blue solid, and is called **Prussian blue**. By these tests ferrous and ferric salts can be distinguished. Hence to **test** for —

Ferrous salts add potassium **ferricyanide**,

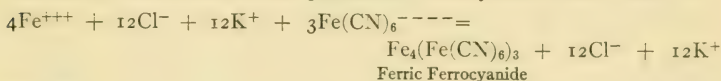
Ferric salts add potassium **ferrocyanide**.

In each test we obtain a dark blue precipitate, but only if we use “**ferrous** with **ferri-**” and “**ferric** with **ferro-**.”

Since these two results are apt to confuse, let us interpret them. Ferrous salts in solution form ferrous ions (Fe^{++}). Potassium ferricyanide in solution forms potassium ions (K^+) and ferricyanide ions ($\text{Fe}(\text{CN})_6^{---}$). When **ferrous** chloride and potassium **ferricyanide** solutions are mixed, ferrous ions unite with ferricyanide ions and form **ferrous ferricyanide**, thus: —



Similarly, ferric chloride and potassium ferrocyanide react thus: —



The dark blue precipitate is formed only by the combination of either **ferrous and ferricyanide ions** or **ferric and ferrocyanide ions**.

Besides the above tests for ferric salts, potassium sulphocyanate (KCNS) produces a *red solution* or ferric sulphocyanate ($\text{Fe}(\text{CNS})_3$) with *ferric salts*, but leaves ferrous salts *unchanged*.

EXERCISES

1. Name the ores of iron. What proportion of the earth's crust is iron? Compare with the abundance of other elements.
2. Describe a blast furnace.
3. Describe the manufacture of cast iron.
4. Apply Exercise 3 to wrought iron.
5. State the characteristic properties of cast iron and wrought iron.
6. Describe the manufacture of steel by (a) the Bessemer process, (b) the open-hearth process, and (c) the crucible process.

7. Compare the composition of cast iron, wrought iron, and steel.
8. Study topics: (a) Production and transportation of iron ore. (b) Uses of steel. (c) Meteorites. (d) Primitive iron smelting. (e) Armor plate. (f) Special steels. (g) Iron objects in the school building. (h) Iron in the home. (i) Tests for iron.
9. What is copperas, rouge, crocus, iron pyrites, green vitriol, hematite, magnetite, yellow prussiate of potash?
10. How are ferrous changed into ferric compounds, and vice versa? Give equations.
11. Practical topics: (a) Cite proofs that iron is widely distributed. (b) How would you test coal ashes for iron? (c) How would you prove by experiment that bluing contains an iron compound?
12. Sketch from memory (a) a blast furnace, (b) a converter in operation, (c) an open-hearth furnace.
13. Starting with iron, how would you prepare in succession ferrous chloride, FeCl_2 , ferric hydroxide, ferric chloride, $\text{Fe}_2(\text{Fe}(\text{CN})_6)_3$?
14. Review these topics by iron compounds: (a) Law of multiple proportions. (See Problem 3.) (b) Oxidation and reduction (502). (c) Valence (502). (d) Hydrolysis (452).
15. Solutions of ferrous sulphate sometimes give a test for ferric iron. Why?

PROBLEMS

1. Calculate the weight of iron in (a) 70 tons of copperas, (b) 3 tons of hematite (95 per cent pure), (c) 2 kg. of pyrite, (d) 1000 lb. of magnetite.
2. Write the formulas of (a) the ferrous and (b) the ferric salts of the following acids: Hydrobromic, hydriodic, carbonic, nitric, orthophosphoric.
3. Calculate the percentage composition of (a) the three oxides and (b) the two chlorides of iron, and show how the two sets of compounds illustrate the law of multiple proportions.
4. Calculate the following: (a) the weight of ferrous carbonate needed to produce 25 l. of CO_2 (standard conditions); (b) the weight of iron formed by the interaction of hydrogen and 220 gm. of Fe_3O_4 ; (c) the weight of pure iron that can be made from 1000 tons of iron ore (94 per cent hematite).
5. Complete and balance the following: (a) $\text{FeCl}_2 + (\text{NH}_4)_2\text{S} = \text{FeS} + \text{---}$; (b) $\text{FeCl}_3 + \text{---} = \text{Fe}(\text{OH})_3 + \text{NH}_4\text{Cl}$; (c) $\text{Fe} + \text{O} = \text{Fe}_2\text{O}_3$; (d) $\text{K}_3\text{Fe}(\text{CN})_6 + \text{---} = \text{---} + \text{K}_2\text{SO}_4$; (e) $\text{K}_4\text{Fe}(\text{CN})_6 + \text{---} = \text{---} + \text{KCl}$.
6. What is the simplest formula of a compound, if 9 gm. of it yielded 4.8 gm. of sulphur and the rest iron?

CHAPTER XXXII

ALUMINIUM AND ITS COMPOUNDS — CLAY AND CLAY PRODUCTS

511. Occurrence. — Aluminium (often called aluminum) compounds are numerous, abundant, and widely distributed. About 8 per cent of the earth's crust is combined aluminium; in abundance it ranks first among the metals and third among the elements (11). All important rocks except limestone and sandstone contain aluminium silicates and other metals. Clay is also aluminium silicate. Corundum and emery are impure aluminium oxide (Al_2O_3). Bauxite is an aluminium hydroxide ($\text{H}_4\text{Al}_2\text{O}_5$); it is often colored red by iron oxide. Cryolite is sodium aluminium fluoride (Na_3AlF_6); it is a white icelike solid.

512. Manufacture of aluminium. — Aluminium is manufactured by the electrolysis of aluminium oxide (Al_2O_3). The purified oxide, which is prepared from bauxite, is dissolved in melted cryolite, and when the current passes, aluminium is deposited at the cathode. This process was discovered in 1886 by the American chemist Hall and perfected by him.

A sketch of the apparatus is shown in Fig. 188. An open iron

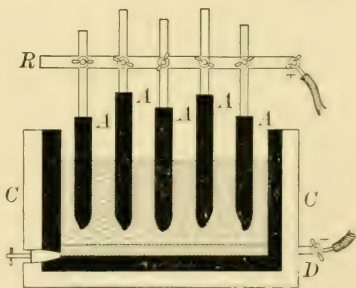


Fig. 188. — Sketch of the apparatus for the manufacture of aluminium by the electrolysis of aluminium oxide

vessel (*C*, *C*) lined with carbon is the cathode. Connection with the cathode is made at *D*. The anode consists of several graphite bars (*A*, *A*, etc.) attached to a copper rod (*R*), which can be lowered as the graphite is consumed (by the liberated oxygen).

The bottom of the box is first covered with cryolite, the anode is lowered, and the box is then filled with cryolite (to which some calcium fluoride is added to reduce the melting point). The current is turned on, and the resistance generates enough heat to melt the cryolite. Pure, dry aluminium oxide is now added, which dissolves in the cryolite and doubtless dissociates somewhat as electrolytes do in water. The oxygen goes to the anode and unites with the carbon. The graphite anodes have to be replaced.

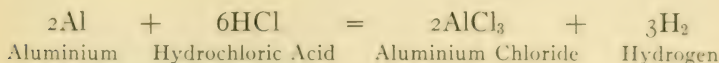
The aluminium is liberated at the cathode, sinks through the cryolite, and collects as a liquid at the bottom of the vessel. The process is continuous, fresh aluminium oxide being added and the molten aluminium being drawn off at intervals. The cryolite is not decomposed as long as aluminium oxide is present.

513. Properties. — Aluminium is a lustrous white metal. It is very light in weight, being in fact the lightest of the common metals. Its specific gravity is only about 2.6 while that of iron is 7.8. It is ductile and malleable, and is extensively made into wire and sheets. It is a good conductor of heat and electricity. Compared with most metals aluminium is rather hard and strong. It melts at about 658°C .

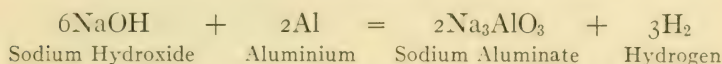
Aluminium in the semi-molten state can readily be extruded, *i.e.* forced or pressed out through an opening into desired shapes. Just below the melting point it is brittle and can be ground into powder. Aluminium can be cast and welded, though it cannot be turned well in a lathe, nor can it be readily soldered to produce a permanent joint.

514. Chemical conduct. — Aluminium is only very slightly tarnished by air, owing to the protecting film of oxide that forms on the surface. It combines vigorously with oxygen at high temperatures. It is a powerful re-

ducing agent (517). Hydrochloric acid reacts readily with it, thus:—



Under ordinary conditions nitric and dilute sulphuric acids do not affect it; concentrated sulphuric acid acts upon it, forming aluminium sulphate. Sodium chloride interacts with it, if dilute acids are present. With sodium and potassium hydroxides it forms aluminates and hydrogen, thus:—



515. Uses.—The varied properties of aluminium, especially its strength, lightness, and durability, adapt it to numerous uses, *e.g.* parts of military outfits, caps for jars, surgical instruments, tubes, fittings of boats, automobiles, and airships, parts of opera glasses and telescopes, framework of cameras, stock patterns for foundry work, hardware samples, and scientific apparatus. Varied forms of aluminium cooking utensils have become very popular.

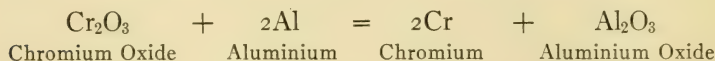
Its attractive appearance leads to its extensive use as an ornamental metal, both in interior decorative work and in numerous small objects. Aluminium leaf is used for lettering book covers and signs, and the foil has largely replaced tin as a wrapper for food and candy. The powder suspended in an adhesive liquid is used as a paint for steam pipes, radiators, smokestacks, and other metal objects exposed to heat or the weather. Aluminium wire is used to some extent as a conductor of electricity.

Large quantities of aluminium are consumed in deoxidizing steel, *i.e.* removing air bubbles from the molten steel, thereby preventing the formation of small holes in the castings (494, 495).

516. Alloys. — Aluminium forms alloys with copper. The proportions of aluminium vary widely (from 5 to 95 per cent) thus giving a great variety of useful alloys. Those containing from 5 to 10 per cent of aluminium are called **aluminium bronze**; they are yellow and are used in making jewelry and statuary. Whereas those containing 90 to 95 per cent of aluminium are silver-white; these alloys are used in making castings and household ware, and are called **duralumin**.

An alloy with magnesium, called **magnalium**, contains from 75 to 90 per cent of aluminium. It is hard, light, attractive, and durable, and is used as parts of chemical balances and scientific instruments.

517. Thermit. — Aluminium is a powerful reducing agent. This property is utilized in the manufacture of certain metals and in welding. When a mixture of chromium oxide and powdered aluminium is ignited at one point, the reduction proceeds rapidly throughout the mixture and the intense heat fuses the chromium, which can be removed from the crucible in a lump; the aluminium oxide rises to the top of the metal as a slag. The equation is: —



Other metals, *e.g.* manganese, hitherto rare or expensive are similarly prepared.

If a mixture of ferric oxide (Fe_2O_3) and powdered aluminium is ignited, molten iron at a temperature of about 3000°C . is produced. By using a special form of apparatus the molten iron can be conducted from the crucible into a mold around a joint or fracture (Fig. 189, right). This method is widely used to weld steel rails and repair fractures in machinery (Fig. 190).

Mixtures of aluminium and oxides, used for this purpose, are called **thermit**, and the method is known as the aluminothermic method.

518. Aluminium oxide (Al_2O_3) is the only oxide of alu-

minium. It is often called **alumina**, as silicon dioxide is called silica. Its native forms are **corundum** and **emery**.

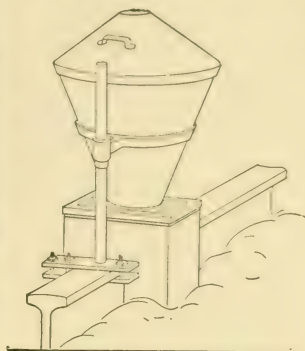


Fig. 180. — Welding a steel rail with thermit. Sketch of the crucible and mold in position (right). The operation is shown on the left

Both are very hard substances, pure corundum ranking next to diamond. The transparent varieties of corundum have long been prized as gems, among them being the



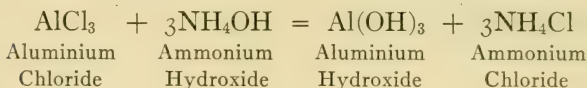
Fig. 190. — A crankshaft repaired by the thermit process

sapphire and ruby. Emery was formerly used as an abrasive. But it has been largely replaced by an artificial

oxide called **alundum**. This product is manufactured by heating more or less pure alumina in an electric furnace. On cooling, the mass forms a hard solid like corundum.

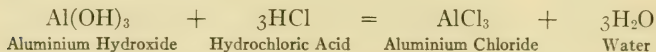
When alumina or any other compound of aluminium is heated on charcoal with a blowpipe, then cooled, moistened with cobaltous nitrate solution, and heated again, the mass turns a beautiful blue color. This is a **test for aluminium**.

519. Aluminium hydroxide $(\text{Al}(\text{OH})_3)$ is a white, jelly-like solid formed by adding ammonium hydroxide to a solution of aluminium salt, thus : —



It is insoluble in water, but it dissolves in strong acids and strong bases (in excess), forming respectively aluminium salts and aluminates.

In aluminium hydroxide, aluminium acts either as a metal or a non-metal (397), that is, aluminium hydroxide has basic and acid properties, though both are weak. An equation illustrating the basic property is : —

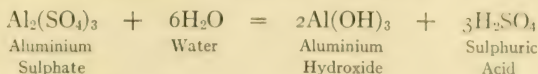


One illustrating the acid property is : —



520. Aluminium sulphate $(\text{Al}_2(\text{SO}_4)_3)$ is a white solid prepared from clay or bauxite by heating with sulphuric acid. The crystallized salt usually has the formula $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$. It is used in dyeing and paper making, in purifying water, in making white leather, and in making alum and other aluminium compounds.

A solution of aluminium sulphate has an acid reaction on account of hydrolysis (452); the equation for the hydrolysis is:—



Practical application is made of this reaction in purifying water. Upon adding aluminium sulphate and lime to impure water, the gelatinous aluminium hydroxide that is precipitated slowly settles and carries with it suspended particles and bacteria (69).

521. Alums.—A mixture of concentrated solutions of aluminium sulphate and potassium sulphate deposits crystals of **potassium alum** or simply **alum** (Fig. 191). Its formula is $\text{K}_2\text{Al}_2(\text{SO}_4)_4$ or $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3$. It is the type of a class of similar salts called **alums**, which can be prepared from sulphates of univalent and trivalent metals (*e.g.* K, Na, NH_4 , and Al, Cr, Fe). For example, chrome (or chromium) alum is $\text{K}_2\text{SO}_4 \cdot \text{Cr}_2(\text{SO}_4)_3$.

Alums are rather soluble in water, and their solutions have an acid reaction owing to hydrolysis (452, 520). They crystallize as octahedrons and contain twenty-four molecules of water of crystallization (Fig. 191). When heated, alums lose their water of crystallization and usually some sulphur trioxide, and become a white powder or a porous mass known as **burnt alum**.

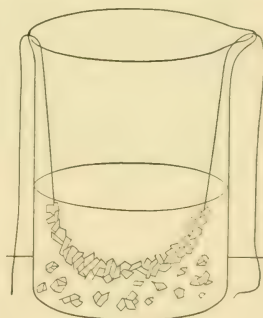


Fig. 191. — Alum crystals deposited from a concentrated solution

Alum (and sometimes aluminium sulphate) is an ingredient of alum baking powders (454); the acid needed to liberate carbon dioxide is formed by the hydrolysis of the alum.

Alums are used in dyeing and printing cloth, in tanning and paper making, as a medicine, for hardening plaster, in making wood and

cloth fireproof, and in preparing aluminium compounds. Aluminium sulphate is displacing aluminium alums for many purposes, especially the purification of water.

522. Mordants. — Aluminium hydroxide is extensively used as a mordant in dyeing. Many dyes must be fixed in the fiber by a metallic substance, otherwise the color would be easily removed.

The cloth to be dyed or printed is first impregnated or printed with an aluminium salt, such as aluminium acetate, and then exposed to steam or treated with aluminium hydroxide. This operation changes the aluminium salt into aluminium hydroxide, which is precipitated in the fiber of the cloth. The mordanted cloth is next passed through a vat containing a solution of the dye, which unites chemically or mechanically (perhaps both) with the aluminium hydroxide, forming a colored compound. The latter is relatively insoluble and cannot be easily washed from the cloth, *i.e.* it is a fast color.

523. Clay is the most common and perhaps the most useful compound of aluminium. It is a more or less impure aluminium silicate, formed by the slow decomposition of rocks containing aluminium compounds, especially the feldspars (**386**). Pure, typical feldspar is potassium aluminium silicate (KAlSi_3O_8). The products of its decomposition are chiefly an insoluble aluminium silicate and a soluble alkaline silicate. The latter is washed away. The pure aluminium silicate which remains is **kaolin** ($\text{H}_4\text{Al}_2\text{Si}_2\text{O}_9$ or $\text{H}_2\text{Al}_2(\text{SiO}_4)_2 \cdot \text{H}_2\text{O}$). Usually kaolin is mixed with particles of mica and quartz, calcium and magnesium carbonates, and iron compounds — the last giving the colors. This mixture, which varies in composition, is known as **clay**.

All grades of wet clay are plastic and can be molded into various objects which retain their shape when dry; if heated, the dried clay does not melt (except at a very high temperature) but becomes a permanently hard mass. These two properties (plasticity when wet and

hardness when heated) have been utilized for ages in making useful and ornamental objects.

524. Clay products. — Porcelain and china are made by mixing kaolin, fine sand, and powdered feldspar, shaping the mass into the desired form by molds or on a potter's wheel, and then heating in a kiln to a high temperature (Fig. 192). The mass when cool is hard and translucent



Fig. 192. — Scene in the largest chemical porcelain works in the United States. Putting porcelain dishes in clay boxes preparatory to heating in the kiln

(if thin), but porous. To be serviceable its surface must be **glazed**. This is done by dipping it into a creamlike mixture of feldspar and silica, similar to that used for making the porcelain but more easily fused, and then heating it again. The thin coating melts, runs over the surface, penetrates the porous mass and fuses with it to some extent, and when cold finally forms a shiny, impervious glaze.

Porcelain is decorated by mixing colored substances with the glaze or by painting designs on the surface with metallic paints or colored glass, and then heating again.

In making **pottery** the raw materials are less carefully selected and prepared, and not heated to such a high temperature. The best grades can hardly be distinguished from porcelain, but usually pottery is much heavier and thicker.

If less pure, plastic clay is used and heated to a moderate temperature, the product is known as **earthenware** or **stoneware**. This is a large class and includes tiles, terracotta, jugs, flowerpots, and chemical ware. This ware is porous and is sometimes glazed by throwing salt into the kiln just before the operation is over. The salt volatilizes and forms a fusible sodium aluminium silicate upon the surface. The special grades of stoneware for use in chemical plants are made by a more careful procedure.

Clay products used for construction include bricks, conduits, drain pipe, etc. They are made from impure clay and heated just enough to harden the mixture. The product varies with the clay, but is often colored red owing to iron oxide formed from the iron compounds in the unburned clay. Buff bricks are made from clay containing a small proportion of iron. Fire bricks and other material designed to withstand high temperatures are made from clay containing considerable silica.

EXERCISES

1. Prepare a summary of (a) aluminium, (b) the oxide and hydroxide, (c) the sulphate and alums.
2. Describe the manufacture of aluminium.
3. Discuss the interaction of aluminium hydroxide with acids and with alkalis.
4. Topics for home study: (a) History of aluminium. (b) Ceramics. (c) Clay. (d) Dyeing with mordants. (e) Uses of aluminium. (f) Aluminium in gems. (g) Use and care of aluminium ware. (h) Hydrolysis of aluminium compounds. (i) Two pans are identical in size and thickness of material, one being of aluminium and the other of iron. Compare their weights.

PROBLEMS

1. Calculate the weight of aluminium in (a) 20 gm. of aluminium oxide, (b) 34 gm. of aluminium hydroxide.

2. (a) Starting with aluminium how would you prepare in succession AlCl_3 , $\text{Al}(\text{OH})_3$, Na_3AlO_3 , AlCl_3 , $\text{Al}(\text{OH})_3$, Al_2O_3 , $\text{Al}^?$ (b) Calculate the percentage composition of two of the compounds in (a).

3. Write the formulas of aluminium nitrate, aluminium bromide, aluminium phosphate (ortho), aluminium fluoride, aluminium silicate (meta), potassium aluminate. Calculate the per cent of aluminium in three of these compounds.

4. How many pounds of aluminium in a ton of pure kaolin?

5. What weight of aluminium can be obtained from 100 kilograms of bauxite (93 per cent $\text{Al}(\text{OH})_3$)?

CHAPTER XXXIII

COPPER

525. Introduction. — Copper has been known for ages. Domestic utensils and weapons containing copper were used before similar objects of iron. The Latin word *cuprum* gives the symbol Cu.

526. Copper ores. — Copper, both free and combined, is an abundant element. Free or native copper, mixed with a hard rock, is found in large quantities in northern Michigan on the shores of Lake Superior. Copper sulphide ores occur abundantly in Montana and Utah, *e.g.* chalcocite (Cu_2S), chalcopyrite (CuFeS_2), and bornite (Cu_3FeS_3). The basic carbonates, malachite ($\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$) and azurite ($2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$) together with the oxide, cuprite (Cu_2O), are mined in Arizona.

527. Metallurgy of copper. — Free copper is easily extracted from the ore. The ore is first crushed, next concentrated by grinding and then washing away the rocky impurities down an inclined plane and on shaking tables, and finally heated until the copper melts and flows to the bottom of the furnace.

Copper carbonate and oxide ores are reduced by heating them with coke in a suitable furnace, somewhat as iron is smelted. The general chemical change may be represented thus: —



The metallurgy of copper-sulphur-iron ores is difficult, although chemically it only involves the removal of sulphur and iron. The result is accomplished by converting the

(b) The fine concentrate, which, after the grinding in *C* and jiggling in *D*, goes to the roasting furnace (*K*).

(c) The very fine concentrate, which is further concentrated by **flotation**. The ground ore from *E* passes through the desliming cone *F* on to the table *G*; here part goes to the roasting furnace (*K*). The rest is ground exceedingly fine in the mill *H* and on into the flotation machine (*I-J*). Here a remarkable change occurs. The fine ore particles are mixed with water containing a little oil (and sometimes sulphuric acid). Air is beaten into the mixture by vigorous agitation. *An oily froth is formed to which the copper mineral particles stick and float on the top of the mass, whereas the rocky particles sink.* The water is removed (by a filter — not shown) and the concentrate goes to the roasting furnace (*K*).

3. *Roasting.* The concentrate from the mechanical concentrator *D* and flotation concentrator *I-J* goes to the roasting furnace *K*. This is a cylindrical steel furnace lined with fire brick. Here the charge is heated red-hot but not melted; the heat, after the furnace is once started, comes from the burning sulphur. By this treatment about 80 per cent of the sulphur is removed and part of the copper and iron sulphides are changed into oxides. The product goes to the reverberatory furnace (*L*).

4. *Smelting.* The product from the roasting furnace *K* is smelted in the reverberatory furnace *L*; and the coarse concentrate from the jig *B* is smelted in the blast furnace *M*. That is, they are heated with a flux until they melt, just as iron is smelted. By this treatment more sulphur (as sulphur dioxide) and iron (as slag) are removed, and the copper and iron sulphides melt together to form copper **matte**. There are two kinds of furnaces for smelting: (1) In the reverberatory furnace *L* the heat radiated down

upon the hearth fuses the charge (Fig. 174). Most of the iron sulphide becomes iron oxide and forms a slag with the lime, silica, and alumina (Al_2O_3) in the charge, while the copper sulphide and the remaining iron sulphide melt together and sink through the slag to the bottom of the mass. The slag runs off continually. The **matte** is tapped off periodically and taken to the converter (*N*). (2) The blast furnace (*M*) is much like that used in making cast iron (Figs. 171, 172), though it is cooled by a constant flow of water through jackets which inclose its sides. The charge consists of the coarse concentrate (see 2 (*a*) above), limestone, and coke. Air is blasted through the furnace. Much heat is supplied by the burning sulphur. By this treatment 60 per cent of the sulphur is removed and most of the iron is changed to an oxide which forms a slag with the limestone in the charge or with the silica and alumina purposely left in the concentrate. The copper sulphide melts with the rest of the iron sulphide into copper **matte**. The slag and matte are drawn off through water-jacketed spouts into settles, where the matte drops through the slag — the slag passing on to the dump and the matte going to the converter (*N*).

5. *Converting*. This is the last stage. **Matte** from the reverberatory and blast furnaces (*L* and *M*) is poured into the converter — 65 tons to a charge (Fig. 194). The converter is much like the kind used in the Bessemer process of making steel (Figs. 176, 177). It is lined with magnesia brick. Air is blown through the liquid mass. The sulphur burns to sulphur dioxide which escapes through the top, while the iron forms a slag with the silica and alumina of ore added to supply these substances. About five hours is needed to burn out the sulphur and “slag the iron.” The product, which is metallic copper together with a little iron,

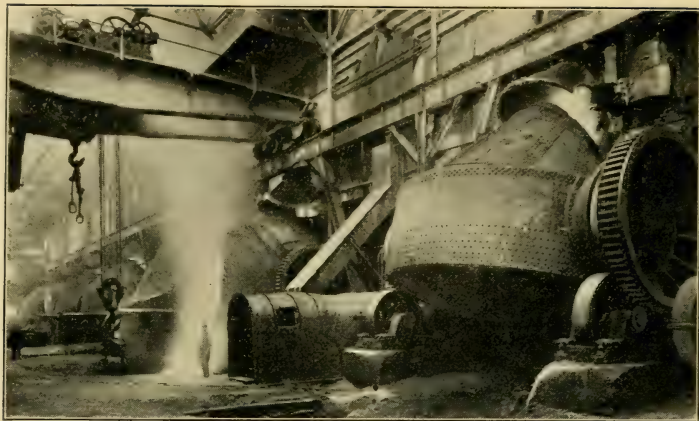
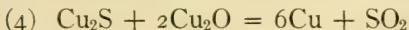
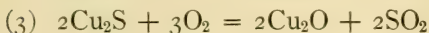
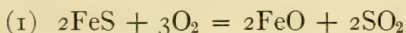


Fig. 194. — A copper converter in action

sulphur, and slag, goes to the refining-casting furnace (*O*).

The chemical changes in the converter may be represented thus:—



6. *Casting into anodes.* The product from the converter (*N*) is further purified in the refining-casting furnace *O* by blowing air through it and then stirring it with poles of green wood to reduce any oxide. When the refining is complete, the copper, now 99.25 per cent pure and called **blister copper**, is cast into **anodes** (Fig. 195). The anodes weigh about 500 pounds each. They are sent to the electrolytic refinery for final purification by electrolysis (529).

529. Refining of copper by electrolysis.— Since very pure copper (at least 99.95 per cent) is needed in electrical industries, the blister copper, as it is called, which is prepared by the process described above, must be further

purified to remove the last traces of impurities, especially arsenic. This is done by **electrolysis**, and the refined metal, which is exceedingly pure (99.98 per cent), is called **electrolytic copper**.

The anodes are suspended in a solution of copper sulphate and sulphuric acid. The cathodes, which are made of thin sheets of pure copper, also dip into the solution (Fig. 196.) When the current passes, copper ions (Cu^{++}) migrate to the cathode, lose their charges, and are deposited as metallic copper, thus building up the cathode (Fig. 197).

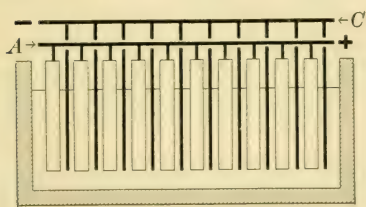


Fig. 196. — Sketch of the apparatus for the preparation of pure copper by electrolysis. A, A, A are anodes, and C, C, C are cathodes

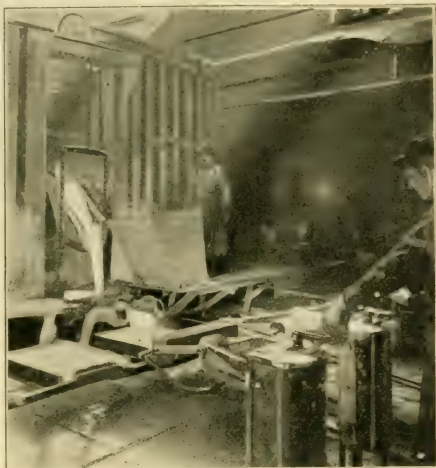


Fig. 195. — Casting refined copper into anodes

An equal weight of copper dissolves from the anode. The impurities drop to the bottom of the cell as a slime; from this slime the gold and silver that were in the copper ore are profitably extracted.

530. Properties of copper. — Copper is distinguishable from all other metals by its peculiar reddish color. It is flexible, ductile, malleable, and tough. It melts at 1083°C . Its spe-

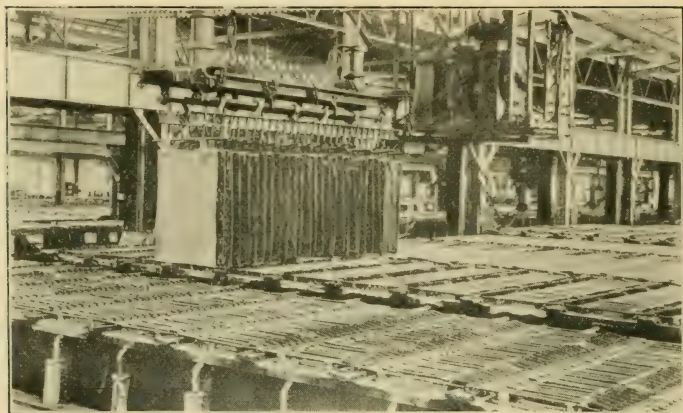


Fig. 197. — Removing cathodes of pure copper from a cell in one of the rooms of an electrolytic refining plant

cific gravity is 8.9. Copper is an excellent conductor of electricity — the best of the cheaper metals.

Exposed to ordinary air, it turns dull owing to a thin film of oxide. In moist air it gradually becomes coated with a green basic copper carbonate. Heated in the air, it is first changed into black copper oxide (CuO), and at a high temperature it colors a flame emerald-green. With nitric acid it forms copper nitrate and nitrogen oxides (**189**, **194**, **195**); with hot sulphuric acid it yields copper sulphate and sulphur dioxide (**260**). Hydrochloric acid has little effect upon it.

Copper displaces some metals if suspended in solutions of their compounds, *e.g.* a clean copper wire, if placed in a solution of any mercury compound, soon becomes coated with mercury; on the other hand, metals like iron, zinc, and magnesium displace copper from its solution, *e.g.* a nail or knife blade soon becomes coated with copper if dipped into a solution of any copper compound. Scrap iron is often used to precipitate copper on a large scale.

531. Tests for copper. — (a) The reddish color, peculiar "coppery" taste, and green color imparted to a flame serve to identify metallic copper. (b) An excess of ammonium hydroxide added to a solution of a copper compound produces a beautiful deep blue solution. (c) A few drops of acetic acid and potassium ferrocyanide solution added to a dilute solution of a copper compound produce a brown precipitate of copper ferrocyanide ($\text{Cu}_2\text{Fe}(\text{CN})_6$).

532. Uses of copper. — Large quantities of copper wire are used to conduct electricity, *e.g.* in operating the telegraph, cable, telephone, electric railway, and electric light. Sheet copper is made into household utensils, boilers, and stills, and is also used for roofs and spouts. All nations use copper as the chief ingredient of small coins. Much copper is utilized in electrical and other apparatus, especially now that copper can be cast. Books are printed and illustrated from electrotypes made by depositing copper upon an impression of the type or design in wax; in a similar way many objects are copper plated (243). Copper is an ingredient of many common and useful alloys, as may be seen from the accompanying table.

TABLE OF COPPER ALLOYS

NAME	COPPER	ZINC	ALUMIN- IUM	SILVER	NICKEL	TIN
Aluminium bronze	90-98		2-10			
Bell metal . . .	78					22
Brass	63-93	5-40				
Bronze	60-95	25				
German silver . .	50-60	25			20-25	
Gun metal . . .	90					10
Gold coin . . .	10			Gold 90		
Monel metal . .	28				60	
Nickel coin . .	75				25	
Silver coin . . .	10			90		

533. Two series of copper compounds. — Copper, like iron, forms two series of compounds — the cuprous and the

cupric. The valence of copper is 1 in cuprous compounds and 2 in cupric.

Cupric salts are more common. Many are soluble in water, and all dilute solutions are blue owing to the presence of the blue cupric ion (Cu^{++}).

Soluble copper compounds are more or less poisonous. Cooking utensils made of copper should be used with care. Vegetables, acid fruits, and preserves, if boiled in them, should be removed as soon as cooked. The vessels themselves should be kept bright to prevent the formation of copper salts, which might contaminate the contents. Certain lower forms of plant life (algæ) are poisoned by copper salts, and copper sulphate is sometimes added to ponds and reservoirs to destroy such growths.

534. Copper sulphate or cupric sulphate (CuSO_4) is a blue solid. It is also called blue vitriol or "blue stone." The crystallized salt ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) effloresces; heated to 240°C ., all the water escapes, leaving a whitish powder called **anhydrous copper sulphate**. Copper sulphate solutions have an acid reaction owing to hydrolysis (452).

Copper sulphate is used in electric batteries (*e.g.* the gravity cell), in making other copper salts, as a mordant in calico printing and dyeing, and in copper plating and electrotyping. A mixture of copper sulphate and milk of lime, called **Bordeaux mixture**, is sprayed upon trees to kill insects.

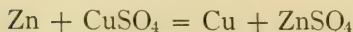
Copper sulphate is prepared by treating copper scrap in the air with dilute sulphuric acid or by oxidizing copper sulphide. Some of the copper sulphate of commerce is a by-product in refining gold and silver with sulphuric acid.

535. Other copper compounds. — **Cuprous oxide** (Cu_2O) is the red mineral cuprite. It is precipitated as a reddish powder by heating Fehling's solution (*i.e.* a mixture of solutions of copper sulphate, Rochelle salt, and sodium hydroxide) with glucose; its formation serves as a **test for glucose** and sugars like it (345). **Cupric oxide**

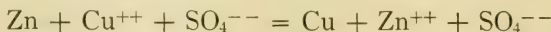
(CuO) is a black solid formed by heating copper in air. It is used to remove sulphur compounds from petroleum. **Copper nitrate** ($\text{Cu}(\text{NO}_3)_2$) is a blue, crystallized solid, formed by the interaction of copper and dilute nitric acid. It is a cupric salt. It is deliquescent, very soluble in water, and is readily decomposed by heat into cupric oxide (CuO) and nitrogen oxides. **Cupric sulphide** (CuS) is the black precipitate formed by passing hydrogen sulphide gas into a solution of a cupric salt. **Malachite** is a bright green mineral and is often used as an ornamental stone. **Azurite** is a magnificent blue crystallized mineral. Both are basic carbonates and are ores of copper (526).

536. Displacement of metals. — We have already seen that iron, zinc, and other metals displace copper from copper salt solutions, and that copper itself displaces mercury (530). The deposition of metallic copper and of mercury are examples of a chemical change in which most metals can participate. The displacing relations of metals have been carefully studied. It has been found that there is a fixed order in which one metal can displace another from its solutions. This order is sometimes called the **displacement series**. The arrangement of the common metals is shown in the accompanying column.

In this series each free metal displaces succeeding metals DISPLACEMENT SERIES OF THE COMMON METALS	from their solutions. For example, zinc displaces most of the metals in the series, while copper displaces only a few.
Magnesium	Let us interpret a case of displacement. In the case of zinc and copper sulphate solution, not only does the zinc displace the copper, but the zinc passes into solution. This fact can be shown by testing the solution for zinc. The action (in the case of zinc and copper sulphate solution) is represented thus : —
Aluminium	
Zinc	
Iron	
Tin	
Lead	
Hydrogen	
Copper	
Mercury	
Silver	
Platinum	
Gold	



In the ionic form, this equation is : —



We notice that the essential changes are (1) metallic zinc to ionic zinc, and (2) ionic copper to metallic copper. This kind of change is sometimes called **electrochemical**. And the displacement series is often called the **electrochemical series of metals**.

Hydrogen is not a metal in the common acceptance of this term. But it is usually included in the displacement series of metals, because the metals that precede hydrogen displace it from most acids. That is, hydrogen behaves in this respect like other members of the series. Recall that hydrogen is like metals in that it forms positive ions (H^+).

537. The electric cell. — If a rod of zinc and a strip of copper are put in a beaker of dilute sulphuric acid, little or no action is observed. But if the outer ends are connected by a copper wire, bubbles of hydrogen rise from the copper. The zinc is slowly “eaten up” but the copper is unchanged. The solution will be found, by testing, to contain zinc ions. The simultaneous liberation of hydrogen and the disappearance of zinc mean that metallic zinc has passed into solution as ionic zinc (Zn^{++}) and ionic hydrogen (H^+) has come out of solution as hydrogen gas (H_2). We might represent this action thus : —



If the wire is cut and the ends connected with a voltmeter, an electric current will be detected flowing from the copper strip (positive electrode) through the wire to the zinc rod (negative electrode). This means that the electric current flows in the solution, by means of ions, from

the zinc to the copper. This arrangement — zinc, acid, copper, — is a simple illustration of an **electric cell**. The electric cell is an example of the transformation of chemical energy into electrical energy (Fig. 198).

All metals have a tendency to pass into solution, *i.e.* to become ionic. This tendency varies. Any two metals in the displacement series may be used with a suitable electrolytic solution. The farther apart they are in the series, the stronger the current produced. Hence the displacement series is also called the **electromotive series**.

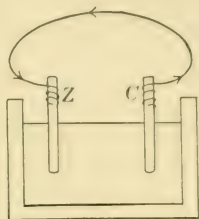


Fig. 198.—Sketch of an electric cell

EXERCISES

1. Prepare a summary of the metallurgy of copper sulphide ores.
2. Interpret the electrolytic refining of copper.
3. State physical properties of copper that fit it for electrical uses.
4. Give several tests for copper.
5. Name five alloys of copper. State the uses of three.
6. What is an electrotype plate? How is it made?
7. Topics for home study: (a) Why is the spark from a trolley wire often colored green? (b) A tin can will displace copper from copper solutions. Why? (c) Nitric acid produces a green-blue stain on a silver coin. Why?
8. Starting with copper, how would you prepare in succession, cupric oxide, $\text{Cu}(\text{NO}_3)_2$, CuO , Cu , CuSO_4 , the metal?
9. Write the formulas of the following compounds by applying the principle of valence: Cupric bromide, cuprous chloride, cupric phosphate, cupric sulphate, cuprous iodide.

PROBLEMS

1. Calculate the weight of copper in (a) 10 gm. of crystallized copper sulphate, (b) 1 kg. of malachite, and (c) 2000 lb. of chalcocite.
2. Calculate the percentage composition of the two copper oxides and show that they illustrate the law of multiple proportions. (Use exact atomic weights.)
3. Calculate the simplest formulas corresponding to: (a) $\text{Cu} = 96.94$, $\text{H} = 3.05$; (b) $\text{Cu} = 57.46$, $\text{H} = 0.91$, $\text{O} = 36.2$, $\text{C} = 5.43$.

4. How much (a) silver and (b) copper can be obtained from an American ten cent coin which weighs 2.44 gm.?

5. How much CuS can be obtained from 24 gm. of CuSO_4 ?

6. A flask full of water weighs 153 gm.; 25 gm. of copper is dropped in. The whole now weighs 175.19 gm. Calculate the specific gravity of copper.

7. A certain weight of copper oxide, when heated in a current of hydrogen, lost 59.789 gm. of oxygen and formed 67.282 gm. of water. If the atomic weight of oxygen is 16, calculate the atomic weight of copper.

8. Copper nitrate is heated. What weights of the products are formed from 150 gm. of copper nitrate?

CHAPTER XXXIV

MAGNESIUM — ZINC — MERCURY

538. Occurrence of magnesium. — Magnesium is never found free. In combination it is widely distributed and very abundant, constituting about 2.5 per cent of the earth's crust. **Dolomite** is magnesium calcium carbonate ($\text{CaMg}(\text{CO}_3)_2$); it forms whole mountain ranges in the Tyrol and vast deposits in many regions. Dolomite closely resembles marble and limestone in its properties, and is sometimes called magnesium limestone. **Magnesite** is magnesium carbonate (MgCO_3); it is also abundant. Several Stassfurt salts (**462**) are magnesium compounds, *e.g.* kainite ($\text{KCl} \cdot \text{MgSO}_4 \cdot \text{H}_2\text{O}$), carnallite ($\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), and kieserite ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$). Magnesium is a constituent of many rocks and minerals, such as serpentine, talc, soapstone, asbestos, and meerschaum; these are silicates (**386**). The sulphate (MgSO_4) and chloride (MgCl_2) are found in sea water and in mineral springs.

539. Manufacture of magnesium. — Magnesium is manufactured by the electrolysis of a fused mixture of magnesium chloride and potassium chloride obtained from carnallite. An air-tight iron vessel is the cathode (Fig. 199). The anode is a carbon rod (*A*). An inert gas is supplied through *DD'*. The chlorine es-

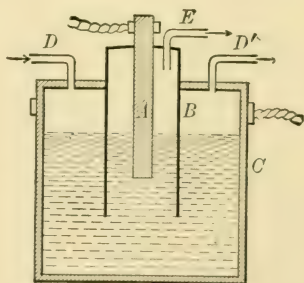
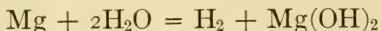


Fig. 199. — Sketch of the apparatus for the manufacture of magnesium by the electrolysis of carnallite

capacities through *E*. Magnesium rises to the surface of the fused electrolyte.

540. Properties of magnesium. — Magnesium is a lustrous, silvery white metal. It is light, the specific gravity being about 1.75. It is tenacious and ductile, and when hot can be drawn into wire or rolled into a ribbon, the latter being a common commercial form. It is easily kindled by a match, melts at 651°C ., and can be cast.

Heated in air, it burns with a dazzling light, producing dense white clouds of magnesium oxide (MgO) together with a little magnesium nitride (Mg_3N_2). It does not tarnish in dry air, but in moist air it is soon covered with a film of the basic carbonate. It liberates hydrogen from acids. It also liberates hydrogen, slowly, from boiling water, thus: —



When heated in dry nitrogen, it forms magnesium nitride; this property was utilized by Ramsay in the separation of nitrogen from argon (124, 125).

Solutions of magnesium salts contain magnesium ions (Mg^{++}).

541. Uses of magnesium. — The light from burning magnesium affects a photographic plate, and magnesium powder (mixed with potassium chlorate) is used in taking flashlight photographs. It is also used in signal lights (*e.g.* star shells) and fireworks. Magnalium, the alloy of magnesium and aluminium, has been described (516).

542. Magnesium oxide and hydroxide. — Magnesium oxide (MgO) is a white, bulky powder. It is formed when magnesium burns in the air, but it is manufactured by gently heating magnesium carbonate, just as lime is made from limestone. It is often called **magnesia**, or calcined magnesia. It combines very slowly with water, forming **magnesium hydroxide** ($\text{Mg}(\text{OH})_2$). Like lime, magnesia

is infusible and is therefore used in making fire brick, crucibles, and furnace linings. It is the main ingredient

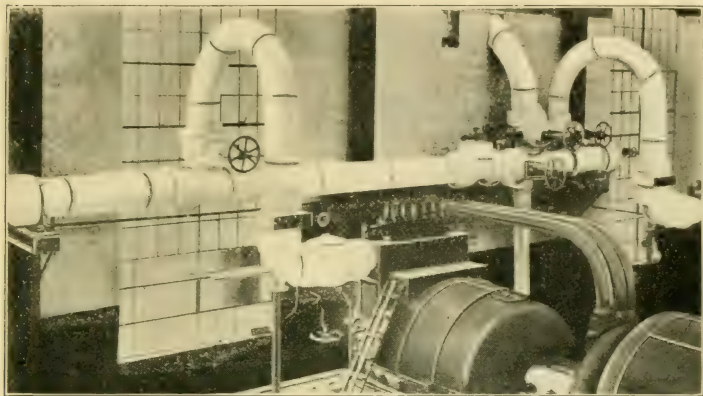


Fig. 200. — Pipes covered with "85 per cent magnesia" to prevent loss of heat

of a mixture used to prevent the loss of heat from steam pipes (Figs. 200, 201).

Magnesium hydroxide is a white solid. It is only very slightly soluble in water, and a suspension, called **milk of magnesia**, is used as a medicine to neutralize acidity in the mouth and stomach.

543. Magnesium sulphate and chloride. — **Magnesium sulphate** (MgSO_4) is a white solid. The commercial form



Fig. 201. — Section of a pipe showing end of protective cover

is often called Epsom salts ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$). It is very soluble in water and its solution has a bitter taste; it is used as a laxative. Magnesium sulphate, like calcium

sulphate, makes water permanently hard (483). Magnesium sulphate is used in manufacturing paints,

soap, and sulphates of sodium and potassium, and as a coating for cotton cloth. **Magnesium chloride** (MgCl_2) is a white solid. The crystallized salt ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) is very deliquescent. Magnesium chloride undergoes hydrolysis with hot water, forming magnesium hydroxide and hydrochloric acid (452).

If water containing magnesium chloride (*e.g.* sea water), is used in a boiler, the insoluble magnesium hydroxide forms a hard scale on the boiler and the liberated hydrochloric acid corrodes the metal. Hence

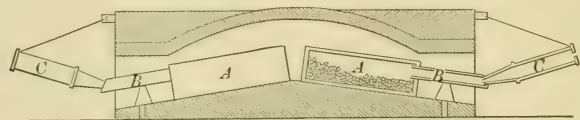


Fig. 202. — Retorts for reduction of zinc oxide (open — right, closed — left)

a hard water containing magnesium chloride (or sulphate) should be softened before use (483).

544. Other magnesium compounds. — **Ammonium magnesium phosphate** (NH_4MgPO_4) is precipitated when disodium phosphate solution and ammonium hydroxide are added to a solution of a magnesium compound. Its formation serves as a **test for magnesium**. **Magnesium carbonate** (MgCO_3) occurs native as magnesite, and combined with calcium carbonate as dolomite. It is extensively used as a lining for furnaces (*e.g.* open-hearth) and converters (494, 495). Like the corresponding calcium compound, it forms the soluble acid carbonate ($\text{MgH}_2(\text{CO}_3)_2$) in water containing carbon dioxide (472). The commercial salt known as *magnesia alba*, or simply **magnesia**, is a complex compound (ordinarily $\text{Mg}(\text{OH})_2 \cdot 3\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$). Many face powders consist chiefly of *magnesia alba*.

545. Occurrence of zinc. — Free zinc is never found. The chief **ores** are zinc sulphide (sphalerite, zinc blende, ZnS), and zinc carbonate (smithsonite, ZnCO_3). Other ores are zinc silicates (calamine, $\text{Zn}_2\text{SiO}_4 \cdot \text{H}_2\text{O}$, willemite, Zn_2SiO_4), red zinc oxide (zincite, ZnO), and franklinite

($\text{Zn}(\text{FeO}_2)_2$). Zinc ores are found in Missouri, Kansas, and New Jersey.

546. Metallurgy of zinc. — The ores are usually concentrated (sulphide ore by the flotation process (528, 2 (c))), then roasted to form the oxide, which is reduced by heating with finely powdered coal.

The reduction is conducted in earthenware retorts (*A*) connected with double receivers (Fig. 202). The retorts are heated by gas above the boiling point of zinc; so at first the zinc (together with some zinc oxide) condenses in *C* as a powder called **zinc dust**, somewhat as sulphur forms flowers of sulphur. But when this receiver becomes hot, the zinc

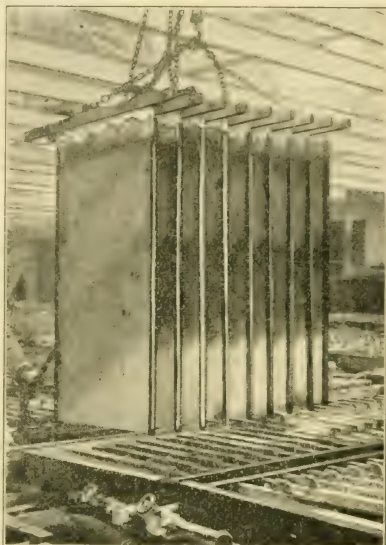


Fig. 203. — Lifting the cathodes of pure zinc from an electrolytic cell

condenses to a liquid in *B*, from which it is drawn off at intervals and cast into bars or plates. The impure zinc thus obtained is called **spelter**. It is freed from carbon, lead, iron, cadmium, and arsenic by repeated distillation; very pure zinc is obtained by the electrolysis of a pure zinc salt (Fig. 203).

547. Properties of zinc. — Zinc is a bluish white, lustrous metal. At ordinary temperatures it is rather brittle, but at $100\text{--}150^\circ\text{C}$. it is soft and can be rolled into sheets and drawn into wire; zinc which has been rolled or drawn does

not become brittle on cooling. Above 150° C. it again becomes brittle. It melts at 419° C. If melted zinc is poured into water, it forms brittle lumps called **granulated zinc**, which is a convenient form for use in the laboratory.

Heated in air above its melting point, zinc burns with a bluish green flame, forming white zinc oxide (ZnO). Zinc does not tarnish in dry air, but ordinarily it becomes coated with a thin film of basic carbonate, which protects it somewhat from further change. Commercial zinc interacts readily with acids and usually liberates hydrogen; pure zinc acts very slowly. Like aluminium, it interacts with hot solutions of sodium and potassium hydroxides (514); it forms zincates and hydrogen, thus:—



Zinc displaces most metals from their solutions (536). Ordinary zinc salts yield zinc ions (Zn^{++}) in solutions.

548. Uses of zinc.—Zinc is extensively used as an electrode in many kinds of batteries. Sheet zinc is used for roofs, gutters, pipes, parts of washing machines, and as a lining for tanks. The chief use of zinc is in making **galvanized iron**. This is iron covered with a thin layer of zinc and is made by dipping clean iron into melted zinc. The zinc protects the iron from air and moisture. Hence galvanized iron does not rust easily and is extensively used for netting, wire, roofs, pipes, cornices, and water tanks. Zinc shavings are used in the cyanide process of extracting gold (591). Zinc is an ingredient of many useful alloys, *e.g.* brass, bronze, and German silver (532).

549. Zinc oxide and hydroxide.—Native **zinc oxide** is red, owing to the presence of manganese. The pure oxide (ZnO) is white when cold and yellow when hot. It

is formed when zinc burns, and is manufactured in this way or by heating zinc carbonate. It is often called zinc white or Chinese white, and large quantities are used in the manufacture of automobile tires and white rubber goods, and to make white paint. Paint made of zinc oxide is not discolored by sulphur compounds in the atmosphere (257, 576). On account of its antiseptic properties, zinc oxide is an ingredient of ointments. **Zinc hydroxide** ($\text{Zn}(\text{OH})_2$) is formed as a dull white precipitate by the interaction of sodium or potassium hydroxide and a solution of a zinc salt. An excess of the alkaline hydroxide changes zinc hydroxide into a zincate (547, end). Zinc hydroxide, like aluminium hydroxide, has both acid and basic properties (519). Unlike aluminium hydroxide, however, it dissolves in ammonium hydroxide owing to the formation of a soluble complex compound ($\text{Zn}(\text{NH}_3)_4(\text{OH})_2$).

550. Zinc sulphide, sulphate, and chloride. — Native **zinc sulphide** is yellow, brown, or black on account of impurities. Pure **zinc sulphide** (ZnS) is white, and is formed as a jelly-like precipitate when hydrogen sulphide is passed into an alkaline or very weak acid solution of a zinc salt. A mixture of zinc sulphide and barium sulphate, called **lithophone**, is used as a white pigment in paints. **Zinc sulphate** (ZnSO_4) is formed by the interaction of zinc and dilute sulphuric acid. Large quantities are also made by roasting the sulphide in a limited supply of oxygen and extracting the sulphate with water. Thus prepared, it is a white, crystallized solid ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) which effloresces in the air, and when heated to 100°C . loses most of its water of crystallization. The crystallized salt is called **white vitriol**. It is used in dyeing and calico printing, as a disinfectant, and as a medicine. Like other zinc salts, it is poisonous. **Zinc chloride** (ZnCl_2) is a white, deliquescent

solid. It is used as a constituent of a mixture for filling teeth. Large quantities are used to preserve wood, especially posts and railroad ties. Mixed with zinc oxide and water, it forms a cement. Cellulose (352) is slowly changed by zinc chloride into a plastic mass, which can be molded into different shapes, *e.g.* tubes, pails, sheets; it is called fiber board.

551. Tests for zinc. — The formation of the sulphide or hydroxide, as above described, serves as a **test for zinc**. A green incrustation is produced when zinc compounds are heated on charcoal and then moistened with cobaltous nitrate solution. (Compare 518, end.)

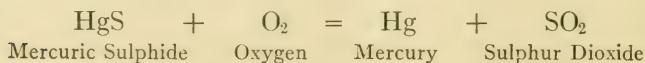
552. Cadmium (Cd) occurs in zinc ores, and is extracted from the zinc dust condensed in the retorts (546). It is a white, lustrous, and rather soft metal. Cadmium is a constituent of certain fusible alloys (441). Wood's metal, for example, contains 12 per cent of cadmium.

The most important compound is **cadmium sulphide** (CdS), which is a bright yellow solid, formed by adding hydrogen sulphide to a solution of a cadmium compound. Its formation serves as the **test for cadmium**. It is used as an artist's color.

553. Occurrence of mercury. — Native mercury is occasionally found in minute globules. The most abundant ore and the chief source of mercury is **mercuric sulphide** (cinnabar, HgS). The ore is extensively mined in Spain, Austria, and Italy; in the United States large quantities are obtained in California and Texas.

Mercury has been known for ages as quicksilver. The Latin name, *hydrargyrum*, which gives the symbol Hg, means "water silver."

554. Metallurgy of mercury. — Mercury is readily prepared by roasting cinnabar in a current of air, and condensing the vapor of the metal, thus:—



The crude mercury is freed from soot by pressing it through linen or chamois leather. For accurate use it must be further purified by distilling or by agitating with nitric acid (or ferric chloride) to remove the dissolved metals, such as lead or zinc. Mercury is sent into commerce in strong iron flasks holding 75 pounds.

555. Properties of mercury. — Mercury is a silvery metal, and is the only common one that is liquid at ordinary temperatures. It solidifies at about -39° C. and boils at about 357° C. It is a heavy metal, the specific gravity being about 13.6. Mercury is a good conductor of electricity.

Mercury does not tarnish in the air, unless sulphur compounds are present. At about 300° C. it combines slowly with oxygen to form red mercuric oxide (HgO). Hydrochloric acid and cold sulphuric acid do not affect it; hot concentrated sulphuric acid oxidizes it, and nitric acid changes it into nitrates. It is displaced from solution by most metals (536).

556. Amalgams are alloys of mercury. — Amalgamated zinc is used in certain electric batteries to prevent unnecessary loss of the zinc. Amalgams of some metals (*e.g.* tin, silver, gold) are used as a filling for teeth. Silver and gold form amalgams readily, and considerable mercury is used in extracting these precious metals from their ores (581, 591). Care should be taken, while using mercury, not to let it come in contact with jewelry.

557. Uses of mercury. — Mercury is used in thermometers, barometers, and some kinds of air pumps. Considerable is used in preparing certain medicines and explosives (*e.g.* mercury fulminate, which is used in caps to explode gunpowder and nitroglycerin. It is also used in one method of making sodium hydroxide (456).

The use of mercury in thermometers depends not only on the fact that it is a bright liquid between a wide range of temperature, but also on the uniform change of volume with change of temperature.

The curve showing the relation of volume and temperature is almost a straight line (Fig. 204), that is, the expansion of mercury is regular.

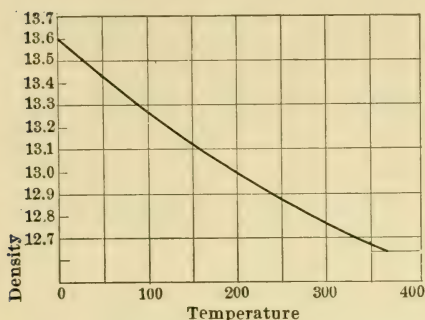
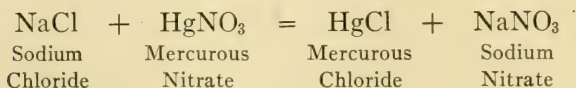


Fig. 204. — Curve showing regular change in volume of mercury with change of temperature

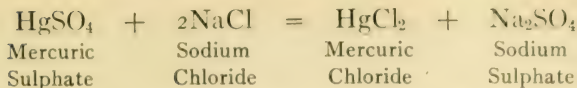
558. Two series of mercury compounds. — Mercury, like copper and iron, forms two classes of compounds — **mercurous** and **mercuric**. The valence of mercury is 1 in mercurous compounds and 2 in mercuric. Solutions of mercurous salts contain

mercurous ions (Hg^+), and of mercuric salts mercuric ions (Hg^{++}).

559. Mercurous and mercuric chlorides. — **Mercurous chloride** (HgCl) is a white, tasteless powder, insoluble in water. It is used as a medicine under the name of **calomel**. It is formed as a white precipitate when a chloride and mercurous nitrate interact — a **test for mercury in mercurous compounds**. The equation is : —

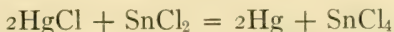
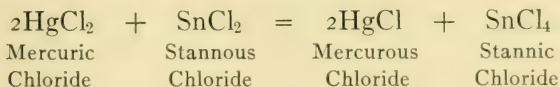


This test is confirmed by adding ammonium hydroxide which blackens the precipitate. **Mercuric chloride** (HgCl_2) is a white, crystalline solid, soluble in water. It is prepared by heating a mixture of mercuric sulphate and sodium chloride, thus : —



Mercuric chloride is a violent poison. The best antidote is the white of a raw egg. The albumin forms an insoluble mass with the poison, which may then be removed from the stomach. The common name of mercuric chloride is **corrosive sublimate** (or bichloride of mercury). It has powerful antiseptic properties, and is extensively used in surgery to sterilize instruments and to protect wounds from the harmful action of germs; taxidermists sometimes use it to preserve skins, and it has many serviceable applications as a medicine and disinfectant. It is usually used as a dilute solution (1 part to 1000 parts of water).

Mercuric chloride, when treated carefully with stannous chloride, is reduced first to white mercurous chloride and finally to a dark gray precipitate of finely divided mercury — the **test for mercury in mercuric compounds**. The equations for these reactions are: —



560. Other mercury compounds. — Native **mercuric sulphide** or cinnabar (HgS) is a red, crystalline solid. When hydrogen sulphide is passed into a solution of a mercuric salt, mercuric sulphide is precipitated as a black powder; this variety, when sublimed, changes into red crystals. **Vermilion** is artificial mercuric sulphide prepared by various processes. It has a brilliant red color and is used to make red paint. **Mercurous nitrate** (HgNO_3) and **mercuric nitrate** ($\text{Hg}(\text{NO}_3)_2$) are prepared by treating

mercury respectively with cold dilute nitric acid, and with hot concentrated nitric acid. They are white solids.

EXERCISES

1. State the properties and uses of magnesium.
2. Starting with magnesium, how would you prepare in succession MgO , magnesium hydroxide, MgCl_2 , magnesium carbonate, magnesium oxide?
3. Write equations for (a) interaction of magnesium and sulphuric acid and (b) heating magnesium in nitrogen.
4. Essay topics: (a) Asbestos. (b) Magnesia as a refractory material. (c) Stassfurt salts containing magnesium. (d) Dolomite. (e) Joseph Black's investigations of "magnesia alba." (f) Properties of zinc and aluminium.
5. Name the chief ores of zinc. Describe the metallurgy of zinc.
6. Summarize the physical chemical properties of zinc.
7. Starting with zinc how would you prepare in succession zinc oxide, ZnCl_2 , zinc hydroxide, Na_2ZnO_2 , zinc sulphide, ZnCl_2 , ZnCO_3 , zinc oxide, zinc?
8. Topics for home study: (a) Zinc paints. (b) Galvanized iron. (c) Amalgams. (d) History of mercury. (e) Cinnabar. (f) Mercuric oxide and oxygen. (g) Alloys of zinc.
9. What are the tests for zinc?
10. Describe the metallurgy and purification of mercury.
11. Practical topics: (a) Suggest a proof of the volatility of mercury at ordinary temperatures. (b) What is the significance of "quick" in the word quicksilver? (c) Etymology of amalgam. (d) In what respect does mercury resemble bromine? (e) Name three metals which will float on mercury. (f) Why is mercury used in a barometer?
12. Describe (a) mercurous chloride and (b) mercuric chloride. What is the commercial name of each? The use?
13. State the tests for mercury.
14. What is (a) magnesia, (b) Epsom salts, (c) galvanized iron, (d) Chinese white, (e) white vitriol, (f) calomel, (g) corrosive sublimate?

PROBLEMS

1. Calculate the per cent of the metallic element in (a) magnesium oxide, zinc oxide, and mercuric oxide; (b) Epsom salts, sphalerite, cinnabar, and smithsonite; (c) $\text{Mg}_2\text{P}_2\text{O}_7$, $\text{H}_2\text{Zn}_2\text{SiO}_5$, $\text{Hg}(\text{NO}_3)_2$.

2. Calculate the percentage composition of mercurous and mercuric iodides, and show that these compounds illustrate the law of multiple proportions. (Use exact atomic weights.)

3. Write the ordinary and the ionic equations for (a) mercuric chloride and hydrogen sulphide form mercuric sulphide and hydrochloric acid, (b) magnesium chloride and sodium hydroxide form magnesium hydroxide and sodium chloride, (c) zinc hydroxide and sodium hydroxide form sodium zincate and water.

4. Write the formulas of the following compounds by applying the principle of valence or by utilizing analogous formulas in this chapter: Magnesium bromide, magnesium nitrate, magnesium sulphide, zinc chromate, zinc carbonate, zinc acetate, zinc phosphate (ortho), mercurous fluoride, mercuric sulphate, mercurous oxide.

5. If the annual production of quicksilver in the United States were 20,600 flasks of 75 pounds each, and if this amount were made into corrosive sublimate, how many metric (2200 lb.) tons would be produced?

6. What (a) weight of mercury, (b) weight of sulphur dioxide, (c) volume of sulphur dioxide (standard conditions) can be obtained from a metric ton of cinnabar (60 per cent pure)?

7. Calculate the atomic weights of magnesium, mercury, and zinc: (a) 16.0263 gm. of MgO give 47.8015 gm. of MgSO_4 ; (b) 16.03161 gm. of zinc give 19.9568 gm. of ZnO; (c) 118.3938 gm. of HgO give 109.6308 gm. of mercury; (d) 177.1664 gm. of mercuric sulphide give 152.745 gm. of mercury. (Use exact atomic weights.)

8. What (a) weight and (b) volume (standard conditions) of oxygen will 79 gm. of mercuric oxide yield?

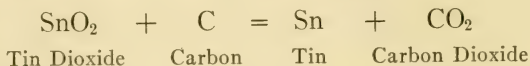
CHAPTER XXXV

TIN — LEAD

561. Only one ore of tin. — Tin dioxide (cassiterite, tin stone, SnO_2) is the only available ore. It is not widely distributed. The ore was formerly mined in England (at Cornwall), but the chief sources now are Australia, Tasmania, Bolivia, and the East Indian Islands, especially Banca and Billiton. None is mined in the United States.

Tin is one of the oldest of metals. Many prehistoric bronzes contain tin. The Latin word *stannum* gives us the symbol Sn and the terms stannous and stannic.

562. Metallurgy of tin. — The ore is roasted to remove sulphur and arsenic, and oxidize any iron present. The tin oxide is then reduced by heating it with coal in a reverberatory furnace (Fig. 174). The equation is: —



The tin collects at the bottom of the furnace and is drawn off and cast into bars or masses, which are often called **block tin**. Usually it is purified by melting it slowly on an inclined hearth, so the low melting tin will flow away from the metallic impurities. This tin may be further purified by stirring the molten metal with a wooden pole, or by holding billets of wood beneath its surface. (Compare 528, 6.) The impurities are oxidized by the escaping gases. Tin is also refined by electrolysis.

563. Properties of tin. — Tin is a white, lustrous metal. It is soft and malleable, and can be readily cut and

hammered. It is softer than zinc, but harder than lead. Its specific gravity is 7.3. It melts at about 232°C ., and when heated to a higher temperature it burns, forming white tin oxide (SnO_2).

Ordinary tin if kept below about 18°C . changes into gray tin, which is a dull looking powder. Sometimes objects containing tin, such as organ pipes, medals, and statues, disintegrate owing to the formation of powdery tin; once started, the "tin disease," as it is called, spreads rapidly (Fig. 205).

Concentrated hydrochloric acid changes it into stannous chloride (SnCl_2); hot concentrated sulphuric acid converts it into stannous sulphate (SnSO_4); and concentrated nitric acid oxidizes it to a white solid known as **meta-stannic acid** or **beta-stannic acid** (usually designated by $(\text{H}_2\text{SnO}_3)_5$). Certain metals precipitate tin from its solutions often as a grayish black, spongy mass filled with bright scales (536).

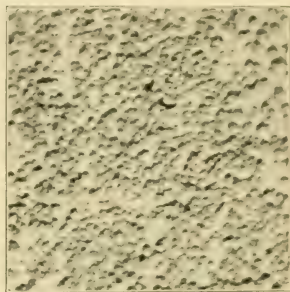


Fig. 205. — Sheet tin affected by "tin disease" (enlarged one and one half times)

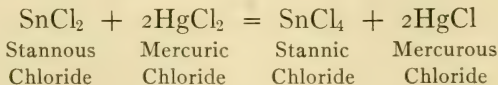
564. Uses of tin. — Tin is so permanent in air, weak acids (like vinegar and fruit acids), and alkalies that it is extensively used as a protective coating for metals. Tin plate (also called sheet tin, or simply "tin") is made by dipping very clean sheet iron into molten tin. Thus coated with a thin layer of tin, it is made into tinware, cans, and many useful objects. Copper coated with tin is made into vessels for cooking, and brass coated with tin is made into pins. Tinned iron or steel does not rust until the iron is exposed, and then the rusting proceeds rapidly. Tin pipes are used to convey liquids, *e.g.* soda water, which act on lead.

Tin is also hammered into thin sheets called tin foil, though much tin foil contains lead.

Tin is used in making useful alloys. Those containing a minor per cent of tin are bronze, gun metal, type metal, and fusible alloys (**441**, **532**). Speculum metal contains about 30 per cent of tin. Alloys containing considerable tin are Britannia metal (90 per cent), pewter (75 per cent), and solder (50 per cent). (Compare **532**.)

565. Two series of tin compounds. — Tin, like iron, copper, and mercury, forms two series of compounds — **stannous** and **stannic**. The valence of tin is 2 in stannous compounds and 4 in stannic. Stannous ions (Sn^{++}) and stannic ions (Sn^{++++}) are found in solutions of the respective salts. Stannous salts pass readily into the corresponding stannic salts.

566. Stannous and stannic chlorides. — **Stannous chloride** (SnCl_2) is formed by the interaction of hydrochloric acid and tin. From the concentrated solution a greenish salt crystallizes ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$), known as **tin crystals** or **tin salt**. Stannous chloride hydrolyzes easily; a strong solution deposits a basic salt ($\text{Sn}(\text{OH})\text{Cl}$), *i.e.* a salt formed by substituting a non-metal for part of the hydroxyl groups of a base. To keep stannous chloride “stannous,” hydrochloric acid and tin must be added to the solution. Stannous chloride can be quickly oxidized to stannic chloride by mercuric chloride, thus: —



By an extension of the simplest idea of oxidation and reduction to include the negative element chlorine, stannous chloride may be said to be oxidized to stannic chloride and mercuric chloride to be reduced to mercurous chloride. (Compare **502**, **559**, end.) An excess of stannous chloride reduces the white mercurous chloride to gray or black metallic mercury; this serves as a **test for tin** (**559**, end).

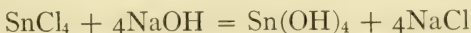
Stannic chloride (SnCl_4) is prepared by passing chlorine into stannous chloride solution, thus:—



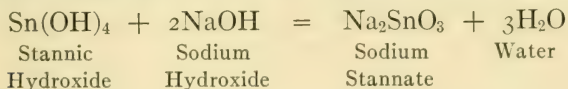
It is obtained industrially by passing dry chlorine over tin scrap (cuttings, cans, etc.). The stannic chloride, which boils at 114°C . is distilled from the other products.

Stannous chloride is used as a reducing agent and as a mordant in dyeing and calico printing (522). Crystallized stannic chloride ($\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$), known commercially as **oxymuriate of tin**, is also used as a mordant. Tin mordants produce brilliant colors.

567. Other tin compounds.—Stannic chloride and bases form unstable **stannic hydroxide**, thus:—



This hydroxide has acid properties. It is unstable, and by loss of water yields first **alpha-stannic acid** (H_2SnO_3) and finally **stannic oxide** (SnO_2). The gelatinous precipitate of stannic hydroxide dissolves in an excess of sodium hydroxide (519, 549), forming **sodium stannate**, thus:—



Sodium stannate is used in preparing fireproof cotton and in weighting silk. The cotton fabric is soaked in sodium stannate solution, washed, and dried, and then treated with ammonium sulphate solution. The ammonium stannate thereby produced becomes stannic acid, which loses water and leaves stannic oxide as a non-inflammable precipitate. Silk fabrics, treated in a similar way, become heavier and more attractive in finish. The added tin compound is much greater (25 to 200 per cent) than the weight of the silk itself. Such silks are not durable.

568. Only one ore of lead. — The most abundant native compound and the chief source of the metal is **lead sulphide** (galena, PbS). Other native compounds are the carbonate (cerussite, PbCO_3) and the sulphate (anglesite, PbSO_4). Lead ore is found in the United States in the Middle West (Illinois, Iowa, Wisconsin, and Missouri), Colorado, Idaho, and Utah.

Lead and its compounds have been used since the dawn of history. The Chinese have used it for ages to line chests in which tea is stored

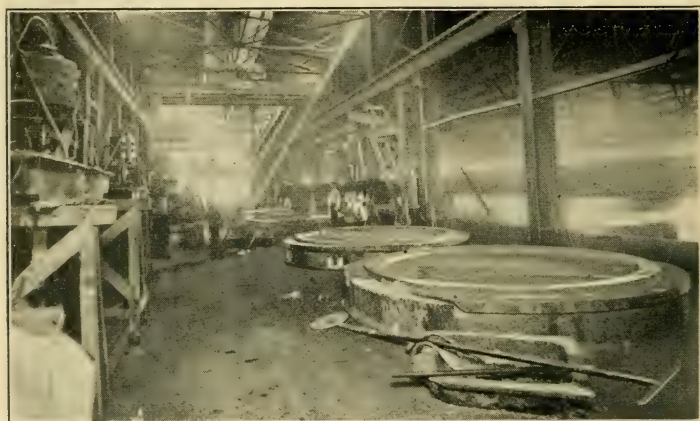


Fig. 206. — Desilverizing kettles in which lead is freed from silver and gold

and transported. The Romans, who obtained it from Spain, called it *plumbum nigrum*, i.e. black lead, and used it for conveying water just as we do today. The symbol Pb comes from *plumbum*.

569. Metallurgy of lead. — Lead is obtained from galena by first roasting the ore to change part of the sulphide to oxide. This product (sulphide and oxide) is then mixed with raw ore, iron oxide, limestone, and coke, and smelted in a blast furnace. Complex changes take place, which consist essentially in (a) reduction of the lead oxide to lead

by the carbon and carbon monoxide, (b) transformation of lead sulphide to lead and iron sulphide, and (c) removal of silica and other impurities as a slag by the limestone.

Lead produced by this process is impure and must be **refined**. The impurities make the lead hard and unfitted for most uses. The lead is first heated in a “softening” furnace at a low temperature to oxidize the arsenic and antimony. The impure lead (containing chiefly gold and silver) is melted with a small proportion of zinc in huge desilverizing kettles (Fig. 206); the silver and gold together with the zinc and some lead form a crust on the top. This is skimmed off and heated in a retort to distill off the zinc; the residue is



Fig. 207. — Casting refined lead into molds

next “cupelled,” *i.e.* heated by a stream of air. By the latter process the lead is oxidized to litharge (PbO) which is skimmed or blown off, leaving the silver and gold (581, second paragraph). These two metals are separated as described in 581 (last paragraph) and 592.

The purified lead left in the desilverizing kettles is cast into molds by machinery (Fig. 207).

Lead is also **refined by electrolysis**. The cathode is a sheet of pure lead, and the electrolytic solution is a mixture of lead fluosilicate (PbSiF_6) mixed with gelatin. When the current passes, pure lead is

deposited on the cathode and the other metals remain attached to the remnant of the anode or sink to the bottom as mud. Subsequently the gold and silver as well as bismuth are recovered from the anode residues. (Compare 529.)

570. Properties of lead. — Lead is a bluish metal. When scraped or cut, it has a brilliant luster, which soon disappears, owing to the formation of a film of oxide and basic carbonate. It is soft, and can be scratched with the finger nail; it also discolors the hands, and when drawn across a rough surface it leaves a black mark. Lead is not tough nor very ductile and malleable, though it can be made into wire, rolled into sheets, and pressed while soft (just below the melting point) into pipe. It is a heavy metal, its specific gravity being 11.4; with the exception of mercury, it is the heaviest of the familiar metals. It melts at 327°C .

571. Chemical conduct of lead. — Lead when heated strongly in air changes into oxides (mainly the monoxide, PbO). Hydrochloric and sulphuric acids have little effect upon compact lead. Nitric acid changes it into lead nitrate ($\text{Pb}(\text{NO}_3)_2$). In the presence of air, weak acids like acetic acid (or vinegar), and acids from fruits and vegetables change it into soluble, poisonous compounds; hence cheap tin-plated vessels, which sometimes contain lead, should never be used in cooking. Soft water containing air, and especially carbon dioxide, dissolves lead; and lead pipes should not be used to convey rain water or water containing ground gases. Certain metals, *e.g.* zinc and iron, precipitate lead from its solutions as a grayish mass, which often has a beautiful treelike appearance (536).

572. Uses of lead. — Lead is extensively used as pipe. Lead pipe is not only used to convey water, but also as a sheath for electric cables, both overhead and underground.

Sheet lead is used to cover roofs and to line sinks, cisterns, and the cells employed in some electrolytic processes. The lead chambers and some evaporating pans used in manufacturing sulphuric acid are made of sheet lead. Shot and bullets are lead (alloyed with a little arsenic or antimony). Spongy lead is used in preparing the plates of storage batteries. Lead wool (very fine wire) is used to calk pipe joints.

Lead is used to make many useful alloys. Those containing considerable lead are type metal (lead, tin, antimony), solder (lead and tin), Britannia and Babbit metals, and pewter (532). Most fusible metals contain lead (441).

573. Lead oxides. — There are three oxides. **Lead monoxide** (PbO) is a yellowish powder known as **massicot**, or a buff-colored crystalline mass called **litharge**. It is formed by heating lead in a current of air. It is made this way, though considerable is obtained as a by-product in separating silver from lead (569). Large quantities are used in preparing some oils and varnishes, in making flint glass, and a glaze for pottery, and as the source of many lead compounds. **Lead tetroxide** (red lead or minium, Pb_3O_4) is a red powder, varying somewhat in color and composition. The pure compound is believed to have the formula Pb_2PbO_4 , *i.e.* plumbous plumbate. It is prepared by heating lead or lead monoxide at the right temperature (about 450°C ., but not over 545°C .). It is used in making flint glass. Pure grades are made into artists' paint, but the cheap variety is used to paint structural iron work (bridges, gasometers, etc.), hulls of vessels, and agricultural implements. A mixture of linseed oil and red lead is used by plumbers and gas fitters to make joints tight. **Orange mineral** has about the same composition as red lead, though

its color is lighter; its uses are the same. **Lead dioxide** (PbO_2) is a brown powder formed by treating lead tetroxide with nitric acid or by the action of bleaching powder on sodium plumbite (Na_2PbO_2 , formed by dissolving lead hydroxide in sodium hydroxide). It is a strong oxidizing agent. It is extensively used as the essential ingredient of the positive plate of electric storage batteries.

574. Lead carbonate (PbCO_3) is found native as the transparent, crystallized mineral cerussite. It is obtained as a white powder by adding sodium bicarbonate solution to a solution of a lead salt. Sodium and potassium carbonates, however, produce basic lead carbonates. The most important of these basic carbonates has the composition corresponding to the formula $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$, and is known as **white lead**.

575. Paints. — A paint consists essentially of a powder suspended in an oil, usually linseed oil, which “dries” (really oxidizes) to a tough film and sticks to a surface. The powder, which is often called a **pigment**, gives opacity and color to the paint. It also fills the minute holes in the dried oil film and thereby assists in protecting the surface of the painted object from the action of oxygen and moisture.

576. White lead is a heavy, white powder which mixes well with linseed oil, and is used extensively as a **white paint**. It is also the basis of many colored paints, pigments being added to give the desired color. White lead paint has a marked covering power, *i.e.* it covers a surface well; it also dries to a good finish. But it darkens on exposure to hydrogen sulphide (which is often present in the air of cities, **257**), owing to the formation of black lead sulphide (PbS). In recent years other paint bodies, as the solids are called, have been mixed with, or substituted for, white lead, *e.g.* zinc oxide (**549**), kaolin, barium sulphate, and lithophone (a mixture of zinc sulphide and barium sulphate).

These are white solids which do not darken in the air, and they often improve the paint in other ways.

577. Manufacture of white lead. — White lead is manufactured by several processes. The Dutch process is the oldest, having been used as early as 1622. It is essentially the same today, though many details have been improved.

Perforated disks of lead, called buckles, are put in earthenware pots, which have a separate compartment at the bottom, containing a weak solution of acetic acid (Fig. 208).

These pots are arranged in tiers in a large building, and spent tan bark is placed between each tier. The building is now closed except openings for the entrance and exit of air and steam. The fermentation of the tan bark produces carbon dioxide and moisture; heat is also liberated. The heat volatilizes the acetic acid which changes the lead into lead acetate. The moist carbon dioxide converts the lead acetate into basic lead carbonate or white lead. The operation is allowed to proceed until the lead is entirely transformed — sixty to one hundred days.

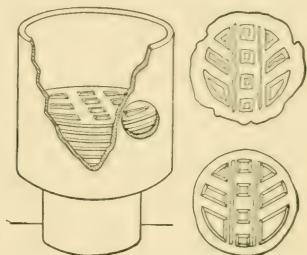


Fig. 208. — Earthenware vessel containing lead buckles to be made into white lead. Buckle before (lower) and after (upper) corrosion

Commercial white lead is manufactured by other processes. In one, melted lead is blown ("atomized") into a very fine powder by a jet of steam, and the powder is treated for several days with acetic acid, carbon dioxide, and air.

578. Other lead compounds. — Native lead sulphide (PbS) is the mineral galena, the chief ore of lead. It resembles lead in appearance, but is harder and is usually crystallized as cubes, octahedrons, or their combinations (Fig. 209). It is obtained as a black precipitate by the interaction of hydrogen sulphide (or other soluble sulphides) and a solution of a lead salt. Its formation is a **test for lead** (and of course for hydrogen sulphide). **Lead**

chloride (PbCl_2) is a white solid formed by adding hydrochloric acid or a soluble chloride to a cold solution of a lead salt. It dissolves in hot water. **Lead sulphate** (PbSO_4) is a white solid, formed by adding sulphuric acid or a soluble sulphate to a solution of a lead salt. It is very slightly



Fig. 209. — Galena crystals (cube, octahedron and cube, octahedron)

soluble in water, but soluble in concentrated sulphuric acid, hence crude sulphuric acid often contains lead sulphate. **Lead chromate** (PbCrO_4) is a yellow solid formed by adding a solution of a lead compound to a solution of potassium chromate or potassium dichromate. It is sometimes called chrome yellow and is used as a pigment. Its formation serves as a **test for lead**.

EXERCISES

1. Describe the metallurgy of (a) tin and (b) lead.
2. Summarize the properties and uses of (a) tin and (b) lead.
3. Name three alloys which contain large proportions of (a) tin and (b) lead. Name several alloys containing a minor proportion of (a) tin and (b) lead.
4. Topics for home study: (a) History of tin. (b) Tin disease. (c) Tin plate industry. (d) Tin mordants. (e) Tin foil and its substitutes. (f) Different processes of making white lead. (g) Paints and painting. (h) History of lead. (i) Lead poisoning.
5. State the tests for (a) tin and (b) lead.
6. What are the properties and uses of each lead oxide?
7. What tin compound is a reducing agent?
8. Practical topics: (a) How would you test paint for lead? (b) What advantage has tin over lead for pipes? Lead over tin? (c) What is "tin"? Block tin? Tin foil? Tinware? (d) What is red lead? White lead? Black lead? (e) How would you show

the presence or absence of lead in a lead pencil? (f) Should lead paint be used on the walls of a chemical laboratory? Why? Zinc paint? Why?

PROBLEMS

1. Calculate the weight of (a) lead in 250 gm. of PbO_2 and (b) of tin in 250 gm. of SnO_2 .

2. How many gm. of lead in (a) 200 gm. of galena, (b) in 1 kg. of litharge, (c) a metric ton (2200 lb.) of red lead?

3. Write the formulas of the following compounds by applying the principle of valence: Lead fluoride, lead acetate, lead dichromate, stannous iodide, stannic bromide, stannous sulphide, stannic sulphide.

4. Calculate the atomic weight of lead or tin from the following: (a) 16.2956 gm. of lead give 17.554 gm. of PbO ; (b) 4.9975 gm. of PbCl_2 require 3.881 gm. of silver to precipitate the lead; (c) 25 gm. of tin give 31.8 gm. of stannic oxide (the specific heat of tin is 0.055); (d) 29.42 gm. of tin unite with 35.4 gm. of chlorine, and the vapor density of the compound is 8.303.

5. Complete and balance the following: (a) $\text{SnCl}_2 + \text{HgCl}_2 = \text{SnCl}_4 + \text{---}$; (b) $\text{Sn} + \text{HNO}_3 = \text{H}_2\text{SnO}_3 + 4\text{NO}_2 + \text{---}$; (c) $\text{SnCl}_2 + \text{H}_2\text{S} = \text{SnS} + \text{---}$; (d) $\text{Pb}(\text{NO}_3)_2 + \text{HCl} = \text{PbCl}_2 + \text{---}$.

6. Calculate the percentage composition of the two chlorides of tin and show how they illustrate the law of multiple proportions.

7. A cube of lead is 6 cm. on each edge. How much does it weigh?

8. A block of tin measures $30 \times 10 \times 5$ cm. and weighs 10.95 kg. What is the specific gravity of the tin?

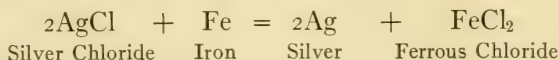
CHAPTER XXXVI

SILVER — PHOTOGRAPHY — GOLD

579. Introduction. — Silver and gold are precious metals. They have been used for ages as ornaments and coins. The Latin names of these metals are *argentum* and *aurum*, from which the symbols Ag and Au are derived.

580. Occurrence of silver. — Free silver occurs as flakes or wire in certain kinds of rock, though generally as alloys of gold and copper. The chief ore is silver sulphide (argen-tite, Ag_2S), which is usually associated with lead sulphide. Copper ores also contain silver. In fact, silver-bearing ores are an important source of silver.

581. Metallurgy of silver. — Ores containing free silver, or silver compounds that can be easily changed into silver, are treated by the **amalgamation process**. The powdered ore is first changed, if necessary, into silver chloride by roasting with sodium chloride. The silver is freed by agi-tation with water and iron (or an iron compound); the simplest equation for this reaction is: —



The silver is extracted by adding mercury, which forms an amalgam with the silver (**556**). When the amalgam is heated, the mercury distils off and the silver — with some gold — remains behind.

Silver is extracted from lead ores by the **Parkes process**. After the sulphur, arsenic, and other impurities have been

removed from the lead ores by roasting, the final mixture of lead, silver, and gold is melted with about 1 per cent of zinc. As the mixture cools, an alloy of silver, gold, zinc, and a little lead rises to the surface, solidifies, and is skimmed off. This process is repeated several times. The skimmings are heated in a retort to volatilize the zinc, and then in a shallow furnace (cupel furnace) to convert the lead into an oxide (PbO), which melts and runs off, leaving an alloy of silver and gold (569 and Fig. 206).

Silver can be separated from the gold by several processes. In the **older process** the alloy is boiled with concentrated nitric (or sulphuric) acid; the gold is not acted upon, but the silver forms a soluble silver salt (nitrate or sulphate). The silver is precipitated from the diluted solution by metallic copper. Silver is also refined by **electrolysis** in much the same way as copper; the anode is rich in silver and the solution is silver nitrate in nitric acid (529).

582. Properties of silver. — Silver is a lustrous, white metal. It is harder than gold, but softer than copper. Like copper, it is ductile and malleable, and can be easily made into various shapes. Silver has a specific gravity of about 10.5, being heavier than copper, but lighter than lead. It melts at about 960°C . Silver conducts electricity the best of all metals, but it is too expensive for general use.

583. Chemical conduct of silver. — Silver does not tarnish in air unless hydrogen sulphide is present, and then the familiar brown (or black) film of silver sulphide (Ag_2S) is produced. It also turns black when in contact with organic sulphur compounds. For example, silver spoons become black in eggs or mustard. The tarnishing of household silver is caused by hydrogen sulphide in illuminating gas or gas from burning coal. So-called "oxidized" silver is not oxidized, but coated with silver sulphide.

Certain metals, especially mercury, precipitate silver from solution in beautiful crystals (536).

Silver is only very slightly acted upon by hydrochloric acid, and not at all by molten sodium hydroxide, potassium hydroxide, or potassium nitrate. Nitric acid and hot concentrated sulphuric acid change it into the nitrate (AgNO_3) and the sulphate (Ag_2SO_4) respectively. Sodium cyanide in the presence of air and water changes it into sodium silver cyanide ($\text{NaAg}(\text{CN})_2$).

Solutions of simple silver salts contain silver ions (Ag^+), whereas complex salts yield complex ions, *e.g.* the silver-cyanogen ion ($\text{Ag}(\text{CN})_2^-$) and the silver-ammonium ion ($\text{Ag}(\text{NH}_3)_2^+$).

584. Cleaning silverware. — Tarnished silverware is usually cleaned by rubbing off the film of sulphide with a very soft abrasive. It can be safely and quickly cleaned by an **electrolytic process**.

A piece of metallic aluminium and the tarnished object are immersed in a hot solution of sodium bicarbonate and sodium chloride, and kept in contact. As soon as the cleaning is accomplished, the object is removed, thoroughly washed in clean, hot water, and dried. The proportions for household use are a teaspoonful each of baking soda and common salt to a quart of water. The best results are obtained when the solution is very hot and the two metals are in good contact.

585. Uses of silver. — Silver is made into coins, jewelry, ornaments, and tableware. Pure silver is too soft for constant use, and is usually hardened by adding a small amount of copper. These alloys are used as coins and for jewelry. Silver coins of the United States and France contain 900 parts of silver to 100 of copper, and are called 900 fine. British silver coins are 925 fine; this quality is called **sterling silver**, and from it much ornamental and

useful silverware is made. Large quantities of silver are used to plate other metals and to make silver compounds, especially silver nitrate.

586. Silver plating. — Metals cheaper than silver, *e.g.* copper, can be readily coated or plated with pure silver. Plated silverware has the appearance of solid or pure silver. The object to be plated is carefully cleaned, and made the cathode in a solution of potassium (or sodium) silver cyanide; the anode is a plate of pure silver (Fig. 210). When the electric current is passed the silver dissolves from the anode and deposits on the cathode. The deposit of silver is dull, but can be brightened by rubbing.

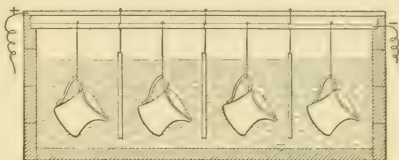
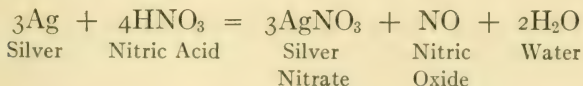


Fig. 210. — Silver plating

Mirrors and reflectors (especially for automobiles) are made by coating glass with silver. A mixture of silver nitrate and ammonium hydroxide is reduced to metallic silver, which sticks to the glass and is protected by varnishing it.

587. Silver nitrate (AgNO_3). — This is the most important compound of silver. It is a white crystalline solid, made from silver and nitric acid, thus: —



It is very soluble in water. It turns dark in contact with organic matter owing to reduction to metallic silver. For this reason it blackens the skin; if applied long enough, it disintegrates the flesh, and is often used by surgeons to cauterize sores or abnormal growths. Silver nitrate is the essential substance used in making some **indelible inks**; the cloth to which the ink is applied reduces the silver compound to black metallic silver.

588. Silver halides. — **Silver chloride** (AgCl) is made by adding hydrochloric acid or a chloride solution to a solution of a silver compound. It is a white, curdy solid, which soon turns violet in the light and finally black. It is converted by ammonium hydroxide into a soluble complex compound ($\text{Ag}(\text{NH}_3)_2\text{Cl}$), from which silver chloride can be reprecipitated by adding an excess of nitric acid. **Silver bromide** (AgBr) and **silver iodide** (AgI) are analogous to silver chloride in their properties and methods of formation; they are used in photography.

The formation and properties of silver chloride constitute the **test for silver**.

589. Photography is based mainly on the fact that silver salts, especially the bromide and iodide, darken when exposed to the light.

The photograph is taken on a glass plate, or celluloid film coated on one side with a thin layer of gelatin containing very fine particles of silver bromide. The plate or film is **exposed** in the camera. The light that comes from the object being photographed passes through the lens and forms an image on the plate or film and changes the silver salt in proportion to the intensity of the light reflected from the object. The exposed plate, however, reveals no change until it is **developed**. This process consists in immersing the plate in a solution of a reducing agent, *e.g.* hydroquinone, pyrogalllic acid, or special mixtures. As the developer acts upon the silver salt on the plate, the image appears. This is really a deposit of finely divided silver which varies in thickness in proportion to the light that fell upon the plate, being thickest where the light was most intense.

After the plate has been properly developed, it still contains some silver salt not altered by the light; and if the salt were left on the plate or film, the image would be clouded and finally obliterated by the light. The image is, therefore, **fixed** by dissolving the silver salt with a solution of sodium thiosulphate (or "hyposulphite") and washing the plate thoroughly. On the fixed plate the dark parts of the object appear light and the light parts dark; and since the image is the reverse of the object, the plate in this condition is called a **negative** (Fig. 211, left).

The **print**, or **photograph**, is made on paper coated with a mixture much like the one on the plate, though less sensitive to light. The paper is laid upon the negative and exposed to the light, so the light

must pass through the negative first. Since the negative obstructs the light in proportion to the thickness of the silver deposit, the dark and light parts are reversed and we thereby obtain a positive, *i.e.* a photograph which has approximately the same shading as the object (Fig. 211, right).



Fig. 211. — Daguerre — a pioneer in photography (negative (left) and positive (right))

On some kinds of paper the image appears at once, but on others it must be developed and fixed. Subsequent treatment called **toning** produces special results.

590. Occurrence of gold. — Gold is widely distributed, but not abundantly in many places. Its native compounds are few and rare; the only important ones are the **tellurides** (compounds of tellurium, *e.g.* AuAgTe_2). It is never found pure, being alloyed with silver and occasionally with copper or iron. It is disseminated in fine, almost invisible, particles among ores of other metals, though not so abundantly as silver, and is recovered in the last stages of their purification (**569**, **581**). Much gold is found in veins of quartz, and in the sand formed by the disintegration of gold-bearing rocks.

591. Mining and metallurgy of gold. — Gold was formerly mined by **washing** the gold-bearing sand in large pans or cradles. Now the sand is scooped up by huge dredgers and washed by machines. In **placer mining** and **hydraulic mining**, streams of water wash away the lighter materials, but leave the heavier gold behind. From this mixture,

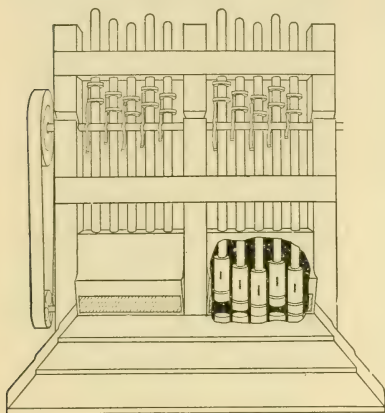


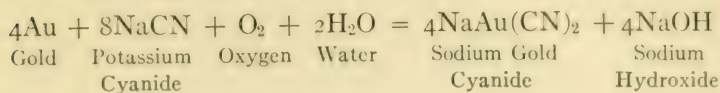
Fig. 212. — Stamp mills for crushing gold ore to a fine powder. Cut away on the right to show stamps (2 and 5 are lifted). Crushed ore passes through sieve (left) and the gold is caught by mercury on the plates (front). The rocky refuse is washed away.

gold and silver are extracted with mercury. In vein or quartz mining the lumps of gold-bearing quartz are crushed to a fine powder in **stamp mills**, *i.e.* in a row of huge iron mortars by hard pestles (Fig. 212). The moistened mass is passed over copper plates coated with mercury which collects or dissolves the gold and other metals. The **amalgam** is heated, as in the metallurgy of silver, to remove the mercury, and the gold is extracted from the residue.

In the **chlorination process** the ore is treated with water containing chlorine or with bleaching powder and sulphuric acid; this operation forms a soluble gold chloride (AuCl_3), from which the gold is precipitated as a fine powder by ferrous sulphate or other reducing agents.

In the **cyanide process** the ore, usually low grade, or the slime from a previous extraction, is mixed with a weak

solution of sodium cyanide and exposed to the air; this operation changes the gold into a soluble cyanide, thus:—



The gold is separated from this solution by electrolysis or precipitated by zinc shavings (536).

592. Refining gold. — Refining is accomplished by parting or by electrolysis. By the old parting process known as **quartation** an alloy of gold and silver, in which the gold is about one fourth of the whole, is treated with nitric acid; this operation changes the silver into the nitrate from which the pure gold may be readily removed. The metals can be parted by the method described under silver, viz. by boiling with concentrated nitric or sulphuric acid (581). By this treatment the silver is dissolved and the gold is left as a brownish, porous mass.

These processes have been largely replaced by **electrolytic processes**. In one, which is used in the United States mints, the solution is a mixture of gold chloride and hydrochloric acid, the anode is an alloy rich in gold, and the cathode is pure gold. Gold is deposited on the cathode, and the silver forms silver chloride around the anode.

The purity of gold is expressed in **carats**. Pure gold is 24 carats fine. An alloy, for example, containing 22 parts of gold and 2 parts of copper is 22 carat gold.

593. Properties of gold. — Pure gold is a yellow metal; the color of commercial gold varies with the alloying metal. It is nearly as soft as lead, and is the most ductile and malleable of all the metals. The **leaf** into which it can be beaten is very thin — in some cases requiring 110,000 leaves to make a thickness of 1 centimeter. Gold is one of the

heaviest metals, its specific gravity being about 19.3. It forms alloys with most metals.

Air, oxygen, and most acids do not attack it, and for this reason it is sometimes called a **noble metal**. It is changed into gold chloride (AuCl_3) by chlorine and *aqua regia* (159, 186). With sodium cyanide, as described in 591, it forms sodium gold cyanide ($\text{NaAu}(\text{CN})_2$).

594. Uses of gold. — Pure gold is too soft for use as jewelry or coins, and it is usually alloyed with copper or silver. Gold coins contain gold and copper. The United States standard gold coins contain 90 per cent gold and 10 per cent copper. Gold leaf of various grades is used to ornament books and signs. Jewelers use gold for many purposes; such gold varies from 12 to 22 carats in purity, though 14 or 18 carat gold is commonly used. Much jewelry is gold plated (595). On account of its malleability, feeble chemical action, and beauty, gold is used by dentists for filling teeth.

595. Gold compounds. — Gold like several other metals forms two series of compounds — **aurous** and **auric**, in which the gold has the valence of 1 and 3 respectively. **Auric chloride** (AuCl_3) is formed when gold is treated with chlorine or *aqua regia*. Auric chloride in dilute solution is reduced by stannous chloride solution to a beautiful purple precipitate; the latter is called "purple of Cassius," and is finely divided gold (a colloidal solution). Its formation is the **test for gold**. In gold plating, which is much the same as silver plating, the solution contains a potassium gold cyanide ($\text{KAu}(\text{CN})_2$ or $\text{KAu}(\text{CN})_4$).

EXERCISES

1. Prepare a summary of the metallurgy of (a) silver and (b) gold.
2. Describe in order the steps in taking a photograph.
3. How is gold purified? What is 14 carat gold?
4. Prepare a summary of the properties of (a) silver and (b) gold.
5. If silver cost only ten cents a pound, for what would it probably be used? What is the present price of (a) silver and (b) gold?

6. Why is gold "valuable"? What is sterling silver?
7. Review topics: (a) *Aqua regia*. (b) Amalgams. (c) Ions and ionization. (d) Valence. (e) Colloidal solutions.
8. State uses of (a) silver and (b) gold that depend on the properties.
9. Write the formulas of these silver compounds by applying the principle of valence: Sulphide, hydroxide, oxide, acetate, carbonate, nitrate, orthophosphate.
10. As in Exercise 9: Auric chloride, aurous bromide, auric sulphide, auric hydroxide, aurous chloride.
11. Complete and balance: $\text{Ag}_2\text{SO}_4 + \text{KBr} = \text{K}_2\text{SO}_4 + \text{---}$. Write the final equation in ionic form.

PROBLEMS

1. Calculate the weight of (a) silver in 1 kg. of silver nitrate and (b) gold in 1 gm. of potassium auricyanide.
2. Calculate the percentage composition of the two gold chlorides and show that they illustrate the law of multiple proportions. (Use exact atomic weights.)
3. How many grams of gold in a 14 carat ring which weighs 14 gm.?
4. (a) What weight of silver can be obtained from an American ten cent piece which weighs 2.44 gm.? (b) How much gold from an American gold coin weighing 3.75 gm.?
5. How much silver chloride can be made from 47 gm. of silver nitrate?

CHAPTER XXXVII

CHROMIUM — MANGANESE — PLATINUM — NICKEL AND COBALT — OTHER METALS

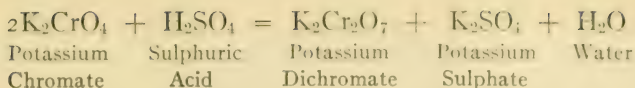
596. Occurrence of chromium. — Metallic chromium is never found free. Its chief ore is ferrous chromite (chrome iron ore, $\text{Fe}(\text{CrO}_2)_2$). Traces of chromium occur in many minerals and rocks, *e.g.* emerald and serpentine, and verd antique marble. Chromite is mined in Greece, New Caledonia, New South Wales, and Turkey.

597. Preparation, properties, and uses of chromium. — Chromium is produced by reducing chromium trioxide (Cr_2O_3) with granulated aluminium (517).

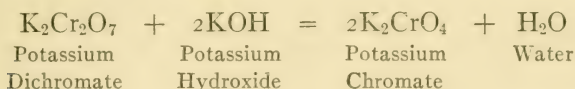
Chromium is a silvery, crystalline, hard, brittle metal. Its specific gravity is about 6.9 and its melting point is about 1520°C . It is not oxidized by air at ordinary temperatures.

Chromium is used to harden the steel made into armor plate, projectiles, safes, vaults, and parts of the stamp mills used to crush gold-bearing quartz (591). This hardened steel is called **chrome steel** (499). It forms other hard alloys. One commercial form of chromium is an alloy of 65 to 80 per cent chromium, a little carbon, and the rest iron; this alloy is called **ferrochrome**. Another alloy, called **nichrome** or **chromel**, contains nickel.

598. Chromates and dichromates. — Chromates are salts of chromic acid (H_2CrO_4) which is formed when the red chromium oxide (chromic anhydride, CrO_3) is dissolved in water. **Potassium chromate** (K_2CrO_4) is the commonest chromate; it is a lemon-yellow, crystalline solid, very soluble in water. Acids change it into the dichromate, thus: —

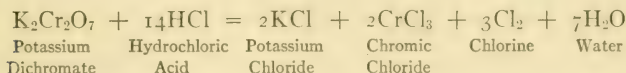


Lead chromate (PbCrO_4) is a yellow solid, formed by adding a lead salt solution to potassium chromate (or dichromate). Its formation is a **test for chromium** (and lead, 578). It is known as **chrome yellow**, and is used in making yellow paint. **Potassium dichromate** (sometimes called **bi-chromate**) ($\text{K}_2\text{Cr}_2\text{O}_7$) is a red solid. It forms large anhydrous crystals. It is less soluble in water than potassium chromate, and its solution contains both chromate (CrO_4^{--}) and dichromate ($\text{Cr}_2\text{O}_7^{--}$) ions. Alkalies change it into a chromate, thus: —

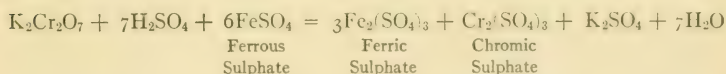


Potassium dichromate is used in dyeing, calico printing, and tanning, in bleaching oils, and in manufacturing other chromium compounds and dyestuffs.

Potassium dichromate is an oxidizing agent. When hydrochloric acid is added to potassium dichromate, the oxygen of the dichromate oxidizes the hydrogen of the acid and liberates chlorine, thus: —



The equation for the reaction in the case of ferrous sulphate is: —



Sodium dichromate ($\text{Na}_2\text{Cr}_2\text{O}_7$) is a red solid much like potassium dichromate, which it has largely displaced.

Potassium chromate is **manufactured** by roasting chrome iron ore with lime and potassium carbonate. The potassium chromate extracted from the mass is changed by sulphuric acid into potassium dichromate.

Potassium chromate is also formed as a yellow mass by fusing on porcelain or platinum a mixture of a chromium compound, potassium carbonate, and potassium nitrate — a **test for chromium**.

599. Chrome alum ($K_2Cr_2(SO_4)_4 \cdot 24H_2O$) is a purple, crystalline solid (521).

Chrome alum is used as a mordant in dyeing and calico printing (522). It is also used in tanning leather because it readily forms chromium hydroxide ($Cr(OH)_3$) which changes the hide into a relatively insoluble compound.

600. Other chromium compounds. — **Chromic oxide** (Cr_2O_3) is a bright green powder prepared by heating chromic hydroxide ($Cr(OH)_3$). It is the basis of the chrome green pigments used to color glass and porcelain. When chromium compounds are heated with borax they color the bead green, owing to this oxide (458).

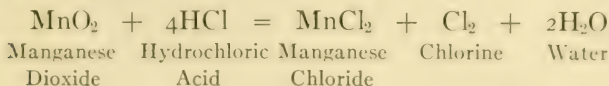
There are several **chromic hydroxides**. The typical one is a bluish solid formed by the interaction of a chromic compound (*e.g.* chrome alum) and an alkaline hydroxide, carbonate, or sulphide. The chromic hydroxide is soluble in an excess of sodium (or potassium) hydroxide. That is, it is changed into a soluble chromite, just as aluminium hydroxide forms soluble aluminates. Unlike aluminates, however, the chromites are changed back into chromic hydroxide by boiling.

When concentrated sulphuric acid is added to a saturated solution of potassium dichromate (or chromate), **chromium trioxide** (CrO_3) separates as long, bright red crystals; this oxide is often called **chromic acid** (598). It is a vigorous oxidizing agent.

601. Occurrence of manganese. — This metal is not found free in nature, but its oxides and hydroxides are widely distributed and rather abundant. The chief compound is **manganese dioxide** (pyrolusite, MnO_2).

602. Preparation, properties, and uses of manganese. — Manganese is prepared by heating manganese dioxide with charcoal in an electric furnace, or by reducing the oxide with aluminium (517). The metal is grayish, hard, and brittle. It melts at $1225^\circ C$. Manganese, alloyed with iron, is used in making steel (499). Spiegel iron contains from 5 to 20 per cent of manganese, while ferromanganese contains 20 per cent or more.

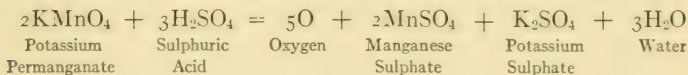
603. Manganese dioxide (MnO_2) is a black solid and is often called black oxide of manganese. It is an oxidizing agent. When heated it yields oxygen. When heated with hydrochloric acid (**144**) manganous chloride, chlorine, and water result, thus: —



It colors glass and borax a beautiful amethyst, and is often used in glass making to neutralize the green color caused by impurities. Large quantities are used in the manufacture of glass, dry batteries, and manganese alloys.

604. Potassium permanganate (KMnO_4) is a dark purple, glistening, crystalline solid. It is very soluble in water, and the solution is red, purple, or black, according to the concentration. The solution contains permanganate ions (MnO_4^-). Potassium permanganate is used as an oxidizing agent, a disinfectant, and an antiseptic.

The uses of potassium permanganate depend mainly upon its oxidizing power. With sulphuric acid the action is thus: —



The liberated oxygen oxidizes any organic matter present, and the solution becomes colorless (or brownish) owing to the reduction of the potassium permanganate to colorless manganese compounds.

605. Other manganese compounds. — The chloride (MnCl_2) and sulphate (MnSO_4) are pink, crystalline salts. The sulphide (MnS) is a flesh-colored precipitate formed by adding ammonium sulphide to the solution of a manganese salt, the color distinguishing it from all other sulphides; its formation serves as a **test for manganese**. Another test is the formation of green **potassium manganate** (K_2MnO_4) by fusing a mixture of a manganese compound, potassium hydroxide (or carbonate), and potassium nitrate. **Sodium manganate** (Na_2MnO_4) is used in solution as a disinfectant.

606. Occurrence of platinum. — Platinum occurs as the chief ingredient of an alloy called platinumore. The associated metals are osmium, iridium, and palladium; iron, gold, and copper are usually present. Only one native compound is known, viz. platinum arsenide (sperrylite, PtAs_2).

607. Preparation of platinum. — Platinum is obtained by boiling the ore with *aqua regia*, then precipitating with ammonium chloride, and heating. This **spongy platinum** is melted, and hammered while hot into a compact form. It is a scarce and expensive metal.

608. Properties and uses of platinum. — Platinum is a lustrous, gray-white, somewhat soft metal. It is malleable and ductile. Sheet platinum is cut into squares — the familiar **platinum foil** of the laboratory, or made into crucibles, dishes, and stills. Its use in these forms is based partly on its high melting point (1755°) and partly on its resistance to acids and other corrosive chemicals. Although it is attacked by fused caustic alkalies (e.g. NaOH), low melting metals (e.g. lead), and *aqua regia*, platinum is practically indispensable in the chemical laboratory and is used in many chemical processes involving accurate analysis.

Platinum is a good conductor of electricity and is made into small electrodes. Formerly large quantities were consumed in electrical apparatus, especially as the “sealed in” wires in electric light bulbs, but this need is now met by an alloy of iron and nickel called **platinite** (499, 610).

Platinum is a very heavy metal. Its specific gravity is about 21. (Lead is 11.4.)

In the form of a black, porous mass it is called **spongy platinum**, and a still finer form is called **platinum black**. Asbestos coated with platinum is used as the catalyzer in the contact method for making sulphuric acid (269, 270).

Platinum forms low melting alloys with other metals, and should never be heated with lead, similar metals, or their compounds. With

iridium, however, it forms a very hard alloy of which certain standard metric apparatus is made. Platinum is used in making rings and as mountings for gems.

609. Occurrence and properties of nickel. — Small amounts of metallic nickel are found in meteorites. The chief ores are nickel-bearing iron sulphides, which are abundant in the Sudbury district, Canada, and the silicates found in New Caledonia.

Nickel is a silver-white metal, which takes a brilliant polish. It is ductile, hard, malleable, tenacious, and does not tarnish in the air. It is attracted by a magnet.

610. Uses of nickel. — Nickel is an important ingredient of coins and alloys.

The per cent of nickel is 12 in the United States cent and 25 in the five-cent piece. German silver contains from 15 to 25 per cent of nickel (532). **Platinite** is an alloy of nickel (46 per cent) and iron; it is used as a substitute for platinum (499, 608). **Monel metal** contains nickel (70 per cent) and copper (28 per cent); it is stronger than ordinary steel, is not attacked by acids, and can be cast and machined.

Nickel is used to coat or plate other metals, especially iron and brass. **Nickel plating** is done by electrolysis, as in silver and gold plating, though the electrolytic solution contains ammonium nickel sulphate ($(\text{NH}_4)_2\text{Ni}(\text{SO}_4)_2$), not a cyanide (586, 594, 595). The deposit of nickel is hard, brilliant, and durable. An important use of nickel is in the manufacture of **nickel steel** (5 per cent nickel) which is used for the armor plate and turrets of battleships (499).

611. Nickel compounds. — Nickel forms two series of compounds — the **nickelous** and the **nickelic**. The nickelous are more common and many of them are green. The **test for nickel** is the formation of apple-green nickelous hydroxide ($\text{Ni}(\text{OH})_2$) by the interaction of an alkali and a dissolved nickel salt.

612. Cobalt (Co) generally occurs combined with arsenic and sulphur in complex minerals, and is often associated with nickel compounds. It is a lustrous metal with a reddish tinge. It is harder than iron but less magnetic.

Cobalt forms two series of compounds — the **cobaltous** and the **cobaltic**. The cobaltous compounds are more common. **Cobaltous nitrate** ($\text{Co}(\text{NO}_3)_2$) is a red solid, which crystallizes with six molecules of water of crystallization. The hydrated compound loses water readily and turns blue when heated.

Some cobalt compounds are used to color glass, porcelain, and paper, especially a complex compound known as **smalt** or smalt blue. The blue color produced by fusing cobalt compounds into a borax bead is a **test for cobalt**. Another test is the precipitation of yellow **potassium cobaltinitrite** ($\text{K}_3\text{Co}(\text{NO}_3)_6$) by the addition of potassium chloride, potassium nitrite, and acetic acid to a solution of a cobaltous compound.

613. Molybdenum (Mo), tungsten (W), and uranium (U) are metallic elements related to chromium. **Ammonium molybdate** ($(\text{NH}_4)_2\text{MoO}_4$) is used to detect and determine phosphorus in fertilizers (426). **Tungsten** and **molybdenum** are used to make special steels (499); and tungsten is the filament of electric light bulbs; **sodium tungstate** is used for making cloth fireproof. Uranium compounds are obtained chiefly from pitchblende and uraninite. Salts of uranium (*e.g.* sodium uranate, $\text{Na}_2\text{U}_2\text{O}_7 \cdot 6\text{H}_2\text{O}$) are used in making fluorescent glass; such glass is green by transmitted light and yellow by reflected light. Uranium is a radioactive element (618).

614. Cerium (Ce) and thorium (Th) are members of the tin-lead family. They are constituents of rare minerals. Their compounds are prepared from **monazite** sand. A mixture of the oxides of thorium and cerium composes the Welsbach mantle (338). In making mantles, a cotton bag is dipped into a solution of thorium and cerium nitrates and burned. The cotton is consumed and the nitrates are changed into a firm mass of oxides. Thorium is a radioactive element (618).

EXERCISES

1. Describe the preparation of (a) chromium and (b) manganese by the aluminothermic method.
2. State test for (a) chromium and (b) manganese.

3. Review topics: (a) Uses of manganese dioxide. (b) Oxidation with potassium permanganate. (c) Special steels. (d) Alums. (e) Lead chromate.

4. Starting with MnO_2 how would you prepare in succession MnCl_2 and manganese sulphide? Starting with $\text{Fe}(\text{CrO}_2)_2$ how would you prepare K_2CrO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, potassium chromate, lead chromate?

5. Write the formulas of the chromate, dichromate, manganate, and permanganate corresponding to NH_4 , calcium, Pb^{II} , Al, magnesium, Ag, Na.

6. What is ferrochrome, black oxide of manganese, chrome yellow, chrome alum, pyrolusite, spiegel iron?

7. Enumerate the uses of platinum based on its properties.

8. Apply Exercise 7 to (a) nickel, (b) tungsten, (c) cerium and thorium.

PROBLEMS

1. What weight of the pure metals can be prepared by the interaction of aluminium and (a) 2 kg. of manganese dioxide, and (b) 2000 gm. of chromium trioxide?

2. How much potassium chromate can be made from potassium hydroxide and 299 gm. of the other compound?

3. What weight of potassium dichromate can be made from 3 tons of potassium chromate?

4. Complete and balance the following: (a) $\text{CaCrO}_4 + \text{K}_2\text{SO}_4 = \text{---} + \text{K}_2\text{CrO}_4$; (b) $\text{Pb}(\text{NO}_3)_2 + \text{---} = \text{PbCrO}_4 + \text{KNO}_3$; (c) $\text{MnO}_2 + \text{K}_2\text{CO}_3 + \text{O} = \text{K}_2\text{MnO}_4 + \text{---}$.

5. What is the atomic weight of chromium, if 6.6595 gm. of ammonium dichromate yield 4.0187 gm. of chromic oxide? (Use exact atomic weights.)

6. A piece of platinum foil measuring 10.5 cm. by 1.5 cm. weighs 0.723 gm. Into how many pieces, weighing 1 dg., may it be divided?

7. The specific heat of platinum is 0.0324. According to analysis, 35.5 gm. of chlorine unite with 48.6 gm. of platinum to form platinum chloride. What is (a) the atomic weight of platinum and (b) the formula of platinum chloride?

CHAPTER XXXVIII

RADIUM AND RADIOACTIVITY

615. What is radium? — Radium is a metallic element which belongs to the calcium family (399). It is a constituent of the rare minerals carnotite and pitchblende. Carnotite is mined chiefly in Colorado and Utah, and pitchblende in Czechoslovakia. The proportion of radium in these minerals is minute, only a few milligrams to the ton. But this small proportion of radium, together with barium, is carefully extracted by a laborious chemical process; the radium is then separated from the other metals as radium chloride or bromide by fractional crystallization.

Radium itself is never extracted. The term *radium* as usually used means a compound, *e.g.* the commercial salt is **radium bromide** (RaBr_2). Since the supply of radium ore is exceedingly limited and the extraction is expensive, the price of radium compounds is high, about \$100,000 a gram (of actual radium in the salt).

616. Discovery of radium. — About 1896 Henri Becquerel discovered that uranium compounds affect a photographic plate wrapped in black paper just as light does. Some minerals containing uranium compounds, particularly pitchblende, were later (1898) found by Madame Curie (Fig. 113) to be more active than uranium compounds. She studied pitchblende carefully, and subsequently in collaboration with her husband extracted from this mineral a minute quantity of a new substance which was exceedingly active. Madame Curie gave the name **radium** to the elementary constituent in it. Since then, although very small amounts of radium compounds are available, radium and its compounds have been zealously studied by Madame Curie and others.



Fig. 213. — Madame Curie (1867-) at work in her laboratory

617. General properties of radium and radium compounds. — The general properties of radium show that it belongs to the alkaline earth family (*i.e.* calcium, strontium, and barium). Metallic radium was isolated by Madame Curie in 1910. It is much like barium. Both are silvery metals which tarnish in the air and decompose water at ordinary temperatures.

Radium forms salts like those of calcium and barium, *e.g.* a soluble chloride (RaCl_2), and an insoluble sulphate (RaSO_4) and carbonate (RaCO_3). Radium compounds like those of calcium and strontium color the Bunsen flame red.

618. What is radioactivity? — Besides the properties just enumerated, radium compounds have special properties which are conspicuously different from those of most substances. Let us consider three of these properties. (1) *Radium compounds spontaneously evolve considerable heat.* It has been calculated that one gram of a pure radium salt gives off over 100 calories per hour, *i.e.* liberates

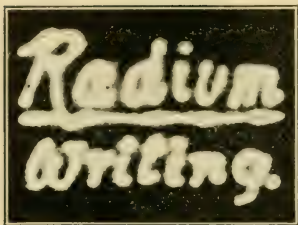


Fig. 214. — Effect of radium compounds upon a photographic plate. (This was produced by slowly moving a small tube containing radium bromide across the plate (wrapped in black paper), and then developing the plate.)

enough heat every hour to raise a little more than its own weight of water from the freezing point to the boiling point. (2) *Radium compounds affect a photographic plate just as light does.* If a tube containing a radium compound is left a short time on a photographic plate wrapped in black paper, or even drawn slowly across it, an image is produced when the plate is developed (Fig. 214). Radium compounds actually photograph themselves

(Fig. 215). (3) *Radium compounds ionize the surrounding air, i.e. make it a conductor of electricity.* Thus, radium compounds discharge an electroscope. An electroscope (Fig. 216) contains two thin strips of metal (*e.g.* gold or aluminium), which separate when the electroscope is charged with electricity. Radium compounds, if brought near a charged electroscope, ionize the air, which permits the escape of electricity from the electroscope; hence the leaves fall together. The electroscope is used to detect radium compounds, and very sensitive instruments are

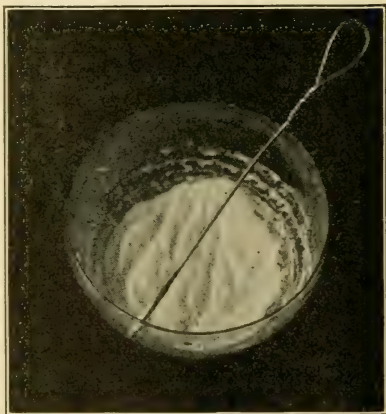


Fig. 215. — Dish of radium bromide photographed by itself in a dark room

essential in determining the proportion of radium in mixtures.

The special properties exhibited by radium compounds are called **radioactive properties**; the term **radioactivity** is often used to include these properties. Similar properties, though less in degree, are possessed by compounds of other elements, *e.g.* uranium and thorium.

619. Interpretation of radioactivity.

It was first thought that the special properties of radium compounds were due to rays or radiations; hence the name radium. Many interesting experiments show that radioactivity is caused by the spontaneous emission of two kinds of electrically charged particles, called alpha (α) and beta (β). The emission of beta particles is accompanied by pulsations in the ether called gamma (γ) rays.

The **alpha particles** are positively charged and move with great velocity — in some cases as great as 14,000 miles a second; the muzzle velocity of a bullet is about $\frac{1}{4}$ of a mile a second. Each alpha particle carries two unit charges of positive electricity. To the alpha particles are due many of the electrical phenomena of radioactive substances, such as ionizing the air. Although alpha particles move very fast in straight lines, they do not travel very far; they are completely stopped by the time they have



Fig. 217. —
Spintharion
scope

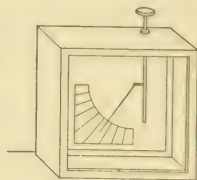


Fig. 216. — Sketch
of an electrostatic
scope

plowed through the air to a depth of 3 to 8 centimeters. They are almost entirely stopped by a thin sheet of paper and by aluminium leaf 0.1 mm. thick. Alpha particles are identical with positively charged helium

atoms (**127, 620, 621**) ; their weight is four times that of a hydrogen atom.

A simple instrument called the **spinthariscopes** (Fig. 217) shows in a striking way that particles are being shot off continuously from a *radium* compound. The screen *S* is coated with zinc sulphide and on the needle *R* there is a minute quantity of radium bromide. Upon looking into the spinthariscopes through the lens, minute flashes of light are seen on the screen. The flashes are due to the impacts of the steady stream of alpha particles which bombard the screen and produce fluorescence in the zinc sulphide.

The **beta particles** are electrons, *i.e.* particles of negative electricity, moving with varying velocity, which sometimes reaches two-thirds the velocity of light (186,000 miles a second). The beta particles are very light, their weight being about $\frac{1}{1846}$ of the weight of a hydrogen atom. The beta particles produce most of the photographic effects. They are stopped by aluminium 1 cm. thick.

The **gamma rays** have the least ionizing and photographic power, but they are the most penetrating. They pass readily through thick layers of metal. Glass tubes containing radium salts are enclosed in thick lead vessels to absorb the gamma rays. Gamma rays are not material particles, but ether waves of the same nature as X-rays.

The **heat evolved** by radioactive substances is due to the fact that the rapidly moving alpha and beta particles are stopped by the air, metals, and the radioactive solid itself.

620. Radium is decomposing spontaneously. — Although radium is an element which possesses many properties like those of the other eighty or more elements, it differs from most of them in being unstable. That is, many observations show that radium is slowly disintegrating. Thus, we have already stated that the alpha

particles are charged helium atoms. Indeed, it has been shown many times, that when alpha particles (collected in a tube) lose their charge of electricity, the spectrum of helium appears. Besides, the rate at which helium is given off by radium has been measured. Another gas has been obtained from radium, viz. **radium emanation** or, as it is more often called, **niton**. It is given off continuously by radium compounds. Moreover, it belongs to the same family as helium and argon (*i.e.* the zero group in the periodic classification, **399**), and has properties much like those of argon.

The two elementary gases, helium and niton, are produced spontaneously. That is, they are coming off continuously from all radium compounds independently of temperature and other conditions. We conclude that the **radium atom** itself is **disintegrating spontaneously**. This means that the atom of one element (radium) is transforming itself into the atoms of two other elements (helium and niton). Unlike other chemical transformations, however, it cannot be hastened or retarded. It goes on unceasingly and unvaryingly at temperatures between liquid air and the electric furnace. Furthermore, this transformation means that radium is slowly disappearing. The change is not rapid. Experiments which we cannot discuss here show that half a given weight of radium will disappear in about 2000 years, half of the residue in another 2000 years, and so on. Niton is also disintegrating. Its rate, however, is rapid; the half period, as it is called, is 5.5 days.

621. The radium disintegration series. — Helium and niton are not the only elements formed by the disintegration of radium. Indeed, radium itself is a product of uranium. Hence uranium, the heaviest of all the elements, is regarded as the parent substance in the disintegration series. The others in the series are uranium X_1 , uranium X_2 , uranium 2,

onium, radium, niton, radium A, B, C, C₁, D, E, F, and G. All of these products are believed to be chemical elements; some are very unstable, the half period being only a few minutes. Helium is not a member of the series, but is given off in some of the transitions. Electrons are also expelled in some cases. Evidence indicates that the final product of disintegration is radio-lead.

622. Atomic weights and the disintegration series. — The disintegration of certain elements in this series is accompanied by the expulsion of an alpha particle, an electron, or both. An electron has a negligible weight, but a helium atom, which is an alpha particle minus the electric charges, has the weight 4. Hence the loss of a helium atom lowers an atomic weight by 4 units. Let us take two examples. (1) In passing from a uranium atom to a radium atom, three helium atoms are lost; and from radium to niton, one is lost. Therefore, the atomic weight of radium should be 12 units (3×4) less than uranium, and of niton 4 less than radium. By the table (back inside cover) we see that uranium has the atomic weight 238.2, radium 226, and niton 222.4. (2) Eight helium atoms are lost in passing from uranium to radium G (the final product). Hence the final product should have the atomic weight 206 (*i.e.* $238 - 8 \times 4$). The atomic weight of the lead isolated from uranium ores was found to be 206.4 by exceptionally accurate experiments by Richards (Fig. 82).

The atomic weight of lead from other (*i.e.* non-radioactive) sources is 207.2, which is actually — not estimated — higher than that of so-called radio-lead. The two forms of lead have identical chemical properties, *e.g.* form compounds exactly alike in exactly the same way. They differ only in atomic weight. Elements which differ in atomic weight but not in properties are called **isotopes** or **isotopic elements**. Other elements besides lead are isotopic.

623. Uses of radium. — The products from radium, especially beta particles and gamma rays, have a powerful effect on living matter, and are utilized to cure certain skin diseases. Much study is being made in this field. The radium compound itself is so expensive, it is seldom used directly. Since radium compounds are constantly giving off radium emanation (**620**) which disintegrates and produces beta particles and gamma rays, the emanation is used. It is collected in tiny glass tubes which can be placed upon or within the flesh.

A luminous mixture containing zinc sulphide and a minute quantity of a radium compound is used on watch dials, push buttons, door numbers, and electric light chains. The cost of the radium is only a few cents for each object. The action is the same as in the spinthariscopes (Fig. 217).

624. Other radioactive elements. — Besides uranium and radium, the element **thorium** is radioactive, though to a much less degree than radium. Thorium disintegrates and yields a series of radioactive products. The first one is moderately radioactive, and is called **mesothorium**. Being cheaper than radium, mesothorium is sometimes used as a substitute, although it lasts only a few years. **Actinium** and **polonium** are very rare radioactive elements.

625. The constitution of matter. — The phenomena of radioactivity are due to the spontaneous decomposition of the atoms of radium and of the other so-called radioactive elements. Radioactivity leads us to conclude that the atoms of radioactive elements are composite, unstable structures. Radium, thorium, etc., to be sure, behave like other elements in chemical changes, *i.e.* they participate in reactions which involve two or more undivided atoms each of which has an unvarying weight. But atoms of many radioactive elements spontaneously emit electrons (beta particles)

and helium atoms (alpha particles), leaving behind an atomic residue of less atomic weight. Many facts besides radioactivity, *e.g.* formation of ions, show that atoms and molecules of elements are more or less unstable.

According to recent views of the constitution of matter, atoms consist of two essential parts: (1) a positively charged nucleus, with which the weight of the atom is associated, and (2) electrons (*i.e.* charges of negative electricity) which, according to most authorities, revolve around the nucleus. This conception of atomic structure finds an excellent illustration in the special properties of radium.

Two other points about the constitution of matter should be noted. *First*, the number of electrons surrounding the nucleus of an atom of many elements has been determined. Thus, hydrogen is 1, helium 2, oxygen 8, niton 86, radium 88, uranium 92. These numbers, and similar ones of other elements, were found by means of the X-ray spectrum of the element. They are called **atomic numbers**.

If elements are arranged in the order of their atomic numbers instead of their atomic weights, anomalies of the periodic classification disappear (402). Hence atomic numbers of the elements are more fundamental than their atomic weights.

Second, experiments show that many **elements** readily **lose or gain** one or more **electrons**. Thus, radium loses electrons; in fact many of the thirty or more radioactive elements have this property. Again, sodium chloride molecules consist of an atom each of sodium and chlorine. When this salt is dissolved in water, each atom forms an ion. Since the sodium ion is charged positively (Na^+), it must have lost one electron, and can be represented by $\text{Na} - e$. Whereas the chlorine ion, since it is charged negatively (Cl^-), must have gained an electron (from the sodium atom) and can be represented by $\text{Cl} + e$.

Finally, we must note the results of two more investigations. *First*, by means of the ultra-microscope, we can see the motion (Brownian movement, 101 and Fig. 55) of particles which are minute enough to be knocked about by the impacts of molecules. *Second*, by a special electrical device, the paths of alpha particles (*i.e.* charged helium atoms) have been instantaneously photographed as these particles shoot through the air (Fig. 218). In the spinthariscopes we see the result of the bombardment of single atoms (619). Moreover, it is possible by means of a supersensitive electroscope to count charged helium atoms as they enter this instrument.



Fig. 218. — Paths of alpha particles (charged helium atoms) in moist air

Whatever may be our interpretation of chemical phenomena, we have little or no reason to doubt that atoms and molecules have been removed from the borderland of theory into the realm of reality.

EXERCISES

1. In what minerals does radium occur?
2. Prepare a summary of (a) radium, (b) radioactivity, and (c) radium disintegration series.
3. State the general properties of radium compounds.
4. State the special properties of radium compounds. In what respect are they striking?
5. Topics for home study: (a) Discovery of radium. (b) Madame Curie. (c) X-rays. (d) Uses of radium. (e) Properties of radium. (f) Ramsay and the discovery of niton. (g) Madame Curie's gram of radium. (h) Electrons.
6. Discuss (a) alpha particles and (b) beta particles. Why was radium so named?

7. Describe (a) a spinthariscopescope and (b) an electroscope. What does each show about radium compounds?
8. Discuss helium, niton, and the disintegration of radium as a connected topic.
9. Review topics: (a) Uranium, thorium, and barium with special reference to radium. (b) Photography. (c) The argon family.
10. Discuss atoms in the light of radioactivity.

PROBLEMS

1. Calculate the weight of radium in a milligram of (a) radium bromide, (b) radium nitrate, (c) radium sulphate.
2. Write the formulas of the following compounds of radium: Iodide, fluoride, carbonate, acid carbonate, oxide, phosphate (ortho), sulphate, nitrate, bromide.
3. If 2.61099 milligrams of radium bromide give 2.00988 milligrams of radium chloride, what is the atomic weight of radium? (Use exact atomic weights of bromine and chlorine.)

APPENDIX

1. The Metric System of weights and measures is based on the **meter**, which is a little longer than a yard (1 meter = 39.37 inches.) The unit of weight is the **gram**, which is about one third of an ounce (1 ounce = 28.35 grams). A five-cent coin weighs approximately five grams. The unit of volume is the **liter**. It is slightly larger than a quart.

Length. 1 meter (m.) = 10 decimeters (dm.) = 100 centimeters (cm.) = 1000 millimeters (mm.). Also, 1 decimeter = 10 centimeters = 4 inches (nearly); and 2.54 centimeters = 1 inch.

Weight. 1 gram (gm.) = 10 decigrams (dgm.) = 100 centigrams (cgm.) = 1000 milligrams (mgm.). Also, 1 kilogram (kg. or kgm.) = 1000 grams (gm.) = 2.2 lb.

Volume. 1 liter (l.) = 1000 cubic centimeters (cc.). Also, 1 cubic centimeter of water (at 4° C.) weighs 1 gram.

2. The Thermometer used in chemistry is the centigrade. The boiling point of water on this thermometer is marked 100, and the freezing point 0. The equal spaces between these points are called degrees. The abbreviation for centigrade is C., and for degree is °. Thus, the boiling point of water is 100° C. Degrees below zero are always designated as minus, *e.g.* — 12° C. means 12 degrees below zero.

3. Weights of Gases. — The weight in grams of one liter of gases at 0° C. and 760 mm. is: —

Acetylene	1.16	Hydrogen chloride	1.64
Air	1.29	Hydrogen sulphide	1.54
Ammonia	0.77	Methane	0.72
Carbon dioxide	1.98	Nitric oxide	1.34
Carbon monoxide	1.25	Nitrogen	1.25
Chlorine	3.22	Nitrous oxide	1.98
Ethylene	1.25	Oxygen	1.43
Hydrogen	0.09	Sulphur dioxide	2.93

4. The Vapor Pressure of water vapor in millimeters of mercury is as follows:—

TEMPERATURE	VAPOR PRESSURE	TEMPERATURE	VAPOR PRESSURE	TEMPERATURE	VAPOR PRESSURE
12	10.5	17	14.4	22	19.7
12.5	10.8	17.5	14.9	22.5	20.3
13	11.2	18	15.4	23	20.9
13.5	11.6	18.5	15.9	23.5	21.5
14	11.9	19	16.4	24	22.2
14.5	12.3	19.5	16.9	24.5	22.8
15	12.7	20	17.4	25	23.6
15.5	13.1	20.5	18.0	25.5	24.3
16	13.6	21	18.5	26	25.0
16.5	14.0	21.5	19.1	26.5	25.7

The numbers in the columns marked Vapor Pressure are the values for a in the formula for the reduction of gas volumes (74).

5. **Books.**—Starred (*) books are primarily for teachers, though many parts of these books are suitable for pupils.

1. * *Alembic Club Reprints*. University of Chicago Press. No. 2 (Dalton, *Atomic Theory*), 3 (Cavendish, *Air*), 4 (Avogadro, *Molecules*), 6 (Davy, *Alkalies*), 7 (Priestley, *Oxygen*), 9 (Davy, *Chlorine*).

2. *Chemical Discovery and Invention in the Twentieth Century*. Tilden. E. P. Dutton & Co. Modern discoveries, principles, inventions, e.g. electrons, radium, catalysis, colloids. Applications of common substances, especially organic compounds. Over 150 illustrations.

3. *Chemistry in America*. Smith. D. Appleton & Co. Vivid story of chemical pioneers in our own country.

4. *Chemistry in the Service of Man*. Findlay. Longmans, Green & Co. Applications of modern principles to chemical industries. Cellulose, catalysis, fixation of nitrogen, colloidal state.

5. *Chemistry of Commerce*. Duncan. Harper & Bros. Interpretation of relation of chemistry to industries.

6. *Chemistry of Familiar Things*. Sadtler. J. B. Lippincott Co.

7. * *Chemistry of the Radio-elements*. Soddy. Longmans, Green & Co. Brief.

8. *Coal and the Coal Mines*. Greene. Houghton, Mifflin Co.

9. *Colloid Chemistry*. Alexander. D. Van Nostrand Co. Concise.

10. *Creative Chemistry*. Slosson. Century Co. Cellulose, rubber, plastics, sugar, fats, electric furnace products.
11. *Discoveries and Inventions of the Twentieth Century*. Cressy. E. P. Dutton & Co.
12. ** Elements of Industrial Chemistry*. Rogers. D. Van Nostrand Co. Comprehensive (1000 pages).
13. *Essays in Historical Chemistry*. Thorpe. Macmillan Co. Includes Boyle, Priestley, Cavendish, Lavoisier, Faraday, Mendeleeff.
14. *Everyman's Chemistry*. Hendrick. Harper & Bros. Useful information interwoven in a course in general chemistry Bibliography.
15. *Famous Chemists*. Tilden. E. P. Dutton & Co. Includes Boyle, Black, Priestley, Cavendish, Lavoisier, Davy, Dalton, Berzelius, Faraday, Avogadro, Cannizzaro, Mendeleeff, Ramsay.
16. *Food and the War*. Blunt and Sprague. Houghton, Mifflin Co. Reliable data on food, nutrition, and diet. Bibliography. Inexpensive.
17. *Food Products*. Sherman. Harper & Bros. Sources, manufacturing processes, standards, pure food regulations. Bibliography.
18. *Fundamentals of Agriculture*. Halligan. D. C. Heath & Co. Fertilizers, soil, insecticides, plant food. Bibliography.
19. *Handbook of Chemistry and Physics*. Chemical Rubber Co., Cleveland, Ohio. Tables of physical and chemical data.
20. *History of Chemistry*. Thorpe. G. P. Putnam's Son. Complete (400 pages). Portraits.
21. *How to Live*. Fisher and Fisk. Funk & Wagnalls Co. Food, physiology, diet, health rules.
22. *How to Make Good Pictures*. Eastman Kodak Co., Rochester, N. Y.
23. *Industrial Chemistry*. Benson. Macmillan Co. Includes water, fuels, iron and steel, alloys, clay products, cement, paint, cellulose, explosives. Condensed (420 pages). Illustrated. Bibliography.
24. ** Inorganic Chemistry*. Newell. D. C. Heath & Co. Advanced book for reference and supplementary reading.
25. ** Laboratory Manual of Inorganic Chemistry*. Newell. D. C. Heath & Co. Experiments based on No. 24.
26. *Modern Chemistry and Its Wonders*. Martin. D. Van Nostrand Co. Explosives, radium, electrochemistry, sugar, coal-tar, salt. Illustrated.
27. ** Nature of Matter and Electricity*. Comstock and Troland. D. Van Nostrand Co. Atoms, electrons, radioactivity, catalysis, constitution of matter.
28. ** New Era of Chemistry*. Jones. D. Van Nostrand Co. Development of chemistry during last three decades. Catalysis, electrons, radioactivity.
29. ** New Knowledge (The)*. Duncan. H. S. Barnes & Co. Applications of physics and chemistry.

30. *Non-technical Chats on Iron and Steel*. Spring. F. H. Stokes Co.
31. *Outlines of Industrial Chemistry*. Thorp and Lewis. Macmillan Co. Between No. 12 and No. 23.
32. *Photography for Students of Physics and Chemistry*. Derr. Macmillan Co. Principles and processes.
33. *Radioactivity*. Venable. D. C. Heath & Co. Brief.
34. *Romance of Modern Chemistry*. Philip. J. B. Lippincott Co. Flame, fuel, explosives, extremes of temperature, crystals, agriculture.
35. *Short History of Chemistry*. Venable. D. C. Heath & Co. Concise.
36. *Some Chemical Problems of To-day*. Duncan. Harper & Bros. Contributions to modern theoretical and industrial chemistry.
37. *Source, Chemistry, and Use of Food Products*. Bailey. P. Blakiston's Son & Co. Practical information about source and manufacture of food. Tables.
38. *Story of Gold (The)*. Meade. D. Appleton & Co. Brief, non-technical.
39. *Story of Iron (The)*. Surface. D. Appleton & Co.
40. *Story of Iron and Steel (The)*. Smith. D. Appleton & Co.
41. *Story of Oil (The)*. Tower. D. Appleton & Co.
42. *Story of a Piece of Coal*. Martin. D. Appleton & Co.
43. **Study of Chemical Composition*. Freund. Macmillan Co. Laws, history, biography.
44. *What We Eat*. Hawk. Harper & Bros. Answers practical questions about physiology, digestion, diet.

INDEX

- Abrasive, alundum, 420
 - Carborundum, 323
 - Emery, 419
- Absolute alcohol, 297
 - Temperature, 51
 - Thermometer, 51
 - Zero, 51
- Acetate, 299
 - Ethyl, 300
- Acetic acid, 250, 298, 461
 - Glacial, 298
 - Ionization, 216
 - Test, 300
- Acetone, 281, 298, 304
- Acetylene, 258, 272, 279, 281-283
 - Burner, 282
 - Flame, 281
 - Oxy-flame, 282, 283
- Acid, acetic, 250, 298, 461
 - Alpha-stannic, 455
 - Antimonic, 355
 - Calcium carbonate, 377
 - Calcium sulphite, 232
 - Capric, 302
 - Caprylic, 302
 - Carbolic, 305
 - Carbonate, 255
 - Carbonic, 30, 254
 - Chromic, 474, 476
 - Citric, 300
 - Colloidal, 321
 - Fluosilicic, 323
 - Formic, 35
 - Fruit, 299, 300
 - Fuming sulphuric, 241
 - Hydriodic, 343
 - Hydrobromic, 341
 - Hydrochloric, 136, 138
 - Hydrocyanic, 371
 - Hydrofluoric, 318, 322, 323, 337, 338
 - Hydrofluosilicic, 323
 - Hydrogen in, 39
 - Hydrosulphuric, 225
 - Hypochlorous, 131-134
 - Lactic, 293, 299
 - Malic, 299
 - Metasilicic, 319, 321
 - Muriatic, 136, 139, 156
 - Nitric, 159-170
 - Nitro-hydrochloric, 140
 - Nitrose, 236
 - Nitrosyl-sulphuric, 234
 - Nitrous, 165
 - Nordhausen, 241
 - Oleic, 300
 - Orthophosphoric, 350
 - Orthosilicic, 319, 321
 - Oxalic, 35, 256, 299
 - Palmitic, 300
 - Phosphate, 350
 - Phosphoric, 347, 349, 352
 - Prussic, 371
 - Pyroligneous, 298
 - Salts, 231, 240, 255, 365
 - Silicic, 319, 321, 323
 - Sodium carbonate, 363, 365
 - Stannic, 453, 455
 - Stearic, 300, 301
 - Steel, 399, 401
 - Sulphuric, 234-238
 - Sulphurous, 68, 230
 - Tartaric, 299
- Acids, 142-146
 - Abnormal behavior, 213
 - And metals, 142

- Acids, anhydrides, 231
 Chlorine, 145
 Common, 142
 Composition, 142
 Detection, 142
 Dibasic, 232
 Dissociation, 202
 Electrolytes, 206
 Exercises, 146
 Finding strength, 145
 Ionic definition, 204
 Ionization, 202
 Metals, 39
 Naming, 145
 Non-oxygen, 145
 Organic, 299-301
 Oxy, 145
 Oxygen, 145
 Problems, 147
 Properties, 142
 Reaction, 142, 206
 Strong, 216
 Tribasic, 350
 Weak, 216, 225, 365
 Actinium, 489
 Adequate diet, 311, 313
 Adhesives, 320
 Agate, 317
 Ware, 370
 Air, 102-113
 A mixture, 106
 Analysis, 107
 And burning, 18, 19
 And carbon dioxide, 29
 And combustion, 19, 20, 265
 And digestion, 309
 And gasoline, 266
 And phlogiston, 18-20
 Argon in, 107
 Blast, 265, 302, 303, 309, 429
 Burning coal, 262, 263
 Carbon dioxide in, 109
 Carbon monoxide in, 256
 Composition, 102, 107
 Constant ingredients, 106
 Currents, 65
 Drafts, 265
 Exercises, 114
 Into nitric acid, 168
 In water, 69, 106
 Liquid, 102, 106, 112
 Mixture, 105, 106
 Nitrogen in, 107
 Normal, 107
 Oxygen in, 107
 Problems, 114
 Saturated, 108
 See Atmosphere
 Test for moisture, 108
 Water vapor in, 107, 108
 Weight of liter, 493
 Airplane, 21, 266
 Airships, 47, 112
 Alchemists, aqua fortis, 163
 Aqua regia, 140
 Alcohol, 297, 298
 Absolute, 297
 And vinegar, 299
 And water, 70
 As fuel, 267, 297, 298
 B.t.u., 267
 Denatured, 297
 Ethyl, 267, 298, 300
 Fermentation, 298
 Grain, 267
 Methyl, 267, 297, 298
 Tax, 298
 Wood, 250, 267
 Alkali, 143, 303
 And hydrogen, 41, 42
 Electrolytic, 367
 Free, 303
 Metals, 360
 Alkaline reaction, 143
 Allotropy, 224
 Carbon, 244

- Allotropy, sulphur, 224
- Alloys, 355
 - Antimony 355
 - Anti-friction, 356
 - Bismuth, 357
 - Chromium, 407, 474
 - Cadmium, 357
 - Copper, table, 433
 - Fusible, 357
 - Iron, 322
 - Lead, 357
 - Silicon, 322
 - Silver, 466
 - Steel, 407
 - Table, 433
 - Tin, 357, 454
- Alpha particles, 485, 487
 - Path, 491
 - Stannic acid, 455
- Alum, 421, 422
 - And water, 60, 422
 - Baking powders, 421, 365, 366
 - Burnt, 421
 - Chrome, 421, 476
 - Hydrolysis, 421
 - Iron, 421
 - Potassium, 421
 - Water purification, 60, 422
- Alumina, 419
- Aluminates, 417, 420
- Aluminium, 415-424
 - Acetate, 422
 - Alloys, 418
 - And sodium hydroxide, 41, 42, 417
 - Bronze, 418, 433
 - Chloride, 417, 420
 - Cleaning by, 466
 - Extruded, 416
 - Family, 332
 - Hydroxide, 420, 421, 422
 - In cleaning silver, 466
 - In steel making, 399, 403, 417
 - Manufacture, 415
 - Metal, 420
 - Non-metal, 420
 - Oxide, 324, 415, 418-420
 - Properties, 416
 - Salts, hydrolysis, 421
 - Sulphate, 420, 421
 - Test, 420
 - Uses, 417
- Alumino-thermic method, 418, 419
- Alundum, 420
- Amalgams, 447, 464
 - Gold, 470
- Amethyst, 316
- Ammonia, 148-157
 - And chlorine, 151, 153
 - And magnesium, 151
 - And water, 151
 - Anhydrous, 150
 - Catalyst, 104, 153
 - Chemical conduct, 150
 - Composition, 153
 - Decomposition, 151
 - Formation, 45, 148
 - Formula, 198
 - Fountain, 150
 - Into nitric acid, 169
 - Liquefied, 150
 - Liquid, 150
 - Manufacture, 152
 - Muriate of, 156
 - Preparation, 148
 - Problems, 157
 - Properties, 150
 - Refrigerant, 154
 - Soda process, 363
 - Softening by, 386
 - Solubility, 150
 - Synthesis, 151
 - Synthetic, 153
 - Term, 148
 - Test, 151
 - Volumetric composition, 153
 - Water, 148, 150

- Ammonia, weight of liter, 150, 493
 Ammoniacal liquor, 149, 277
 Ammonium, 155
 As metal, 155, 214, 215
 Carbonate, 157
 Chloride, 103, 105, 150, 156
 Compounds, 155, 156
 Dichromate, 103
 Ferric citrate, 412
 Hydroxide, 148-150, 155
 Magnesium phosphate, 442
 Molybdate, 350, 480
 Nickel sulphate, 479
 Nitrate, 156, 165
 Nitrite, 103
 Oxalate, 386
 Phosphomolybdate, 350
 Sulphate, 105, 156, 239
 Stannate, 455
 Test, 156
 Amorphous, 223, 247
 Carbon, 247
 Sulphur, 223
 Amyl acetate, 300
 Valerate, 300
 Analysis, water, 79
 Anæsthetic, 166, 304
 Anglesite, 456
 Anhydride, 68, 231
 Acid, 399
 Carbonic, 255
 Phosphoric, 350
 Silicic, 321
 Sulphuric, 233
 Sulphurous, 231
 Anhydrite, 384
 Anhydrous, 74
 Copper sulphate, 434
 Animal charcoal, 250
 Anions, 202, 209, 215
 Annealing glass, 327
 Anode, 209, 367, 368, 387, 416, 430,
 431, 439
 Anthracene, 305
 Anthracite coal, 248
 Antichlor, 135, 232
 Antimonic acid, 355
 Antimony, 355, 356
 Alloys, 355
 Oxychloride, 356
 Sulphide, 225, 355
 Test, 356
 Trichloride, 355, 356
 Trioxide, 355
 Trisulphide, 356
 Antimonyl, 356
 Antiseptic, 304, 305
 Apatite, 337
 Apparatus, aluminium, 415
 Blast furnace, 392, 393, 427-429
 Bromine, 340
 Burning hydrogen, 44
 Carbon dioxide, 28
 Coal gas, 276
 Collecting hydrogen, 41
 Composition of air, 107
 Composition of ammonia, 153
 Contact acid, 237
 Converter, 398, 400, 430
 Copper sulphide ores, 427
 Distillation, 62
 Electrolysis of salt, 129
 Electrolysis of water, 78
 Four-ply paper, 320
 Gasolene, 270
 Glass making, 325, 326
 Hydrochloric acid, 136
 Hydrogen, 40
 Ice, 154
 Ionization, 206
 Kipp, 40
 Lavoisier's, 19
 Liter of oxygen, 55, 56
 Magnesium, 439
 Morley's, 80
 Nitric acid, 159, 160, 168, 169

- Apparatus, oxygen, 14
Oxygen in water, 78
Oxygen rescue, 21, 22
Petroleum, 379
Rescue, 21, 22
Silica, 318
Sodium hydroxide, 367, 368
Sulphuric acid, 235, 237
Vapor pressure, 65, 66
Water, 81, 82
Water gas, 274
Aqua fortis, 163
Aqua regia, 139, 355, 356, 357
Dissolves gold, 472
Nitric acid, 162
Argol, 299
Argon, 110, 335, 440
And nitrogen, 107, 111
Family, 332
In air, 107
Monatomic, 179
Name, 110
Preparation, 111
Properties, 110
Arrhenius, 201, 202
Arsenic, 354, 355
Sulphide, 225, 355
White, 354
Arsenious oxide, 354
Arsenopyrite, 354
Arsine, 356
Asbestos, 319
Asphalt base, 271
Atmosphere, 102
Carbon dioxide, 31
Deliquescence, 75
Efflorescence, 74
Nitrogen, 104
Rare gases, 111
Atmospheric pressure, 52
And boiling point, 67
Normal, 67
Atomic number, 490
Atomic theory, 89
And chemical change, 91, 92
Conservation of matter, 92
Constant composition, 92
Exercises, 94
Multiple proportions, 93
Atomic weights, 93, 182-190
Accurate, 187
And equivalent weights, 186
And molecular weights, 179
And periodic classification, 331, 333
And properties, 334
Approximate, 94, 182, 184
Atomic numbers, 490
Determination, 182, 183, 189
Dulong and Petit, 185
Exercises, 190
From molecular weights, 182
How found, 182, 183
International, 188
Learning, 335
Oxygen, 94
Problems, 190, 191, 228
Radium series, 488
Ratio in molecule, 100
Relative, 94
Specific heat, 185
Standard, 94
Summary, 189
Symbols, 97
Table, Back cover
Atoms, 89, 90
And ions, 202
And molecules, 90, 91
Combining capacity, 193
Constitution, 490
Groups, 143, 193
In molecule, 174, 175, 222, 348, 354
Nucleus, 490
Real, 489-491
Review, 182
Same as molecules, 179

- Atoms, small, 94
 Symbols, 96, back cover
 Unstable, 489, 490
 Valence, 198
 Weight of single, 183
 Auric chloride, 472
 Automobile, 266
 Carbon monoxide, 34
 Reflector, 292, 467
 Tail lights, 324
 Tires, 218
 Avogadro, 172
 Theory, 172, 174
 Azote, 104
 Azurite, 426, 435

 Babbit metal, 356
 Bacteria, nodules, 105
 Water, 61
 Baking powder, 30, 365
 Alum, 421
 Ingredients, 157
 Phosphate, 350
 Tartrate, 366, 374
 Baking soda, 299, 365
 Balancing equations, 116
 Balard, 340
 Balloons, 47, 112
 Barite, 240
 Barium, 388
 Chloride, 74, 388
 Chromate, 388
 Nitrate, 388
 Sulphate, 240, 338, 460
 Test, 388
 Barometer, 53
 Height, 53
 Normal, 53
 Reading, 53
 Barytes, 240, 388
 Base, 142-146
 Ammonium hydroxide, 148
 Ionic definition, 204
 Bases, 142-146
 Abnormal behavior, 213
 Composition, 143
 Electrolytes, 206
 Exercises, 146
 Ionization, 202
 Names, 146
 Naming, 145
 Problems, 147
 Properties, 143
 Strong, 216, 365
 Weak, 216, 365
 Basic reaction, 143
 Salt, 454
 Steel, 401
 Battery, dry, 477
 Bauxite, 415
 Becquerel, 482
 Beet sugar, 289, 290
 Bell metal, 433
 Benzene, 272, 279, 305
 Benzine, 268, 271
 Beryl, 319
 Berzelius, 96
 Bessemer process, 398-401
 Steel, 398-401
 Thomas-Gilchrist, 401
 Beta particles, 486, 489
 Beta-stannic acid, 453
 Beverage, charged, 69
 Bicarbonate, 255
 Bichromates, 475
 Bismite, 356
 Bismuth, 356-358, 458
 Alloys, 357
 Basic chloride, 358
 Test, 358
 Bismuthinite, 356
 Bittern, 340
 Bituminous coal, 248
 Bivalent element, 193
 Black, 254
 Damp, 273

- Black, lead, 246, 456
- Blast furnace, 392
 - Copper, 427, 428
 - Lead, 456
- Blast lamp, 48, 265
- Bleaching, 133-135
 - Apparatus, 135
 - Chlorine, 133-135
 - Fruits, 232
 - Hydrogen peroxide, 84
 - Nuts, 232
 - Ozone, 22
 - Powder, 133-135
 - Process, 134, 135
 - Sodium peroxide, 371
 - Straw, 233
 - Sulphurous acid, 232, 233
 - Vegetables, 232
- Block tin, 62, 452
- Blood, 20
 - Carbon monoxide, 33
 - Iron in, 391
- Blooms, 396
- Blowpipe flame, 286
 - Acetylene, 282, 283
 - Glass, 325
 - Mouth, 286
 - Oxy-hydrogen, 47
- Blue print, 412
- Blue, Prussian, 413
- Blue stone, 240, 435
- Blue vitriol, 434
- Bluing, 412
- Body, elements in, 8
- Boiling point, 64, 67
 - Abnormal, 213
 - Normal, 67
 - Raising, 213
 - Water, 64, 67
- Bomb calorimeter, 262
- Bornite, 391, 426
- Boneblack, 250, 290
- Bones, 346, 350
- Books, list, 494-496
- Borax, 369, 370
 - Bead, 370, 476
 - Hydrolysis, 370
 - Softening by, 386
- Bordeaux mixture, 434
- Boron family, 332
 - Oxide, 324
- Boyle, 53, 54
 - Law, 53, 55, 57, 58
- Brass, 433
- Bread, 28, 294, 295
 - And carbon dioxide, 28, 294, 295, 365, 366
 - Composition, 308
- Breathing, 20
 - Oxygen, 21
 - Oxygen apparatus, 21, 22
- Bricks, 424
- Brimstone, 219
- Brine, 136
 - Ice, 154
- Britannia metal, 356, 454
- British thermal unit, 261
 - Charcoal, 265
 - Coal gas, 276
 - Coke, 261, 265
 - Fuel gases, 261
 - Fuel oil, 261, 266
 - Natural gas, 274
 - Producer gas, 274
 - Soft coal, 261
 - Water gas, 275
 - Wood, 265
- Bromides, 339, 341
- Bromine, 339-341
 - Molecular formula, 179
 - Water, 341
- Bronze, 433
 - Aluminium, 418, 433
- Brownian movement, 91, 491
- B.t.u., 261
 - Problems, 288

- B.t.u., see British thermal unit
 Bullets, 459
 Bunsen, 284
 Burner, 275, 283, 284
 Flame, 284, 285
 Burettes, 144-145
 Burner, acetylene, 282
 Bunsen, 275, 283, 284
 Gas stove, 275
 Oil, 266
 Burning, 17-19
 Coal, 262, 263
 Equations, 264
 Wood, 265
 Butane, 272
 Butter, 302
 Butyric, 302

 Cadmium, 446
 Alloy, 357, 446
 Atom in molecule, 179
 Test, 446
 Calcite, 376
 Calcium, 376, 387
 Acid carbonate, 377
 Acid sulphite, 232
 And hard water, 385
 Borate, 369
 Carbide, 198, 257
 Carbonate, 28, 124, 125, 139, 178, 255, 364, 376-379
 Chloride, 75, 108, 386
 Compounds, 386, 388, 389
 Cyanamide, 104, 105, 387
 Family, 332
 Fluoride, 337, 338
 Hydrogen and, 40
 Hydroxide, 70, 133, 198, 379, 381
 Light, 47
 Nitrate, 105, 386
 Nitride, 387
 Oxide, 257, 379-381
 Oxalate, 386
 Phosphate, 250, 325, 346, 347, 350, 352
 Silicate, 324, 347
 Sulphate, 218, 219, 240, 384
 Sulphide, 386
 Test, 386
 Calculation, equations, 121
 Gravimetric, 121-125
 Volume from weight, 123
 Caliche, 371
 Calomel, 448
 Calorie, 261
 Food, 310
 In food servings, 312, 313
 Large, 261
 Small, 261
 Calorimeter, 262, 310
 Candle flame, 279, 281
 Power, 279
 Candles, 270
 Candy, 289, 295
 Cane sugar, 289-293
 Cannizzaro, 185
 Capric acid, 302
 Caprylic acid, 302
 Caramel, 290
 Carat, diamond, 245
 Gold, 471
 International, 245
 Carbides, 252
 Calcium, 252, 257
 Silicon, 252, 322
 Carbohydrates, 289
 Food, 307, 309, 311-313
 Quantity needed, 311
 Carbolic acid, 305
 Carbon, 25-35, 244-252
 Allotropic, 244
 Amorphous, 244, 247
 As fuel, 260, 262-265
 Atomic weight, 184
 Chemical conduct, 252

- Carbon, compounds, 25-35, 252-258,
289-305
Crystalline, 244
Cycle, 32
Diamond, 244
Disulphide, 226, 227
Electric light, 251
Exercises, 37
Family, 332
Finding atomic weight, 183
Gas, 247, 251
In fuels, 260
In iron, 395, 397
Minimum weight, 183
Occurrence, 25
Oxides, 26, 34, 35, 36, 37, 88, 89,
97, 393
Problems, 258, 259
Reduction by, 252, 394
Test, 250
Tetrachloride, 135, 305, 341
- Carbon dioxide, 26-33, 252-255, 461
And bread, 28, 294, 295, 365, 366
And combustion, 252
And life, 253, 254
And weathering, 319
Atmosphere, 31
By fermentation, 253
By oxidation, 253
Chemical conduct, 30
Choke damp, 273
Decay, 27
Detection in air, 110
Discovery, 254
Experiments, 28
Extension, 252-255
Fire extinguisher, 28, 32, 33
Formation, 26
In air, 109, 110
In breath, 27
Liquid, 30
Life, 30, 31, 253, 254
Manufacture, 28
- Mole, 176
Molecular weight, 172, 173, 174
Not poisonous, 30
Plants, 31
Preparation, 28, 253
Problems, 38, 259
Properties, 29, 253
Review, 252-255
Solid, 30
Test, 27, 30, 110, 253, 382
Vapor density, 173
Weight of liter, 29, 253, 493
- Carbon monoxide, 33-35, 198, 256,
283, 393
In gases, 274
In illuminating gas, 33, 278
Mole, 176
Poisonous, 33, 256
Preparation, 35, 256
Properties, 33, 257
Reducing agent, 34
Reduction by, 256
Review, 256
Test, 257
Weight of liter, 33, 493
- Carbona, 135, 305
Carbonates, 255
Acid, 255
Acid calcium, 255
Normal, 255
Normal calcium, 255
Carbonated water, 29
Carbonic acid, 30, 254, 319, 365
Anhydride, 255
Ions, 254
Carborundum, 252, 322, 323
Carboy, 139
Carburetor, 275
Carnallite, 372, 439
Carnelian, 317
Carnotite, 482
Casein, 293
Cassiterite, 452

- Cast iron, 395
 Catalysis, 45, 104, 233
 Enzymes, 295
 Sulphur trioxide, 233
 See Catalyst
 Catalyst, 45, 153
 Ammonia, 104
 Iron oxide, 237
 Nitric oxide, 235
 Platinum, 237
 Poisoning, 238
 Cathode, 209, 367, 368, 387, 416, 439
 Cations, 202, 209
 List, 215
 Caustic, 366
 Lime, 379
 Potash, 373, 374
 Soda, 366
 Caves, 255, 377
 Cavendish, 111
 Cell, diaphragm, 367
 Electric, 436
 Non-diaphragm, 368
 Celluloid, 296
 Cellulose, 232, 265, 289, 295-297
 Derivatives, 296
 Fiber board, 446
 Nitrates, 296
 Cement, 382-384
 Portland, 384
 Zinc, 446
 Cementite, 395
 Centigrade thermometer, 51, 493
 Cerium, 480
 Oxide, 286
 Cerussite, 456
 Chalcedony, 317
 Chalcocite, 218, 426
 Chalcopyrite, 218, 391, 426
 Chalk, 378
 Precipitated, 379
 Change, chemical, 1, 2, 5, 9, 14, 16,
 17, 41, 42, 89, 91, 115, 309
 Electrochemical, 436
 Physical, 65
 Charcoal, 247, 249
 Animal, 250
 Burning, 265
 In gunpowder, 373
 Sugar, 290
 Uses, 249
 Wood, 249, 250
 Charles' law, 51, 52, 55, 57
 Checkerwork, 401
 Cheese, 293
 Chemical change, 1, 2
 And equation, 115
 And oxygen, 16
 Atoms, 89
 Attraction, 6
 Characteristics, 2, 3
 Compounds, 5-10, 35-37, 77-83,
 88, 89, 91-93, 96-100, 121-125
 Elements, 5-10
 Hydrogen, 41
 In body, 309
 Interpretation, 91
 Mercury oxide, 5
 Other names, 9
 Oxidation, 17
 Potassium chlorate, 14
 Substitution, 42
 Chemical conduct, 2
 Chemical engine, 32
 Chemistry, 1
 Organic, 25, 198, 289
 Chile salt-peter, 341, 342, 370, 371
 China ware, 423
 Chinese white, 445
 Chloride, 132, 140
 Aqua regia, 140
 Composition, 143
 From hydrochloric acid, 139
 Hydrogen, 132
 Insoluble, 140
 Ions, 202, 203, 207

- Chloride, lime, 133
Names, 140
Preparation, 139
Properties, 140
Sulphur, 218
Test, 140
- Chlorinator, 61
- Chlorine, 129-135
Acids, 145
And ammonia, 151
And bromides, 340
And hydrogen, 45, 132, 138, 180
And water, 61
Atomic weight, 184, 188
Atoms in molecule, 175
Bleaching, 133-135, 232
By electrolysis, 129, 130, 366-369
Chemical conduct, 132
Compounds, 61
Discovery, 130
Electrolytic, 368, 369
Equivalent weight, 186
Exercises, 141
In World War, 131
Ion, 490
Liquid, 61, 131
Nascent, 139, 140
Occurrence, 129
Preparation, 129, 130
Problems, 141
Properties, 130
Purification by, 61
Salts from acids, 146
Uses, 135
Water, 77, 78, 131
- Chloroform, 304
- Chlorophyll, 31, 391
- Choke damp, 273
- Chromates, 474, 475
Ions, 475
Lead, 462
- Chrome alum, 476
Iron ore, 474
- Steel, 404, 407, 474
Yellow, 475
- Chromel, 474
- Chromic acid, 474, 476
Anhydride, 474
Oxide, 476
- Chromite, 474
- Chromites, 476
- Chromium, 474-476
Alloys, 474
Family, 333
Hydroxide, 476
Ions, 475
Oxide, 418
Steel, 404, 407, 474
Test, 475
Thermit, 418
Trioxide, 474, 476
- Cinnabar, 218, 446, 449
- Citric acid, 300
- Classification, elements, 329-336
Periodic, 330-336
- Clay, 246, 319, 383, 415, 422
Filler, 297
Products, 423
- Climate, 65
- Clinker, 384
- Clouds, 59, 65, 107
- Coal, anthracite, 248
Beds, 248
Brown, 248
Burning, 262, 263
Bituminous, 248, 250, 272
Composition, 248
Fire, 34, 35, 263-265
Formation, 248
Fossil, 249
Gas, 149, 264, 272, 275-279
Hard, 248, 263
Microscopic section, 249
Soft, 18, 248, 250, 261
Sulphur in, 219
Tar, 277, 278, 305

- Coal, varieties, 247
 - Water gas from, 275
- Cobalt, 480
 - Nitrate, 420, 446, 480
 - Potassium nitrite, 480
 - Test, 480
- Cocanut oil, 302
- Coke, 247, 250, 261, 265, 323, 392
 - Blast furnace, 34, 392, 393
 - Ovens, 149, 251
 - Petroleum, 271
 - Products, 251
- Cold storage, 154
- Colemanite, 369
- Collodion, 296
- Colloid, 77
 - Gold, 472
 - Graphite, 246
 - Particles, 91
 - Silicic acid, 321
 - Solution, 76, 77, 90, 91
 - State, 76
 - Suspension, 76, 294
- Combination, 16, 91
 - Oxygen, 15
- Combining numbers, 186
 - Weights, 186
- Combustion, 17, 26
 - Ammonia, 151
 - And carbon dioxide, 30
 - And air, 19
 - And oxygen, 20
 - Broad meaning, 45, 132
 - Fuels, 264
 - Oxidation, 17
 - Products, 263
 - Spontaneous, 18
- Common salt, 362
- Composition, ammonia, 153
 - And formulas, 97, 98
 - Constant, 6, 88, 92
 - Carbon oxides, 36
 - Gravimetric, 6, 36, 79, 80, 98-100
- Ocean, 8
- Per cent, 99
- Percentage, 99
- Volumetric, 79, 81, 138, 153, 179, 180
- Compound, 6
 - And elements, 9
 - Carbon oxides, 35
 - Formula, 9, 96-100, 121, 122, 177, 178
 - Percentage composition, 99
 - See Chemical compound
- Concentration, ore, 427
- Concentrated solution, 69
- Concrete, 383
 - Reënforced, 383
- Condenser, coal gas, 276
 - Water, 62
- Cones, Bunsen flame, 285
- Conservation of matter, 3, 10, 87, 92
 - Atomic theory, 92
 - Law, 3, 10, 87, 92, 121
- Constant composition, 6, 88, 92
 - Air, 106
 - And mixture, 106
 - Atomic theory, 92
 - Carbon oxides, 36
 - Law, 6, 88
- Converter, copper, 429, 430
 - Iron, 395, 398-401
- Cooking, 28, 30
 - Soda, 30, 365
- Copper, 426-435
 - Alloys, 433
 - And nitric acid, 163
 - And sulphuric acid, 229, 230
 - Anodes, 430, 431
 - Blister, 430
 - Carbonates, 426
 - Chemical change, 91
 - Converter, 429, 430
 - Cupric compounds, 434
 - Cuprous compounds, 433, 434

- Copper, displacement, 432
 Electric cell, 436, 437
 Electrolysis, 211, 430
 Electrolytic, 431
 Family, 332
 Ferrocyanide, 433
 Flame test, 432, 433
 Flotation, 428
 Ions, 431, 434, 436
 Matte, 428, 429
 Metallurgy, 426-430
 Nitrate, 435
 Oxide, 46, 252, 432
 Paris green, 355
 Poisonous compounds, 434
 Refining, 430
 Sulphate, 73, 74, 98, 211, 239, 240, 431, 434
 Sulphide, 218, 426-430
 Smelting, 428
 Test, 370, 433
 Uses, 433
Copperas, 240, 411
Coquina, 378
Coral, 379
Cordite, 303, 304
Corrosive sublimate, 449
Corundum, 415, 419, 420
Cotton, 295
 Gun, 296
Cottonseed oil, 301, 302
Courtois, 341
Crisco, 302
Cream of tartar, 299, 366, 374
Crocus, 410
Crucible, 246
 Steel, 404, 405
Cryolite, 325, 337, 415
Crystallization, 71, 72
 Efflorescence, 74
 Water of, 73, 74
Crystals, 71-74
 Ice, 63, 64
Cullinan diamond, 245
Cupel, 457
Cupric oxide, 434, 435
 See Copper
 Sulphate, 434
 Sulphide, 435
Cuprite, 426, 434
Cuprous compounds, 433, 434
 Oxide, 292, 434
Curie, 482, 483
Cutting metals, 283
Cyanamide, calcium, 105, 387
Cyanide process, 470
Cyanogen iron compounds, 412
Cycle, carbon, 32
 Oxygen, 32
 Phosphorus, 351
Daguerre, 469
Dalton, 89
Dampers, 264
Davy, 273
 Chlorine, 130
 Iodine, 342
 Lamp, 273
 Nitrous oxide, 166
 Sodium, 360
Decay, 27
Decomposition, 14
 Double, 144
 Potassium chlorate, 14
Decrepitation, 363
Definite proportions, 88
 Law, 88
 See Constant composition
Deflagration, 163
Dehydrated, 74
Deliquescence, 75
 Vapor pressure, 75
Denatured alcohol, 297
Deoxidizing agent, 417, 418
Desiccator, 75
Developer, 468

- Dew, 59, 107, 108
 Point, 108
 Dewar flask, 112, 292
 Dextrin, 294, 295
 Dextrose, 291, 292, 294
 Test, 292
 Diamond, 244
 And carborundum, 323
 Carat, 245
 Cullinan, 245
 Drill, 25, 245
 Uses, 25
 Diastase, 293, 295, 298
 Diatoms, 317
 Diatomaceous earth, 317
 Dibasic acid, 232
 Dichromate, 475
 Ions, 475
 Diet, adequate, 311, 313
 Diffusion, 43
 Gases, 57
 Hydrogen, 43
 Digestion, 27, 309
 Products, 27
 Dilute solution, 69
 Disinfectant, carbolic acid, 305
 Chlorine, 135
 Formaldehyde, 304
 Phenol, 305
 Displacement, 42
 And valence, 196
 Interpretation, 436
 Metal and acid, 42
 Metals, 432, 435
 Series, 435
 Dissociation, 202-216
 Acids, bases, salts, 202-216
 Degree of, ions, 215
 Electrolytic, 205, 206
 Ionization, 202-216
 See Ions
 Distillate, 62
 Distillation, 62
 Alcohol, 298
 Dry, 250
 Fractional, 268
 Water, 62
 Wood, 298
 Distilled water, 62, 63
 Divalent element, 193, 195
 Dolomite, 439, 442
 Lining, 401
 Double decomposition, 144
 Dough, 28, 30, 294, 295, 365, 366
 Drying, 65
 Dulong, 185
 Dulong and Petit, 185
 Dumas, 80
 Duralumin, 418
 Duriron, 322
 Dutch process, paint, 461
 Dyad, 193, 195
 Dyeing, 422
 Dyes, 422
 Dynamite, 303, 319

 Earthenware, 424
 Effervescence, 69
 Efflorescence, 74
 Eggs, 219
 Decayed, 224
 Preserving, 320
 Sulphur in, 226
 Electric cell, 436
 Electric charge, ions, 214, 215
 Valence, 215
 Electric furnace, 247
 Calcium carbide, 257
 Carbon disulphide, 227
 Carborundum, 323
 Graphite, 247
 Phosphorus, 346
 Steel, 405
 Electrical energy, 437
 Electricity, attraction, 209
 Kinds, 209

- Electricity, minus, 209
Plus, 209
- Electrochemical change, 436
Series, 436
- Electrodes, 25, 209, 247
- Electrolysis, 206, 208-212
Applications, 212
Calcium chloride, 387
Carnallite, 354
Copper sulphate, 211, 305, 431
Example, 209
Fluorine, 337
Gold, 315
Hydrochloric acid, 209
Illustrations, 148, 209
Interpretation, 148, 212
Ionic interpretation, 208, 209
Lead, 369
Migration, 212
Secondary products, 210
Sodium chloride, 73, 129, 130, 293, 366
Sodium hydroxide, 210, 211
Water, 78, 211
- Electrolytes, 136, 148, 204, 205
Boiling point, 139
Chemical behavior, 140
Examples, 206
Freezing point, 139
Molecular weight, 214
- Electrolytic cell, 148
Dissociation, 137
Solutions, 213
- Electromotive series, 437
- Electrons, 486, 488, 489, 490
And ions, 490
Around nucleus, 490
Change of, 490
- Electroplating, 212
Gold, 472
Silver, 467
- Electroscope, 484, 485, 491
- Electro-silicon, 318
- Electrotyping, 212, 246
- Elements, 6
Allotropic, 224, 244
And atomic weights, 97, 182-190, 330, 333
And compounds, 9
Bivalent, 193, 195
Chemical change, 9
Chemically equivalent, 186
Classification, 329-336
Distribution, 7, 8
Divalent, 193, 195
Electrons, 490
Equivalent weight, 185
Families, 332
Gaseous, 179
Groups, 332
Halogen, 332, 333
Hexavalent, 193
Human body, 8
In body, 8, 218
Inert, 87, 104, 110, 111
Ions, table, 214
Isotopic, 488
Latin name, 9
Molecular formulas, 123, 179
Molecular weights, 123
Molecules, 90
Monatomic, 179
Negative, 409
Number, 7
Oxides, 17
Pentavalent, 193, 195
Periodic classification, 330-336
Positive, 410
Quadrivalent, 193, 195
Quinivalent, 193, 195
Radioactive, 489
Symbols, 8, 97
Table, 7, Back cover.
Tetravalent, 193, 195
Trivalent, 193, 195
Univalent, 193, 195

- Elements, valence, 193-195, 336
 Emery, 331, 415, 419
 Emulsion, 76, 77
 Soap, 304
 Enamel, 370
 Energy, chemical, 437
 Electrical, 437
 From food, 218, 307, 309
 Heat, 261
 Engine, gasoline, 266
 Enzymes, 196, 216, 295
 Zymase, 298
 Epsom salts, 240, 356, 441
 Equation, 9, 10, 115-126
 Arrow in, 119, 152
 Balanced, 121
 Balancing, 116
 Calculations, 121
 Exercises, 141, 157, 170
 Factors, 115
 For reactions, 125
 Gas, 180
 Gaseous, 151
 Gravimetric, 120, 121, 180
 Ionic, 141, 205, 207, 368
 Molecular, 179, 180
 Not algebraic, 119
 Preliminary, 9, 10, 115
 Problems, 147, 158
 Products, 115
 Quantitative, 121
 Reading, 10, 119
 Reading reversible, 152
 Reversible, 152
 Signs, 119
 Steps in writing, 116
 Symbols, 115
 Terms, 119
 Thermal, 261, 262
 Thermo-chemical, 262
 Verbal, 9
 Volume and weight, 123
 Volumetric, 180
 Writing, 115-119
 Equilibrium, 152
 Ammonia, 152
 Completion, 152
 Equivalents, 186
 Equivalent weights, 185-187
 And atomic weights, 186
 Element, 185
 Exercises, 190, 199
 Finding, 186
 Table, 187
 Esters, 207, 300, 302
 Fats, 208
 Etching, 268, 338, 339
 Ethane, 184, 272
 Ether, 214, 304
 And water, 43, 70
 Ethyl, 300
 Acetate, 207, 300
 Alcohol, 267, 298, 300
 Butyrate, 300
 Ether, 214, 304
 Radical, 300
 Ethylene, 172, 241, 272, 278, 391
 Eudiometer, 81
 Evaporation, 65, 107
 From body, 109
 Exercises, acids, 146
 Air, 114
 Alcohols, 306
 Alloys, 462
 Aluminium, 424
 Ammonia, 157
 Atomic weights, 190
 Bases, 146
 Calcium compounds, 388
 Carbon, 37, 258
 Carbon oxides, 38, 258
 Chemical change, 10
 Chlorine, 141
 Chromium, 480
 Composition, 101
 Compounds, 10

Exercises, copper, 437

Electrolysis, 217

Elements, 10

Equations, 126, 141, 157, 170, 228,
414

Equivalent weights, 190, 199

Fats and soap, 306

Food, 314

Formulas, 100, 180

Fuel, 287

Fuel value, 314

Gases, 57

Glass, 328

Gold and silver, 472

Halogens, 344

Home study, 23, 48, 58, 85, 114,
141, 157, 217, 242, 258, 288, 344,
375, 389, 414, 424, 437, 450, 462

Hydrocarbons, 287

Hydrochloric acid, 141

Illuminants, 287

Ions, 217

Iron compounds, 413

Lead, 462

Magnesium, 450

Manganese, 480

Menus, 314

Mercury, 450

Metals, 336

Mole, 180

Molecular weight, 101

Molecular weights, 180

Molecules, 180

Neutralization, 217

Nitric acid, 170

Nitrogen, 114

Nitrogen oxides, 170

Non-metals, 336

Organic compounds, 306

Oxygen, 23

Periodic families, 336

Phosphorus, 358

Potassium compounds, 375

Practical topics, 414, 450, 462

Radium, 491

Reactions, 126

Review, 344, 389, 414

Salts, 146

Silicon, 327

Sodium compounds, 374

Sugars, 305

Sulphates, 242

Sulphides, 228

Sulphur, 227

Sulphuric acid, 241

Sulphur oxides, 241

Symbols, 100

Tin, 462

Valence, 199

Volume equation, 181

Zinc, 450

Exhauster, 276

Explosions, coal mine, 171

Hydrogen 40, 43

Factors, 115

Fahrenheit, 63

Families, elements, 332

Faraday, 209, 210

Fat, 261, 300-304

Butter, 302

Edible, 48

Food, 307, 309, 311-313

Hydrogenation, 302

Natural, 301

Quantity needed, 311

Fehling's solution, 292, 434

Feldspar, 319, 422

Fermentation, 28, 295

Acetic, 299

Alcoholic, 298

Lactic, 293

Ferric chloride, 408-413

Compounds, 408-413

Hydroxide, 354, 410

Ions, 413

- Ferric chloride, iron, 408-413
 Oxide, 410, 418
 Sulphide, 411
 Sulphocyanate, 413
 Ferricyanides, 412, 413
 Ferrite, iron, 410
 Ferro-chrome, 474
 Manganese, 396, 399, 403
 Silicon, 322
 Ferroso-ferric oxide, 410
 Ferrous chloride, 408-413
 Chromite, 474
 Compounds, 408-413
 Ferric oxide, 410
 Hydroxide, 410
 Ions, 413
 Iron, 408-413
 Oxide, 410
 Sulphate, 164, 165, 224, 240, 241, 411
 Sulphide, 411
 Ferrocyanides, 412, 413
 Copper, 433
 Fertilizer, 105
 Artificial, 351
 Complete, 352
 Cyanamide, calcium, 105, 387
 Ingredients, 156
 Manufacture, 236
 Nitrate, 371
 Phosphate, 351, 401
 Potassium, 374, 375
 Results, 352, 353
 Fiber board, 320
 Filter paper, 295
 Water, 60
 Fire, 17
 Damp, 273
 Regulating, 264
 Extinguisher, pyrene, 135, 305
 Extinguishers, 32, 33
 Fireproof fabrics, 455, 480
 Fireworks, 218, 373
 Fixing, photography, 468
 Flame, 277-287
 Acetylene, 281
 And nitrogen, 103
 Blowpipe, 286
 Bunsen, 284
 Candle, 279-281
 Carbon monoxide, 34
 Hydrogen, 44, 47
 Lamp, 279
 Luminous, 277
 Non-luminous, 283
 Oxidizing, 285, 286
 Oxy-acetylene, 21, 282, 283
 Oxy-hydrogen, 20, 47
 Reducing, 285, 286
 Structure, 279-281, 283-286
 Flint, 317
 Flotation, 427, 428
 Flour, 294, 295
 Flower pots, 424
 Fluorescence, 486, 489
 Fluorides, 338
 Fluorine, 266, 337-339
 Fluorite, 266, 337
 Fluor spar, 266, 325, 337
 Fluosilicic acid, 255, 323
 Flux, 392
 Fog, 59, 107
 Food, 307-314
 And energy, 307, 309
 And tissue, 20
 Baking powder, 366, 374
 Composition, 308, 309, 311-313
 Digestion, 27, 309
 Energy, 309
 Exercises, 314
 Fuel value, 261, 307, 309-313
 Function, 307
 Heat from, 310-313
 Infants, 293
 Kind needed, 313, 314
 Nitrogenous, 104, 105
 Phosphorus in, 351

- Food, plants, 31
 Quantity needed, 311
 Salt, 363
 Servings, 312, 313
 Table, composition, 309, 311-313
 Water in, 59
- Fool's gold, 349
- Formaldehyde, 304
 Para-, 304
- Formalin, 304
- Formic acid, 35
- Formula, 60, 97
 Air, 106
 And valence, 195-197
 Calculation, 62
 Composition, 62, 63
 Compound, 9, 96-100, 121, 122, 177, 178
 Expresses composition, 98, 99
 Graphic, 198
 Groups, 97
 Meaning, 97
 Molecular, 122
 Molecular weight, 61
 Molecules, 97
 Simplest, 62, 99, 100, 121, 122, 177, 178
 Structural, 198
- Formulas and symbols, 97
 Correct, 177
 Exercises, 100, 199
 From valence, 196, 197
 Salts, 197
 Structural, 198
 Writing, 97, 196, 197, 199
- Fossils, 378
- Fourdrinier machine, 297
- Franklinite, 442, 443
- Free alkali, 211
- Freezing point, abnormal, 213
 Lowering, 213
 Solutions, 212
 Water, 63
- Frost, 59, 107
- Fructose, 292
- Fruit sugar, 292
- Fuel oil, 266
 B.t.u., 266
 Burner, 266
 Plant, 270
 Separation, 272
- Fuels, 260-277
 Alcohol, 267, 298
 Combustion, 261
 Composition, 260, 261
 Exercises, 287
 Gases, 261, 273
 Hastening combustion, 264
 Heat from, 261, 262
 Heat units, 261
 Kerosene, 266
 Kinds, 260
 Liquid, 265
 Oil, 261, 266, 270, 272
 Saving, 263
 Value, 261
- Fuel value, calorimeter, 262
 Exercises, 314
 Food, 310-313
 Physiological, 310
- Fumigation, 232
- Fuming nitric acid, 167
 Sulphuric acid, 241
- Furnace, blast, 392, 427, 428, 456
 Electric, 227, 247, 257, 346, 405
 Reverberatory, 396
- Fusible link, 285, 357
 Metals, 285
- Gain of electrons, 490
- Galena, 218, 368, 372, 456, 462
- Gallium, 335
- Galvanized iron, 358, 444
- Gamma rays, 485, 486, 489
- Gangue, 392

- Garage, unventilated, 256
 Ventilation, 34
- Gas, 56
 Air, 104
 And pressure, 52, 53
 And temperature, 50
 Carbon, 160, 247, 251
 Carbonic acid, 254
 Coal, 149, 264, 272, 275-279
 Flame, 277, 278
 Holder, 277
 Illuminating, 278, 279
 Inert, 30, 104, 110, 111
 Laughing, 166
 Liquor, 149, 277
 Mantles, 185
 Marsh, 272
 Measurement, 50-55
 Natural, 39, 273
 Oil, 278
 Pintsch, 278
 Poison, 131
 Producer, 35, 39, 274
 Range, 26
 Stove burner, 275
 Volume change, 50, 52
 Water, 35, 39, 274, 275, 278
- Gases, alike, 56
 Atoms in molecule, 175
 Elementary, 118
 Formulas, 118
 Molar volume, 176, 177
 Monatomic, 179
 Nature, 56
 Solution, 69
 Theory, 57
 22.4 liters, 176, 177
 Volumetric combination, 171
 Weight of liter, 493
- Gasolene, 26, 39, 175, 266, 268
 And carbon monoxide, 35
 Boiling point, 268
 Burning, 35, 266
- Composition, 272
 Engine, 266
 Extinguishing fire, 305
 Hydrocarbons, 272
 In water, 69
 Plant, 270
 Separation, 271
- Gay-Lussac, 83
 Tower, 235, 236, 237
- Gay-Lussac's law, 82, 83, 114, 115, 138
 Ammonia, 153
 Atoms in molecule, 174
 Summary, 171
- Gas volumes, 50-56
 And pressure, 52
 Corrected, 55
 Finding weight, 55
 Inverse relation, 54
 Temperature, 50
- Gelatin, 457
 Blasting, 303
- Gems, 332
- Germanium, 335
- German silver, 307, 433
- Geyserite, 254, 319
- Ginger ale, 29
- Glacial acetic acid, 298
 Phosphoric acid, 278
- Glass, 323-327, 354
 Annealing, 327
 Composition, 324
 Cut, 324
 Etching, 338, 339
 Flint, 324, 459
 Fluorescent, 377
 Green, 324
 Ingredients, 323, 324
 Kinds, 324
 Lead, 324, 459
 Machine, 326, 327
 Manufacture, 323, 325
 Plate, 327

- Glass, properties, 325
 - Pyrex, 324
 - Red, 324
 - Soft, 324
 - Sheet, 325, 326
 - Stoppers, 318
 - Water, 320
 - White, 325
 - Window, 325, 326
 - Wire, 407
- Glauber's salt, 240, 294
- Glazing porcelain, 423
- Glover tower, 235, 236, 237
- Glucose, 292
 - Test, 292, 434
- Gluten, 295
- Glycerin, 206, 300-303
 - And water, 69
- Glycerol, 302
- Glyceryl, 301
 - Butyrate, 302
 - Oleate, 300
 - Palmitate, 300
 - Stearate, 300, 301
- Glycogen, 307
- Gold, 469-472
 - Alloys, 472
 - Auric compounds, 472
 - Chloride, 470-472
 - Chlorination, 470
 - Coin, 472
 - Colloidal, 472
 - Compounds, 472
 - Cyanide process, 371, 470, 471
 - Electrolysis, 471
 - Fool's, 349, 411
 - In copper ore, 431
 - In lead ore, 457
 - Leaf, 471
 - Metallurgy, 470, 471
 - Mining, 470
 - Noble metal, 140, 472
 - Ore, 469
 - Plating, 472
 - Potassium cyanide, 472
 - Properties, 471
 - Quartation, 471
 - Refining, 431, 465, 471
 - Separation from silver, 465, 471
 - Sodium cyanide, 471, 472
 - Solubility, 140
 - Telluride, 469
 - Test, 472
 - Uses, 472
 - Valence, 472
- Grain alcohol, 267
- Gram, 493
 - Molecular volume, 175-177
 - Molecular weight, 175-177, 212, 213
- Granite, 319
 - Ware, 370
- Grape sugar, 292
- Graphic formulas, 198
- Graphite, 25, 245, 246
 - Artificial, 246, 247
 - Colloidal, 246
 - In iron, 395
 - Manufactured, 247
 - Occurrence, 247
 - Uses, 25, 246
- Gravimetric composition, 6, 36, 79, 80, 98-100
 - Equation, 120, 121, 180
 - Problems, 101
- Green fire, 388
 - Glass, 324
- Grindstones, 318
- Groups, periodic, 332
- Gun cotton, 296
 - Metal, 307, 433
- Gunpowder, 218, 250, 297, 373
- Gypsum, 219, 240, 373, 384
- Hail, 107
- Hall, 415

- Halogens, 337
 - Elements, 332, 333
 - Exercises, 344
 - Family, 266, 337
 - Periodic classification, 343
- Hardness of water, 324
 - Calcium compounds, 385
 - Magnesium compounds, 385
- Hardness, permanent, 385
 - Temporary, 385
- Hard water, 167, 324, 385
 - Magnesium, 356
- Heat and condensation, 65
 - And evaporation, 65
 - Of neutralization, 144
- Heavy spar, 240
- Helium, 111
 - And atomic weights, 488
 - And radium, 386, 485, 487, 488
 - Atoms, 485, 486, 490
 - Atoms and radium, 488
 - Balloons, 47
 - Counting atoms, 491
 - Formula, 179
 - In atmosphere, 109
 - Monatomic, 179
 - Symbol, 179
- Helmet, oxygen, 19
- Hemaglobin, 213, 391
- Hematin, 213
- Hematite, 337, 391
- Hexad, 127, 193
- Hexane, 272
- Hexavalent element, 127
- Home study, 23, 48, 58, 85, 114, 141, 157, 242, 258, 288, 344, 358, 375, 389, 414, 424, 437, 450, 462
- Hornblende, 319
- Horseradish, 219
- Human body, elements, 8
 - And evaporation, 109
 - And water vapor, 109
- Heat, 20
- Hydrogen, 39
 - Oxidation, 13, 20
 - Steam engine, 20
 - Temperature, 27
 - Tissue, 31
 - Water in, 59
- Humidity, 108
- Hydrates, 46, 74
- Hydraulic main, 276
 - Mining, 470
- Hydriodic acid, 343
- Hydrobromic acid, 341
- Hydrocarbons, 26, 170, 248, 265, 268, 271-273
 - From tar, 305
- Hydrogen, 39
 - In petroleum, 267, 268
- Series, 272
- Hydrochloric acid, 137, 138, 179
 - And hypochlorous acid, 131, 132
 - Commercial, 136
 - From magnesium chloride, 442
 - Electrolysis, 148, 208-209
 - Exercises, 141
 - Formula, 98
 - Ionic test, 207
 - Ionization, 210
 - Ions, 209
 - Manufacture, 136
 - Preparation, 136
 - Properties, 137
 - Test, 140
- Hydrocyanic acid, 371
- Hydrofluoric acid, 267, 318, 322, 323, 337, 338
- Hydrofluosilicic acid, 255, 318, 324
- Hydrogen, 39-48, 335, 391
 - And aluminium, 333
 - And chlorine, 45, 132, 138, 180
 - And combustion, 45, 46
 - And electrolysis, 149, 150
 - And fats, 302
 - And nitric acid, 163

Hydrogen, and water, 44

Apparatus, 40

Atomic weight, 184

Bromide, 341

Burning, 43-45, 77

Calculation of volume, 124

Chemical conduct, 43-45

Dioxide, 54, 84

Diffusion, 43

Displacement series, 436

Equation, 116, 119

Equivalent weight, 186

Exercises, 48

Explosion, 40, 43

Flame, 44, 47, 77

Fluoride, 267, 338

Forms ammonia, 151

From alkalis, 41

From sodium hydroxide, 289

From steam, 41

From water, 40, 41, 42, 77

Generator, 40

In acids, 142

In coal gas, 275, 278

In water, 77, 81

Iodide, 343

Ions, 143

Ions from acid, 204

Iron by, 407

Lightness, 43

Like metals, 436

Molecular formula, 123

Name, 41

Nascent, 409

Occurrence, 39

Peroxide, 83, 84

Plant, 13

Preparation, 39, 40, 41, 42

Preparation, equation, 116

Problems, 49

Properties, 43

Reduces, 46

Reduction by, 46

Replacing, 145

Sodium and, 40

Sulphide, 219, 224-226, 229-231,
276, 391

Test, 46

Uses, 47

Water gas, 35, 274-275

Weight of liter, 43, 493

Hydrogenation, 48, 302

Hydrogen chloride, 132, 136-138, 391

Chemical conduct, 137

Composition, 138

Formula, 120

Fountain, 137, 138

Fumes, 132, 133, 137

Preparation, 136

Properties, 137

Solubility, 137

Test, 132, 138

Weight of liter, 137, 493

Volume equation, 180

Hydrolysis, 364

Aluminium, 421

Antimony trichloride, 284, 356

Bismuth chloride, 286, 358

Borax, 370

Copper sulphate, 308, 434

Ferric chloride, 412

Magnesium chloride, 442

Maltose, 198

Potassium carbonate, 373

Salts, 365

Soap, 303

Sodium carbonate, 364

Sodium cyanide, 371

Stannous chloride, 454

Sugar, 195

Hydroquinone, 468

Hydrosulphuric acid, 225, 230

Hydroxides, 83, 146

Hydroxyl, 83, 143

Groups, 145

Ions, 143, 211

- Hydroxyl, ions from base, 204
 Hypochlorous acid, 131, 134
 Chlorine water, 131
 Sodium hypochlorite, 134
 Hypo, 241, 468
 Hyposulphite, 241, 468
- Ice, 59, 63
 Machine, 154
 Manufacture, 150, 154
 Melting point, 63
 Specific gravity, 63
- Iceland spar, 376
- Illuminants, 260, 276-282
- Illuminating gas, 278-279
 Blast lamp, 48
 Candle power, 279
 Carbon monoxide, 33
 Composition, 278
 Diffusion, 57
 Flame, 277
 Luminosity, 279
- Indelible ink, 467
- Indigo, 241
- Inert gas, 30, 104, 110, 111
- Infusorial earth, 317, 318
- Ingots, 399, 400, 404
- Ink, 411
 Indelible, 467
 Printing, 25, 252
- Insecticides, 354, 355
- Interaction, 9
- Invar, 407
- Iodides, 343
- Iodine, 335, 341-343, 371
 And starch, 294
 Compounds, 343
 Solution, 343
 Test, 343
 Tincture, 343
 Variable formula, 179
- Iodoform, 305, 343
- Ionic equation, 365, 368
- Ionium, 488
- Ionization, 201-216
 And concentration, 215
 Defined, 202
 Degree, 215
 Degree, table, 216
 Experiment, 206
 Interpretation, 213
 Per cent, 216
 Theory, 201, 206
- Ions, 201-216
 Acid sodium carbonate, 365
 And electrons, 490
 And molecules, 202
 And oxidation, 410
 And radicals, 202
 And reduction, 410
 And rusting, 408
 And valence, 410
 At electrodes, 210
 Atoms and molecules, 210
 Balanced sum, 203
 Charges on, 203, 214, 215
 Defined, 202
 Ferric, 413
 Ferrous, 413
 From water, 211, 212
 Hydrogen sulphide, 225
 Hydrolysis, 364
 In solutions, 213
 Kind in solution, 214
 Meaning, 209
 Migration, 210, 211
 Movement, 210
 Negative, 202, 215
 Not atoms, 202
 Phosphoric acid, 350
 Positive, 202, 215
 Representation, 203
 Sodium carbonate, 364
 Sulphuric acid, 240
 Table, 214
 Valence of, 215

- Iridium, 479
 Iron, 391-398, 407-413
 And sulphuric acid, 239
 Burning, 15
 By hydrogen, 407
 Carbon monoxide, 34
 Cast, 395
 Chlorides, 411
 Composition, 395, 397
 Compounds, 408-413
 Displaces copper, 432
 Disulphide, 411
 Electrolytic, 408
 Exercises, 413
 Family, 333
 Ferric, 408-413
 Ferrite, 410
 Ferrous, 408-413
 From ores, 392
 Galvanized, 444
 Hydroxides, 410
 In glass, 324
 Ions, 408, 410
 Manufacture, 392-394
 Metallurgy, 392
 Occurrence, 391
 Ore reduction, 392, 393
 Oxides, 391, 410
 Painting, 459
 Pig, 395
 Pure, 397, 407
 Pyrites, 219, 229, 391, 411
 Russia, 410
 Rust, 408
 Rusting, 398
 See Ferric
 See Ferrous
 Spiegel, 396, 399
 Sulphate, 240, 411
 Sulphide, 2, 3, 9, 10, 218, 411
 Valence, 408
 Wrought, 396-398
 Isomerism, 292
 Isomers, 292
 Isotope, 488
 Jugs, 424
 Kainite, 372, 439
 Kaolin, 422
 Karo, 292
 Kerosene, 39, 266, 367
 And alcohol, 298
 Boiling point, 268
 Composition, 272
 Emulsion, 76
 Flashing point, 270
 Hydrocarbons, 272
 Illuminant, 268
 Lamp, 279
 Refining, 268
 Kieserite, 439
 Kiln, cement, 383
 Lime, 380, 381
 Rotary, 383
 Porcelain, 423
 Kilogram, 493
 Kinetic theory, 57
 Kipp apparatus, 40
 Krypton, 111
 Lactic acid, 293, 299
 Ferment, 293
 Lactose, 292, 293
 Lampblack, 25, 247, 251
 Lard, 301
 Large calorie, 261
 Laughing gas, 166
 Laundry, 134
 Lava, 319
 Lavoisier, 18, 19, 41, 104
 Law, 87
 Boyle's, 53, 55, 57
 Charles', 51, 52, 55, 57
 Conservation of matter, 3, 87, 121
 Constant composition, 6, 88

- Law, definite proportions, 88
 Dulong and Petit, 185
 Exercises, 94
 Gay-Lussac, 138, 153, 171, 172, 174
 Multiple proportions, 37, 84, 88, 89
 Periodic, 334
 Specific heat, 185
- Lead, 354, 456-462
 Acetate, 299, 461
 Alloys, 356, 357, 459
 And radium, 488
 Arsenate, 355
 Atomic weight, 488
 Atomizing, 461
 Basic carbonate, 460
 Black, 246, 456
 Buckles, 461
 Carbonate, 456, 460
 Casting, 457
 Chambers, 235, 236
 Chloride, 140, 461, 462
 Chromate, 462, 475
 Desilverizing, 457
 Dioxide, 460
 Electrolysis, 457
 Fluosilicate, 457
 History, 456
 Metallurgy, 456
 Monoxide, 459
 Nitrate, 98, 458
 Oxides, 458-460
 Pencils, 25, 246
 Pipe, 458
 Plumbate, 459
 Poisonous compounds, 458
 Properties, 458
 Radio-, 488
 Radioactive, 488
 Red, 459
 Refining, 457
 Spongy, 459
 Sulphate, 456, 462
 Sulphide, 218, 226, 456, 460, 461
- Test, 461, 462
 Tetroxide, 459
 Uses, 458, 459
 White, 460, 461
 Wool, 459
- Leblanc process, 137, 363
 Leclanché batteries, 156
 Legumes, 105
 Lemonade, 300
 Levulose, 292
 Life and nitrogen, 104
 And phosphorus, 350
 Carbon dioxide, 30, 31
 Light, lime, 47, 379
 Welsbach, 286
 Lignin, 232
 Lignite, 248
 Lime, 379-381
 And water, 379
 Caustic, 379
 Chloride, 133
 Hydrated, 379, 381
 Kiln, 380, 381
 Light, 47, 379
 Manufacture, 380
 Milk of, 382
 Quick, 379
 Slaked, 133, 379, 380, 381
 Superphosphate, 352
 Sulphur spray, 218
 Water, 27, 381, 382
 Limestone, 376, 380
 Magnesium, 439
 Limonite, 391
 Lining, basic, 401, 403
 Dolomite, 401
 Magnesia, 441
 Magnesite, 442
 Link, fusible, 357
 Linolein, 301
 Liquid air, 102, 112
 Boiling, 106
 Manufacture, 113

- Liquid air, properties, 112
 Liquids, solution, 69
 Liquor, ammoniacal, 149
 Gas, 149
 Liter, gases, weight, 493
 Liters, 22.4, 176, 177
 Litharge, 459
 Lithophone, 445, 460
 Litmus, 142
 Loadstone, 410
 Lockyer, 111
 Look boxes, 271
 Loss of electrons, 490
 Louisiana sulphur, 219
 Lubricant, 246
 Luminosity, 279
 Lungmotor, 21
- Magnalium, 418, 440
 Magnesia, 440, 442
 Alba, 442
 Calcined, 440
 Covering, 441
 Milk of, 441
 Magnesite, 439, 442
 Magnesium, 439-442
 Acid carbonate, 442
 Ammonium phosphate, 442
 Bromide, 340
 Carbonate, 439, 441, 442
 Chloride, 439, 441, 442
 Equivalent weight, 186
 Flame, 281, 440
 Hardness of water, 385
 Hydroxide, 440
 Ions, 440
 Manufacture, 439
 Minerals, 439
 Nitride, 104, 151, 440
 Oxide, 116, 120, 440
 Rocks, 439
 Sulphate, 240, 439, 441
 Test, 442
- Magnetic oxide, 410
 Magnetite, 391, 410
 Malachite, 426, 435
 Malic acid, 299
 Malt, 293
 Maltose, 293, 294
 Manganese, 476-477
 Dioxide, 324, 476, 477
 Family, 333
 Ferro-, 396, 399, 403, 476
 Steel, 407, 476
 Sulphide, 225, 477
 Test, 477
 Manganous chloride, 477
 Mantle, Welsbach, 286, 287
 Marble, 376
 Marsh gas, 272
 Massicot, 459
 Matches, 348, 373
 Phosphorus, 15
 Matte, 428, 429
 Matter, conservation, 3, 87
 Constitution, 489
 Mendelejeff, 330, 334
 Mercuric compounds, 446, 448, 449
 Oxide, 5, 9, 19, 92, 120, 447
 Mercurous compounds, 448, 449
 Chloride, 140, 448
 Mercury, 446-450
 Alloys, 447
 Amalgams, 447
 Atom in molecule, 179
 Barometer, 53
 Bichloride, 449
 Chloride, 141, 448, 454
 Compounds, 448, 449
 Displacement, 432
 Frozen, 113
 Fulminate, 447
 In electrolytic cell, 368
 Ions, 448
 Metallurgy, 446
 Nitrates, 449

- Mercury, oxide, 5, 9, 19, 92, 120, 447
 Poisonous salts, 449
 Problems, 141, 450, 451
 Properties, 447
 Sulphide, 218, 446, 449
 Tests, 448, 449
 Thermometer, 447
 Uses, 81, 82, 447
 Valence, 448
- Mesothorium, 489
- Metal, Babbit, 356
 Bell, 433
 Britannia, 356, 454
 Gun, 433
 Monel, 433, 479
 Newton's, 357
 Noble, 140, 472
 Positive element, 410
 Rose's, 357
 Speculum, 454
 Substitution, 42
 Type, 356
 Typical, 334
 Wood's, 357
- Metallurgy, 392
 Copper, 426-430
 Gold, 470
 Iron, 392
 Lead, 456
 Silver, 464
 Tin, 453
 Zinc, 443
- Metals, 329, 330, 360
 Alkali, 360
 And acids, 142
 And non-metals, 329, 330
 And ions, 329
 And steam, 41
 And sulphuric acid, 239
 And water, 40
 Bead test, 370
 Defined, 329
 Displacement, 435
- Earth, 332
 Fusible, 357
 Rusting, 15, 408
 Table, 330
- Metaphosphoric acid, 347
 Silicic acid, 319, 321
 Stannic acid, 453
- Meteorites, 391
- Meter, gas, 277
 Metric, 493
- Methane, 184, 272, 274
 Flame, 283
 In coal gas, 275, 278
 Series, 272
- Methanol, 250
- Methyl alcohol, 250, 267
 B.t.u., 267
 Salicylate, 300
- Metric system, 493
 Problems, 11
- Mexican onyx, 377
- Mica, 319
- Migration of ions, 212
- Milk, 292
 Composition, 308
 Lactose, 292
 Of lime, 382
 Of magnesia, 441
 Sour, 299
 Sugar, 292
- Mineral matter, 308, 309
 In body, 308
- Minium, 459
- Mispickel, 354
- Mist, 59, 107
- Mixture, 4
 Air, 106
 Bordeaux, 434
- Moissan, 245, 337
- Molar volume, 176
- Molasses, 290, 298
- Mole, 175, 212, 213
 And boiling point, 212

- Mole, and freezing point, 212
 Carbon dioxide, 176
 Carbon monoxide, 176
 Exercises, 180
 Molecular weight, 176
 Nitric oxide, 176
 Problems, 181
 Oxygen, 176
 Volume, 176, 177
 Molecule, 90
 Atoms in, 174
 Chloride, 140
 Compound, 90
 Elements, 90
 Represents volume, 180
 Same as atom, 179
 Molecules and atoms, 90, 91
 And ions, 202, 203
 Atoms in, 175, 222
 Gas, 56
 Impacts of, 491
 In liquid, 90
 In solution, 213
 Real, 489-491
 Sulphur, 222
 Unstable, 490
 Molecular equations, 179, 180
 Molecular formula, 178
 And simplest formula, 178
 Elements, 179
 Molecular volume, gram, 176, 177
 Molecular weights, 98
 And atomic weights, 98, 179, 182, 183
 And formula, 177, 178
 And mole, 175
 And temperature, 179
 Approximate, 173, 174
 By Avogadro's theory, 172
 By boiling point, 213
 By freezing point, 213
 By vapor density, 173, 174
 Calculation, 176
 Correct formula, 177, 178
 Determination, 174
 Electrolytes, 214
 From mole, 176, 177
 Gram, 175
 How found, 172, 173
 Insoluble substances, 174
 Non-electrolytes, 214
 Oxygen, 173
 Variable, 179
 Molybdenum, 480
 Steel, 404, 407
 Monad, 193, 195
 Monatomic elements, 179, 222
 Monazite, 480
 Monel metal, 433, 479
 Monoclinic sulphur, 223
 Mordants, 442, 455
 Morley, 79
 Mortar, 379, 382
 Moth balls, 305
 Motor boat, 266
 Motor cycle, 266
 Mucilage, 295
 Multiple proportions, 37, 84, 88, 89
 Atomic theory, 93
 Muria, 136
 Muriatic acid, 136, 139, 156
 Mustard, 219
 Sulphur in, 226
 Naphthalene, 272, 305
 Nascent state, 134
 Chlorine, 139, 140
 Hydrogen, 409
 Oxygen, 133, 134, 140, 164, 409
 Natural gas, 39, 111, 273
 B.t.u., 274
 Nature of gases, 56
 Negative electricity, 490
 Electrode, 209. See Cathode
 Photography, 468, 469
 Neon, 111, 179

Neutralization, 143, 144, 204, 205

And salts, 144

Equation, 144, 205

Ionic, 204, 205

Ionic equation, 205

Problems, 147

Water in, 204, 205

Neutral reaction, 143

Newton's metal, 357

Nichrome, 474

Nickel, 479

Alloys, 433, 474

Catalyst, 302

Coin, 433, 479

Plating, 479

Steel, 406, 479

Test, 479

Nickelic salts, 479

Nickelous salts, 479

Niter, 372

Pots, 236

Niton, 487, 488

Nitrates, 162

And nitrites, 165

Cellulose, 296

Decomposition, 162, 163

Oxides from, 167

Test, 164

Nitric acid, 159-170

And copper, 163

And metals, 163

Aqua regia, 139

Arc process, 168, 169

Boiling point, 161

Chemical conduct, 161

Commercial, 160

Duriron, 322

Exercises, 170

Formation, 159

From air, 167

From ammonia, 169

From nitrogen oxides, 167

Fuming, 167

Manufacture, 160, 167-169

Norway, 159

Oxygen from, 161

Preparation, 159

Problems, 170

Properties, 160

Strong acid, 216

Test, 164, 165

Uses, 162

Valence formula, 198

Nitric oxide, 166

And oxygen, 166

By catalysis, 169

Into nitric acid, 170

Mole, 176

Sulphuric acid, 234, 235

Test, 166

Volume relations, 174

Nitrides, 104

Nitrification, 163

Nitrites, 165

And nitrates, 165

Nitrogen, 102-105

And argon, 111

And life, 104

Atomic weight, 184

Atoms in molecule, 175

Boiling point, 111, 112

Chemical conduct, 103

Dioxide, 166, 167

Family, 333

Forms ammonia, 151

From ammonia, 151

In air, 107

Inert element, 104

Name, 104

Occurrence, 102

Oxides, 104, 161, 163-169, 234

Preparation, 102

Properties, 103

Test, 104, 148

Tetroxide, 167

Uses, 104

- Nitrogen, weight of liter, 103, 493
 Nitroglycerin, 302, 319
 Nitro-hydrochloric acid, 140
 Nitrose acid, 236
 Nitrosyl-sulphuric acid, 234
 Nitrous acid, 165
 Oxide, 157, 165, 166
 Noble metal, 140, 472
 Nodules, plant, 105
 Non-electrolytes, 205
 Molecular weight, 214
 Non-electrolytic solutions, 213
 Non-metals, 329, 330
 Aluminium, 420
 And anhydrides, 231
 And ions, 329
 Negative elements, 409
 Typical, 334
 Normal conditions, 55
 Gas volume, 54
 Salts, 231, 255
 Nucleus, atom, 490
 Nutrients, 307
 Nutrition, 307, 314

 Ocean, elements in, 8
 Water, 59
 Oil, cocoanut, 302
 Cottonseed, 301, 302
 Fats, 300, 301
 Fuel, 266
 Gas, 278
 Hydrogenation, 48, 302
 Lubricating, 270
 Olive, 301
 Oleic acid, 300
 Olein, 300, 301, 302
 Oleomargarine, 302
 Olive oil, 301
 Onions, 219
 Onyx, 317, 377
 Ooze, 378
 Opal, 317

 Open hearth furnace, 401, 402
 Lining, 442
 Process, 401-404
 Charge, 403
 Orange mineral, 459
 Ore, 391
 Organic acids, 299, 300, 301
 Chemistry, 25, 198, 289
 Organic matter, 372
 Fertilizer, 105
 Oxidation, 60
 Sewage, 60
 Water, 59
 Orpiment, 354, 355
 Orthophosphates, 350
 Orthophosphoric acid, 347, 350
 Orthorhombic sulphur, 223
 Orthosilicic acid, 319, 321
 Osmium, 478
 Oxalic acid, 35, 256, 299
 Oxidation, 16, 17, 286, 409, 410, 454
 And ions, 410
 And oxides, 16
 And reduction, 46
 And valence, 409, 410
 Broad use, 409, 410, 454
 Hydrogen, 44
 In body, 20
 Iron chloride, 411
 Iron compounds, 408-413
 Nascent state, 134
 Of compounds, 17
 Organic matter, 60
 Ozone, 22
 Rapid, 17
 Slow, 17, 18
 Sulphuric acid, 239
 Sulphurous acid, 231
 Tin salts, 454
 Tissue, 309
 Oxides, 17
 And water, 68
 Common, 17

- Oxides, names, 17
- Oxidizing agent, 16, 408
- Hydrogen peroxide, 84
 - Nitric acid, 161
 - Potassium dichromate, 475
 - Potassium permanganate, 477
- Oxidizing flame, 285, 286
- Oxy-acetylene burner, 283
- Flame, 47, 48, 282, 283
 - Outfit, 283
 - Torch, 283
- Oxy acid, 145
- Oxygen, 12-23
- Acetylene flame, 282, 283
 - Acids, 140
 - Administering, 21
 - And body, 20
 - And digestion, 309
 - And iron, 15
 - And life, 20
 - And mercuric oxide, 19
 - And molecular weight, 174
 - And nitrous oxide, 165
 - And ozone, 22
 - And sulphur, 15
 - Atomic weight, 173, 184
 - Atoms in molecule, 175
 - Boiling point, 112
 - Breathing, 21
 - Breathing apparatus, 21, 22
 - By electrolysis, 211
 - Calculation of weight, 123
 - Chemical change, 91
 - Chemical conduct, 15, 16
 - Compounds, 13, 15
 - Cycle, 32
 - Discovery, 12, 19
 - Distribution, 12
 - Equivalent weight, 185
 - Exercises, 23
 - Family, 333
 - Formula, 97
 - From chlorine water, 131
 - From nitric acid, 161
 - In air, 107
 - In water, 77-82
 - Manufacture, 20
 - Mole, 176
 - Molecular weight, 173
 - Name, 19
 - Nascent, 133, 134, 140, 164, 409
 - Oxidizing agent, 16
 - Plant, 13
 - Plants, 31
 - Preparation, 12, 13
 - Properties, 14
 - Removing from steel, 403
 - Standard weight, 188
 - Storing, 21
 - Test, 16
 - Uncombined atoms, 134
 - Uses, 20
 - Weight of liter, 14, 50, 56, 67, 493
- Oxy-hydrogen flame, 47, 48, 317
- Ozone, 22
- And oxygen, 22
 - And water, 61
 - Bleaching, 22
- Paint, 460
- Black, 25, 252
 - Blackening, 460
 - Green, 354
 - Red, 459
 - White, 388, 445, 460
 - Yellow, 475
- Palladium, 478
- Palmitic acid, 300
- Palmitin, 300, 301
- Paper, 296-297
- Beater, 296
 - Filter, 295
 - Making, 232, 296
 - Parchment, 296
- Paraffin, 270
- Base, 270

- Paraffin, series, 272
 - Wax, 272
- Para-formaldehyde, 304
- Parchment paper, 296
- Paris green, 299, 355
- Parkes process, 457, 464, 465
- Particles, alpha, 485, 487, 491
 - Beta, 486, 489
 - In solution, 91
- Pearlash, 373
- Pencils, lead, 246
- Pentad, 193, 195
- Pentahydrate, 97
- Pentane, 272
- Pentavalent element, 193
- Percentage composition, 99
 - And formula, 99, 100
 - Problems, 101, 141
- Periodic classification, 330-336, 490
 - Halogens, 343
 - Law, 334
 - Table, 331, 333
- Permanent hardness, 385
- Permanganate ions, 477
- Permutit, 386
- Petit, 185
- Petrified wood, 317
- Petroleum, 39, 267-271
 - Agitators, 269
 - Coke, 271
 - Cracking, 268
 - Distillates, 268, 271
 - Industry, 267
 - Look boxes, 271
 - Properties, 267
 - Refining, 268-271
 - Sources, 267
 - Stills, 269
 - Well, 268
- Pewter, 454
- Phenol, 305
- Phlogiston, 18
- Phosphates, 346, 347, 350
 - Acid, 350
 - And life, 350, 351
 - Calcium, 350-352
 - Dicalcium, 352
 - Normal, 350
 - Rock, 351
 - Silver, 350
 - Sodium, 350
 - Test, 350
 - Tricalcium, 352
- Phosphoric acid, 347, 349, 352
 - Anhydride, 350
 - Ions, 350
 - Test, 350
- Phosphorus, 346-354
 - And air, 103
 - And life, 350
 - Burning, 15, 281, 347, 348
 - Cycle, 351
 - Dangerous, 348
 - Exercises, 358
 - Fertilizer, 351
 - Formula, 179, 348
 - In food, 351
 - In iron, 395
 - In steel, 399
 - Manufacture, 346, 347
 - Matches, 15, 348, 349
 - Ordinary, 347
 - Pentoxide, 80, 103, 349
 - Poisonous, 348
 - Problems, 358
 - Red, 348
 - Sulphide, 349
 - Variable formula, 179, 348
 - White, 347
 - With air, 107
 - Yellow, 348
- Photography, 241, 341, 343, 468, 469
 - Film, 296
 - Flash light, 440
 - Radium, 484
- Photomicrographs, 397, 406

- Phylloxera, 218
- Physical change, 65
 - Properties, 2
- Pickles, 142
- Picromerite, 372
- Pig iron, 395
- Pigment, 460, 462, 476
- Pintsch gas, 278
- Pitchblende, 480, 482
- Placer mining, 470
- Plant, hydrogen, 39
 - Ice-making, 154
 - Oxygen, 13
 - Sulphuric acid, 235
- Plants, carbon dioxide, 31, 110
 - Food, 31, 105
 - Leguminous, 105
 - Sunlight, 31
- Plaster of Paris, 384
- Platinum, 236, 407, 478
 - Alloys, 478
 - Arsenide, 478
 - Black, 478
 - Catalyst, 45, 169, 233
 - Family, 333
 - Foil, 478
 - Melting, 47
 - Spongy, 478
 - Substitute, 407, 478, 479
- Platinite, 407, 478, 479
- Plumbago, 246
- Plumbous plumbate, 459
- Poison gas, 131
 - Hydrocyanic acid, 371
- Polonium, 489
- Porcelain, 423
 - Lined vessels, 370
- Portland cement, 384
- Positive nucleus, 490
 - Electrode, 209
 - Photography, 469
- Potash, 373
 - Caustic, 373, 374
- Prussiate of, 412
- Potassium, 371-374
 - Acid fluoride, 337
 - Acid tartrate, 374
 - Aluminium silicate, 422
 - And life, 374
 - And water, 40
 - Antimonyl tartrate, 356
 - Atom in molecule, 179
 - Bichromate, 475
 - Bromide, 340, 341
 - Carbonate, 373, 374
 - Chlorate, 13, 14, 71, 97, 99, 117, 120, 123, 207, 373
 - Chloride, 14, 372, 373
 - Chromate, 474
 - Cobaltinitrite, 480
 - Cyanide, 374
 - Dichromate, 475
 - Equivalent weight, 186
 - Ferricyanide, 412, 413
 - Ferrocyanide, 412, 413
 - Fertilizer, 374, 375
 - Fluoride, 338
 - Gold cyanide, 472
 - Hydroxide, 373
 - Iodide, 342, 343
 - Manganate, 477
 - Nitrate, 104, 372
 - Nitrite, 165, 372
 - Permanganate, 231, 477
 - Sulphate, 374
 - Sulphocyanate, 413
 - Tartrate, 299, 366
 - Test, 372
- Pottery, 424
- Powder, baking, 30, 157, 350, 365, 366, 374, 421
 - Bleaching, 133
 - Smokeless, 296
- Precautions, equation writing, 117
- Precipitate, 140
- Precipitation, 140

- Pressure and gases, 29, 30
 Atmospheric, 52
 Cooker, 67
 Corrected, 67
 Normal, 55
 Standard, 55
 Vapor, 65, 494
 Priestley, 12, 18
 Print, blue, 412
 Photographic, 468
 Problems, acids, 147
 Air, 114
 Aluminium, 424
 Ammonia, 157
 Atomic weights, 190, 191, 228, 243
 Balancing equations, 126
 Bases, 147
 Boyle's law, 54, 58
 Calcium compounds, 389
 Calories, food, 315
 Carbon, 258, 259
 Carbon dioxide, 38, 259
 Charles' law, 52, 58
 Chlorine, 141
 Composition, 11
 Copper, 437
 Equations, 147, 158
 Equivalent weights, 190
 Food, 315
 From equations, 127
 Fuels, 288
 Gas volumes, 58
 Gold and silver, 473
 Halogens, 344
 Hydrogen, 49, 58
 Hydrogen sulphide, 228
 Iron, 414
 Lead, 462
 Magnesium, 450
 Mercury, 451
 Metric system, 11
 Mole, 181
 Molecular formula, 181
 Molecular weight, 101
 Neutralization, 147
 Nitric acid, 170
 Oxygen, 23, 58
 Percentage composition, 101, 141
 Phosphorus, 358
 Potassium, 375
 Radium, 492
 Review, 217, 336
 Silicon, 328
 Simplest formula, 101, 141, 181,
 243, 259, 328
 Sodium, 375
 Sulphur, 228
 Sulphuric acid, 242
 Tin, 462
 Vapor density, 181
 Volume from equations, 127
 Volumetric, 158, 181, 228, 243,
 259
 Water, 85
 Weight from equations, 127
 Process, regenerative, 402
 Producer gas, 39, 274
 Propane, 272
 Properties, 1
 Chemical, 2
 Compounds, 6
 Physical, 2
 Protein, 102
 Food, 308, 309, 311-313
 Function, 307
 Quantity needed, 311
 Prussian blue, 413
 Prussic acid, 371
 Ptyalin, 295
 Puddling, 396
 Pulmotor, 21, 34
 Pulp, wood, 296
 Purifier, gas, 275, 277
 Purple of Cassius, 472
 Putty, 379
 Pyrene, 135, 305

- Pyrex glass, 324
 Pyridine, 298
 Pyrites, 219, 391, 411
 Pyroligneous acid, 298
 Pyrolusite, 476
 Pyrosulphates, 241
 Pyrosulphuric acid, 241
 Pyrrhotite, 391

 Quadrivalent elements, 193
 Quartation, 471
 Quartz, 316, 318, 322
 Fused, 236, 317
 Quartzite, 318
 Quicklime, 379
 Quicksilver, 446
 Quinivalent elements, 193

 Radiation, 485
 Radical, 143, 193
 Ammonium, 155
 And ions, 202
 Antimonyl, 356
 Hydroxyl, 143
 Ions, 215
 Table, 194
 Table, ions, 214
 Valence, 193
 Valence rules, 196, 197
 Radioactivity, 483-487
 Radio-lead, 488
 Radium, 482-491
 And electrons, 490
 And uranium, 488
 Atom, 487
 Bromide, 482
 Carbonate, 483
 Chloride, 483
 Cost, 489
 Decomposing, 486
 Discovery, 482
 Disintegration products, 488
 Emanation, 487, 489
 Flame test, 483
 General properties, 483
 Half period, 487
 Ionizes air, 484
 Isolation, 483
 Luminous mixtures, 489
 Photography, 484
 Series, 487
 Sulphate, 483
 Uses, 489
 Rain, 59, 65, 107
 Water, 59
 Ramsay, 110, 111
 Rayleigh, 110
 Rays, 485
 Gamma, 485
 Reaction, 9, 115
 Acid, 142
 Alkaline, 143
 And equations, 125
 Basic, 143
 Ionic, 206, 207
 Neutral, 143
 Reversible, 152, 168
 Velocity, 152
 Reading equations, 119
 Realgar, 354, 355
 Red fire, 388
 Glass, 324
 Lead, 459
 Reducing agent, 34, 46, 409
 Aluminium, 417, 418
 Carbon monoxide, 34
 For gold, 470
 Hydrogen, 46
 Hydroquinone, 468
 Pyrogallie acid, 468
 Sulphurous acid, 231
 Reducing flame, 285, 286
 Reduction, 34, 46, 286
 And ions, 410
 And oxidation, 46
 And valence, 409, 410

- Reduction, broad use, 409, 410, 454
 By carbon, 34, 252, 394
 Carbon monoxide, 34, 394
 Dextrose, 292
 Fehling's solution, 292
 Flame, 285, 286
 Hydrogen, 46
 Iron chloride, 411
 Iron compounds, 408-413
 Iron ore, 394
 Lead ore, 456, 457
 Mercury chlorides, 454
 Silver solution, 292
 Tin ore, 452
 Zinc ore, 443
Refining petroleum, 268-271
Refrigeration, 150
Regenerative process, 402
Relative humidity, 108
Replacement, 42
 See Substitution
Rescue apparatus, 21, 22
Respiration, 20, 21
Retorts, gas, 276
 Zinc, 443
Reverberatory furnace, 396, 428
Reversible equation, 152
Reaction, 152, 168
Rhombic sulphur, 223
Richards, 187, 188, 488
River water, 59
Rock phosphate, 351
 Shell, 378
Rocks, 59, 319
Rose's metal, 357
Rosin, 297
Rouge, 410
Royal water, 140
Ruby, 419
Rust, iron, 408
 Tin, 453
Rusting, 15, 408
Rutherford, 104
Safety lamp, 273
Sal ammoniac, 156
Saleratus, 366
Sal soda, 364
Salt, common, 59, 362
 Dairy, 362
 Deliquescent, 75
 Glaze, 424
 Moist, 75, 362
 Standard, 362
 Table, 362
 Water, 59
Saltpeter, 370, 371, 372
 Chile, 341, 342, 370, 371
Salts, 142, 145, 204
 Abnormal behavior, 213
 Acid, 231, 240, 255, 365
 And ionization, 206
 And litmus, 142
 And valence, 197
 Basic, 454
 Composition, 143
 Dissociation, 202-216
 Electrolytes, 206
 Epsom, 240, 441
 Exercises, 146
 Formation, 139, 144, 145, 156, 207
 Formulas, 197
 Glauber's, 240, 369
 Hydrolysis, 365
 Ionic definition, 204
 Ionization, 202
 Naming, 145, 146
 Normal, 231, 255
 Properties, 143
 Rochelle, 434
 Smelling, 157
 Stassfurt, 372
Sand, 316, 318
 Paper, 318
 See Silica
 See Silicon dioxide
 Uses, 318, 323

- Sandstone, 318
- Saponification, 303
- Sapphire, 419
- Saturated solution, 70
- Scandium, 335
- Scrubber, 237, 276
- Seaweed, 341, 342
- Selenite, 384
- Selenium, 324
- Series, displacement, 435
 - Electrochemical, 436
 - Electromotive, 437
 - Periodic, 332
- Serpentine, 319
- Shells, 378
- Shoe-blackening, 250
- Shot, 354, 459
- Sicily, sulphur, 218, 219
- Siderite, 391
- Silica, 316-318
 - And alkalies, 318
 - Etching, 339
 - Fused, 317
 - Lining, 399
- Silicates, 319-321, 324
 - Decomposition, 319
 - Etching, 338-339
 - Fusible, 392
 - Of soda, 320
 - Slag, 392, 393, 394
 - Sodium, 320
- Silicic acid, 319, 321, 323
 - Colloidal, 321
 - Meta-, 319, 321
 - Ortho-, 319, 321
- Silicic anhydride, 321
- Silicides, 322
- Silicon, 316, 322
 - And sodium hydroxide, 41, 322
 - Carbide, 252, 322
 - Electro-, 318
 - Ferro-, 322
 - In iron, 395, 396
 - In steel making, 403
 - Test, 323
 - Tetrafluoride, 318, 323, 338, 339
- Silicon dioxide, 316-318, 321
 - See Silica
- Silk, weighted, 455
- Silver, 464-468
 - Alloys, 466
 - Amalgamation, 464
 - Ammonia chloride, 468
 - Ammonium ion, 466
 - Atomic weight, 185
 - Bromide, 341, 468
 - Chloride, 140, 468
 - Cleaning, 466
 - Coins, 466
 - Complex ions, 466
 - Cyanogen ion, 466
 - German, 433, 479
 - Halogen compounds, 241, 468
 - In copper ore, 431
 - In lead ore, 457
 - Iodide, 343, 468
 - Ion, 466
 - Ionic test, 207
 - Metallurgy, 464
 - Nitrate, 466, 467
 - Oxidized, 465
 - Parkes process, 464, 465
 - Phosphate, 350
 - Photography, 241, 468, 469
 - Plating, 467
 - Properties, 465
 - Quick-, 446
 - Refining, 434, 465
 - Separation from gold, 465, 471
 - Sodium cyanide, 466, 467
 - Specific heat, 185
 - Sterling, 466
 - Sulphate, 466
 - Sulphide, 226, 464, 465
 - Tarnishing, 226, 465, 466
 - Test, 468

Silverware, tarnished, 226, 466
 Simplest formula, 99, 100, 177, 178
 And molecular formula, 178
 Problems, 101, 141
 Siphon, 29
 Sizing, 297
 Slag, 347, 392, 393, 394
 Aluminium oxide, 418, 419
 Copper, 429
 Thomas, 401
 Slaking lime, 380
 Slate, 319
 Sleet, 107
 Small calorie, 261
 Smalt, 480
 Smelting, 392
 Copper, 428
 Iron, 392
 Lead, 456
 See Metallurgy
 Smithsonite, 442
 Smoke, 27, 263
 Consumer, 263
 Smokeless powder, 296
 Snow, 59, 65, 107
 Crystals, 63, 64
 Soap, 301, 303, 320
 Cleansing, 303
 Hard water, 385
 Kettle, 303
 Manufacture, 303
 Soft, 373
 Soda, 365
 Ash, 363
 Baking, 299, 365
 Calcined, 364
 Caustic, 366
 Cooking, 30, 365
 Sal, 364
 Silicates, 320
 Washing, 30, 364
 Water, 29, 69
 Sodium, 360-371

Acetate, 300
 Acid carbonate, 363, 365
 Acid sulphite, 232
 And chlorine, 132
 And water, 40, 41, 361, 362
 Atom in molecule, 179
 Bicarbonate, 30, 32, 255, 365, 374
 Carbonate, 30, 255, 318, 363-365,
 369
 Carbonate, hydrolysis, 364
 Chloride, 129, 362, 363, 372, 490
 Chlorine salts, 146
 Cyanide, 371
 Dichromate, 475
 Equivalent weight, 186
 Family, 332
 Glass, 324
 Gold cyanide, 471, 472
 Hydrogen and, 40, 41, 361, 362
 Hydroxide, 13, 41, 129, 130, 210,
 211, 303, 360, 366-369
 Hypochlorite, 134
 Hyposulphite, 241, 468
 Iodate, 341
 Ions, 202, 490
 Lactate, 299
 Manganate, 477
 Manufacture, 360
 Nitrate, 105, 159, 341, 370, 372
 Nitrite, 103, 165
 Oleate, 303
 Palmitate, 303
 Peroxide, 13, 361, 371
 Phosphates, 350
 Plumbite, 460
 Properties, 361
 Silicate, 320, 324
 Silver cyanide, 466, 467
 Stannate, 455
 Stearate, 303
 Sulphate, 240, 363, 364, 369
 Sulphide, 364
 Sulphite, 134, 230, 232, 342

- Sodium, test, 361
 Tetraborate, 369
 Thiosulphate, 72, 73, 241, 468
 Tungstate, 480
 Uranate, 480
 Soft coal, 18, 248, 250, 261
 Steel, 398, 405, 406
 Water, 385
 Solder, 370, 454, 459
 Solubility, and temperature, 70
 Curve, 71, 72
 Limited, 70
 Mutual, 70
 See Solution
 Table, 71
 Soluble glass, 320
 Solute, 69
 Solution, 68-77
 And electric current, 205
 And pressure, 69
 Aqueous, 69
 Chemical behavior, 206-208
 Colloidal, 76, 77
 Concentrated, 69
 Conductors, 205
 Crystallization, 71, 72
 Dilute, 69
 Electrolytes, 205, 213
 Electrolytic, 204, 205
 Freezing point, 212
 Gases, 69
 Ions in, 206, 213
 Liquids, 69
 Molecules in, 213
 Nature, 75-77
 Non-electrolytes, 205, 213
 Particles in, 76, 77, 91
 Saturated, 70
 Solids, 70-75
 Supersaturated, 72, 73
 True, 76
 Two classes, 201
 What ions in, 214
 Solvay process, 363
 Solvent, 68, 69
 Sour milk, 293, 299
 Speculum metal, 454
 Spelter, 443
 Sperrylite, 478
 Sphalerite, 218, 442
 Spiegel iron, 396, 399
 Spintharoscope, 485, 489, 491
 Spontaneous combustion, 18
 Sprinkler head, 357
 Stalactites, 255, 377
 Stalagmites, 255, 377
 Stamp mill, 470
 Standard condition, 54, 55
 Stannic acids, 453, 455
 Chloride, 454, 455
 Compounds, 454, 455
 Hydroxide, 455
 Oxide, 325, 452, 453
 Stannous chloride, 452, 454
 Compounds, 454, 455
 Sulphate, 452
 Starch, 261, 293-295
 Alcohol from, 298
 And dextrin, 295
 And dextrose, 294
 And iodine, 294
 In baking powder, 374
 Plants, 31
 Solution, 75
 Suspension, 76
 Test, 294, 343
 Stassfurt salts, 339, 372, 439
 Steam, 64
 And metals, 41
 Stearic acid, 300, 301
 Stearin, 300, 301
 Steel, 398-407
 Alloys, 407
 Aluminium in, 417
 And monel metal, 479
 Bessemer, 398-401

- Steel, brittle, 406
 - Chromium, 404, 407
 - Composition, 405
 - Crucible, 404, 405
 - Electric process, 405
 - Hard, 404, 405, 406
 - Hardness, 406
 - Heat treatment, 406
 - High speed, 407
 - Manganese, 407
 - Manufacture, 398-405
 - Mild, 405
 - Molybdenum, 407
 - Nickel, 406, 479
 - Open hearth, 35, 401-404
 - Properties, 405-407
 - Soft, 398, 405, 406
 - Special, 406
 - Structural, 405
 - Tempering, 406
 - Tool, 405
 - Tungsten, 407
 - Vanadium, 407
 - Wool, 15
- Sterling silver, 466
- Stibine, 356
- Stoneware, 424
- Storage battery, 459, 460
- Stove, 34, 35, 263-265
 - Blast furnace, 393
 - Fire in, 34, 35, 263-265
 - Polish, 246
- Strontium nitrate, 388
 - Salts, 388
 - Test, 388
- Structural formulas, 198
- 'Stucco, 384
- Sublimate, 156
- Sublimation, 156
 - Ammonium chloride, 156
 - Iodine, 342
- Substances, 1
 - And chemical change, 16
 - Burning, 18, 19
 - Chemical, 4
 - Substitution, 42
 - And valence, 196
 - Copper oxide, 46
 - Metal and acid, 42
 - Sucrose, 289
 - Suffix, acid, 146
 - ate, 146
 - ic, 141, 145, 195
 - ide, 145
 - ite, 145
 - ous, 141, 145, 195
 - Salt, 146
 - Sugar, 289-293
 - Beet, 289, 290
 - Cane, 289-291
 - Charcoal, 290
 - Evaporation, 67, 290, 291
 - Fermentation, 298
 - Fruit, 292
 - Granulated, 291
 - Grape, 292
 - Manufacture, 290
 - Milk, 292
 - Raw, 290
 - Reducing, 292
 - Refined, 291
 - Sulphates, 240
 - Acid, 240
 - Ionic test, 208
 - Insoluble, 240, 241
 - Normal, 240
 - Pyro-, 241
 - Soluble, 240
 - Test, 208, 241
 - Thio-, 241, 468
 - Sulphides, 218, 222, 225
 - Hydrogen, 224
 - Iron, 391
 - Sulphite, 232
 - Acid, 231, 232
 - Normal, 231, 232

- Sulphur, 218-224
 Allotropic, 224
 American industry, 220
 Amorphous, 223
 And oxygen, 15
 Brimstone, 219
 Candle, 232
 Chemical conduct, 222
 Crystals, 223
 Deposits, 219
 Dioxide, 219, 229, 230, 232
 Flowers, 219
 From calcium sulphate, 218
 Heated, 222
 Industry, 219
 In gunpowder, 373
 In iron, 395
 In steel, 399
 Louisiana, 219
 Mining, 219
 Modifications, 222
 Molecules, 222
 Monatomic, 222
 Monochloride, 218, 221, 222
 Monoclinic, 223
 Occurrence, 218
 Orthorhombic, 223
 Oxidation, 15-17, 222
 Oxides, 17, 229-234, 237
 Plastic, 223
 Properties, 221
 Pure, 220
 Purification, 219
 Rhombic, 223
 Roll, 219
 Springs, 224
 Texas, 219
 Trioxide, 233, 237
 Uses, 218
 Variable formula, 179
 Well, 219, 220
 Sulphuretted hydrogen, 224, 225
 Sulphuric acid, 234-241
 And copper, 229, 239
 And iron, 239, 396
 And metals, 39, 40, 239
 And water, 238, 239
 Anhydride, 233
 Chamber process, 234
 Contact process, 237
 Electrolysis, 41, 211, 212
 Equation, 121, 122
 Fire extinguisher, 32, 33
 Formula, 99, 100
 Ionic test, 208
 Ions, 211, 212, 216, 240
 Manufacture, 234-238
 Nordhausen, 241
 Oxidation, 239
 Plant, 235
 Problems, 242
 Properties, 238
 Pyro-, 241
 Specific gravity, 236
 Test, 208, 241
 Use carefully, 238
 Uses, 240
 Sulphurous acid, 230, 231
 Anhydride, 231
 Superheater, 275
 Superphosphate, 352
 Supersaturation, 72, 73
 Suspension, 76, 77
 Sylvite, 372
 Symbols, 8
 Atomic weights, 97
 Exercises, 100
 Formulas, 97
 Ions, 203
 Meaning, 96, 97
 Table, 7, Back cover
 Synthesis, 79
 Ammonia, 151-153
 Water, 79-82
 Table, atomic weights, Back cover

- Table, earth's crust, 7
 Elements, 7
 Human body, 8
 Ions, 214
 Metals, 330
 Ocean, 8
 Periodic, 331, 333, 335
 Solubility, 71
 Symbols, 7, Back cover
 Valence, 194, 195
 Weight of liter, 493
- Talc, 319
- Tallow, 301
- Tapping blast furnace, 394
- Tar, 276, 277
 Products, 305
- Tartar, 299
 Cream of, 299, 366, 374
 Emetic, 356
- Tartaric acid, 299
- Tartrates, 299
- Tellurium, 335
- Temperature and vapor pressure, 66
 Body, 27, 109
 Climate, 65
 Normal, 54
 Solubility, 70
 Standard, 54
- Tempering steel, 406
- Temporary hardness, 385
- Terracotta, 424
- Test, 16
 Acetic acid, 300
 Aluminium, 420
 Ammonium compounds, 156
 Antimony, 356
 Arsenic, 355
 Barium, 388
 Bead, 370
 Bismuth, 358
 Cadmium, 446
 Calcium, 386
 Carbon, 250
 Carbon dioxide, 27, 30, 253, 382
 Carbon monoxide, 257
 Chloride, 140
 Chromium, 475
 Cobalt, 480
 Combined nitrogen, 148
 Copper, 433
 Dextrose, 292
 Ethyl alcohol, 300
 Ferric compounds, 412, 413
 Ferrous compounds, 412, 413
 Flame, 362, 372, 386, 388
 Glucose, 292, 434
 Gold, 472
 Hydrochloric acid, 140
 Hydrogen, 46
 Hydrogen chloride, 138
 Hydrogen sulphide, 226
 Ionic, 207, 208, 413
 Magnesium, 442
 Manganese, 477
 Mercury, 448, 449
 Moisture in air, 108
 Nickel, 479
 Nitrate, 164
 Nitric acid, 164, 165
 Nitrite, 165
 Oxygen, 16
 Potassium, 372
 Radium, 483
 Silicon, 323
 Silver, 468
 Sodium, 361
 Starch, 294
 Strontium, 388
 Sulphate, 208, 241
 Sulphuric acid, 241
 Tin, 454
 Zinc, 446
- Tetrad, 193, 195
- Tetravalent element, 193
- Texas sulphur, 219
- Theory, 87

- Theory, atomic, 89
 Disintegration of radium, 487
 Electrolytic dissociation, 201, 206
 Gases, 57, 90
 Ionization, 201, 206
 Kinetic, 57, 90
 Kinetic-molecular, 57, 90
 Molecular, 57, 90, 172
 Phlogiston, 18
 Thermal equation, 261, 262
 Thermit, 418, 419
 Thermo-chemical equation, 262
 Thermometer, 493
 Absolute, 51
 Centigrade, 51, 493
 High boiling, 104
 Scales, 51
 Thiosulphate, 241
 Photography, 468
 Thomas-Gilchrist process, 401
 Thorium, 480
 Meso-, 489
 Oxide, 286
 Radioactive, 489
 Tiles, 424
 Tin, 452-455
 Alloys, 356, 357, 433, 454
 And silk, 455
 Basic salt, 454
 Block, 62, 63, 452
 Crystals, 454
 Dioxide, 452, 455
 Disease, 453
 Family, 332
 Foil, 454
 Hydrolysis, 454
 Hydroxide, 455
 Ions, 454
 Metallurgy, 452
 Mordants, 455
 Oxymuriate, 455
 Plate, 453
 Properties, 452
 Salt, 454
 Stannic compounds, 454, 455
 Stannous compounds, 454, 455
 Test, 454
 Uses, 453
 Valence, 454
 Toluene, 305
 Toning, 469
 Travertine, 377
 Triad, 193, 195
 Tribasic acid, 350
 Tripoli powder, 317
 Trivalent element, 193
 Tungsten, 407, 480
 Steel, 407
 Turnbull's blue, 412
 Turpentine, 132
 Tuyères, 392
 Type metal, 356, 459
 Ultra microscope, 91, 491
 Univalent element, 193
 Upward displacement, 149
 Uraninite, 480
 Uranium, 480
 And radium, 487, 488
 Atomic weight, 488
 Vacuum vessel, 67
 Valence, 192-199
 And atomic weight, 198
 And combination, 195
 And ions, 215-410
 And oxidation, 409, 410
 And reduction, 409, 410
 Defined, 193
 Determination, 198
 Displacement, 196
 Equivalent weights, 198
 Exercises, 199
 From atomic weights, 198
 Groups by, 333, 334
 Importance, 199

- Valence, interpretation, 195, 196
Learning, 336
Of ion, 215
Radicals, 193
Representation, 193, 197
Rules, 195, 197
Salts, 197
Substitution, 195
Tables, 194, 195
Terms, 193
Variable, 195
Writing formulas, 196, 197
Vanadium, 404, 407
Steel, 404, 407
Vapor, 65
Water, 65-67, 179
Vapor density, 173, 174
And atomic weights, 187
And molecular weight, 174
And oxygen, 173, 174
Carbon dioxide, 173
Method, 173
Molecular formula, 178
Vapor pressure, 65, 494
And mercury, 66
And temperature, 66
Application, 67
At boiling point, 67
At 100° C., 66, 67
Deliquescence, 75
Efflorescence, 74
Experiments, 65, 66
Maximum, 67
Table, 494
Water, 65
Varnish, 298
Vaseline, 270, 272
Velocity and pressure, 152
And catalyst, 153
Hastening, 153
Reaction, 152
Vermilion, 449
Vinegar, 142, 299
Vitamins, 314
Vitriol, blue, 240, 434
Green, 240, 411
White, 240, 445
Volume, gram molecular, 176, 177
Molar, 176
Mole, 176
Volumetric composition, 79, 81, 138,
153, 179, 180
Equation, 179, 180
Problems, 127, 181
Wall board, 320
Washing soda, 30, 385
Water, 59-84
Ammonia, 148, 150
Analysis, 61
And alcohol, 70
And chlorine, 61
And copper oxide, 46
And ether, 70
And heat, 68
And hydrogen, 44
And ions, 211, 364
And metals, 40
And oxides, 68
And ozone, 61
And sodium, 40, 361, 362
And steam, 64
And sulphuric acid, 238, 239
Bacteria in, 61
Beverage, 63
Boiled, 61
Boiling point, 64
Bromine, 341
Chemical conduct, 68
Chemical treatment, 61
Chlorine, 77, 78, 131
Composition, 41, 77-83
Condenser, 62, 63
Crystallization, 73, 74
Decomposition, 13, 68
Distillation, 62

- Water, distilled, 62, 63
 Drinking, 60, 61
 Electrolysis, 78, 211
 Exercises, 84
 Expansion, 63
 Filtering, 60
 Foods, 59
 Formula, 198
 Freezing point, 63
 From ions, 205
 Gas, 35, 39, 274, 275, 278
 Gases from, 13
 Glass, 320, 324
 Gravimetric composition, 79, 80
 Hard, 385, 386, 441
 Hardness, 385, 386, 441
 Household, 61
 Hydrogen in, 77, 81
 Hydrogen sulphide, 224
 Impure, 59
 In body, 59, 308
 In food, 309
 Ions, 205, 211, 212, 364
 Keeping, 61
 Lime, 381, 382
 Mineral, 69, 439
 Natural, 59, 69
 Need in body, 313
 Neutralization, 204, 205
 New York, 60, 61
 Occurrence, 59
 Ocean, 59
 Oxygen in, 77-82
 Ozone, 23
 Problems, 85
 Properties, 63
 Purification, 23, 59, 60, 61, 62, 434
 Qualitative composition, 77-79
 Quantitative composition, 79-81
 Rain, 59
 River, 59
 Royal, 140
 Salt, 59
 Sea, corrosive, 442
 Soda, 29, 69
 Sodium peroxide, 13
 Soft, 385, 386
 Softening, 385, 386
 Solvent power, 68
 Spraying, 60
 Stored, 60
 Synthesis, 79-82
 Three states, 64
 Underground, 69
 Vapor, 63, 64, 107-109, 179
 Vapor pressure, 65-67, 74, 75, 494
 Volumetric composition, 79, 81, 179
Wax, paraffin, 270
Weathering, 319
Weight of liter, 55, 493
 Acetylene, 493
 Air, 493
 Ammonia, 150, 493
 And molecular weights, 172, 493
 Carbon dioxide, 29, 253, 493
 Carbon monoxide, 33, 493
 Chlorine, 131, 493
 Ethylene, 493
 Hydrogen, 43, 493
 Hydrogen chloride, 137, 493
 Hydrogen sulphide, 493
 Methane, 493
 Nitric oxide, 493
 Nitrogen, 103, 493
 Nitrous oxide, 493
 Oxygen, 14, 50, 56, 67, 493
 Sulphur dioxide, 253, 493
Welding, 47, 283, 395
 By thermit, 418
 Oxy-acetylene, 283
 Wrought iron, 397
Welsbach light, 286
 Mantle, 480
Whetstone, 318, 323
Whey, 293
White lead, 460

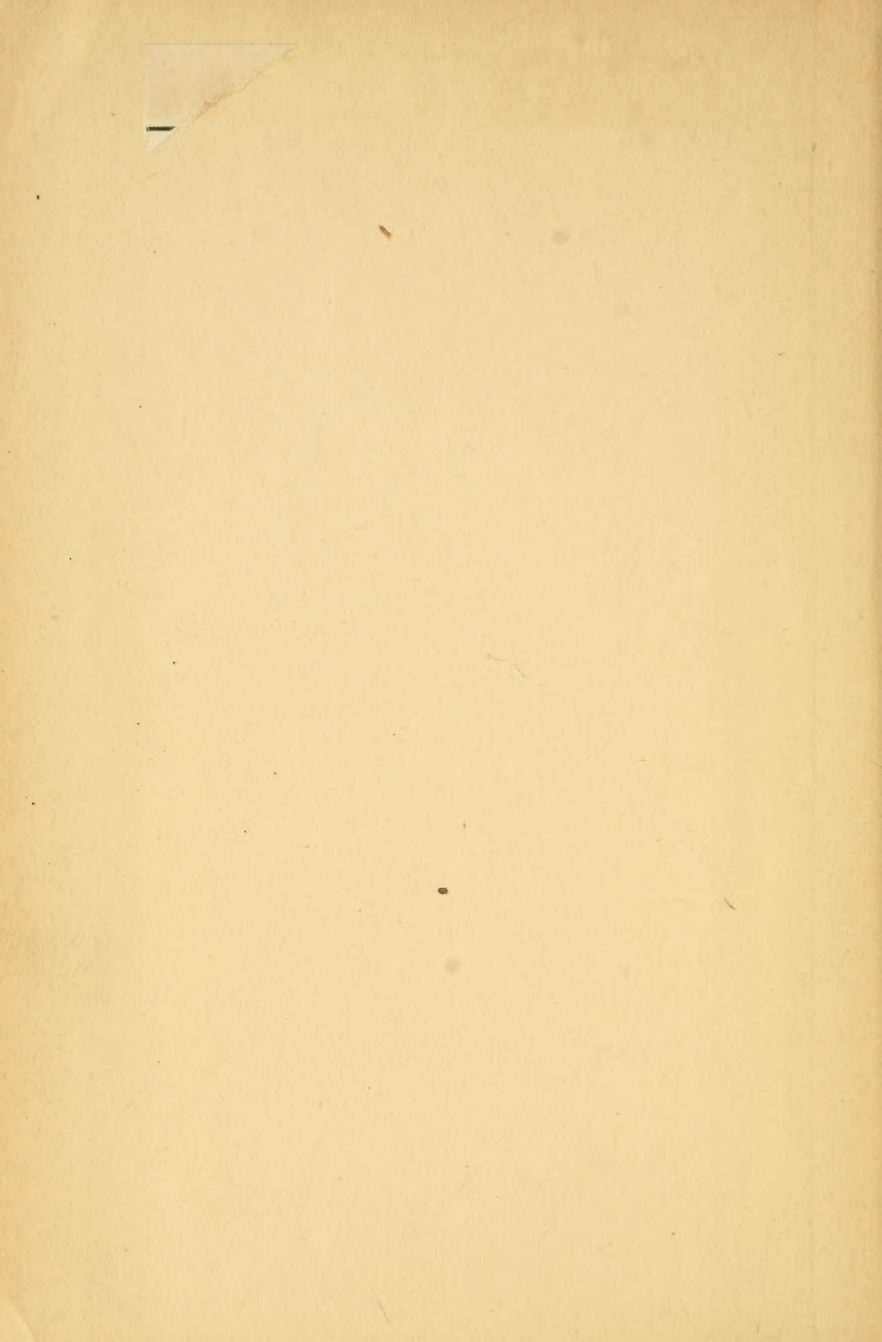
- White lead, blackening, 226
 Manufacture, 461
White vitriol, 445
Whitewash, 382
Whiting, 379
Willemite, 442
Wintergreen, 300
Wood alcohol, 250, 267
Wood and paper, 232
 Ashes, 371, 373, 374
 B.t.u., 267
 Burning, 265
 Cellulose, 295
 Paper, 296, 297
 Petrified, 317
 Pulp, 218
 Silicified, 317
Wood's metal, 357
World War, 131
Writing equations, 115-119
Wrought iron, 396-398

Xenon, 111
X-rays, 486
 Spectrum, 490

Yeast, 295
 And alcohol, 298
 And bread, 295
Yellowstone Park, 319

Zero, absolute, 51
 Group, 487

Zinc, 442-446, 471
 Alloys, 433, 444
 Amalgamated, 447
 And sulphuric acid, 42
 Atom in molecule, 179
 Blende, 218, 442
 Carbonate, 442
 Chloride, 445
 Complex compound, 445
 Dust, 443
 Electric cell, 436, 437
 Electrolytic, 443
 Equivalent weight, 186, 189
 Family, 332
 Flame test, 446
 Granulated, 444
 Hydroxide, 445
 Ions, 436, 444
 Metallurgy, 443
 Ores, 442
 Oxide, 442, 444, 445, 460
 Poisonous salts, 445
 Properties, 443
 Silicates, 442
 Sulphate, 240, 445
 Sulphide, 218, 225, 442, 445, 486
 Test, 446
 Uses, 444
 White, 445
Zincates, 444, 445
Zincite, 442
Zones, blast furnace, 394
Zymase, 298

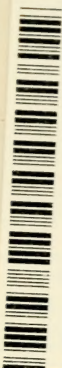


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