THE

SCHOOL CHEMISTRY

A NEW TEXT-BOOK

FOR HIGH SCHOOLS AND ACADEMIES

BY

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AVERY'S PHYSICAL SCIENCE SERIES.

FIRST LESSONS IN PHYSICAL SCIENCE.
FOR USE IN GRAMMAR SCHOOLS.
(By Dr. Avery and Professor Sinnott.)

ELEMENTARY PHYSICS.
A SHORT COURSE FOR HIGH SCHOOLS.

SCHOOL PHYSICS.
FOR HIGH SCHOOLS AND ACADEMIES.

SCHOOL CHEMISTRY.
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TO TEACHERS.

If possible, have a well-ventilated room set apart for chemical operations. It is very desirable that this room be provided with a ventilating hood (see Appendix, § 23) connected with the chimney flue or the ventilating shaft. If you can not do this, keep an open fire burning, so that offensive gases and vapors may be removed from the room as well as possible in that manner. Provide working benches or tables, about 75 cm. (2½ feet) wide. Each pupil should be allotted about a meter of working space at these tables, and *held responsible for its condition.*

If the room is provided with gas and water, a gas-cock and a water-cock, to which flexible tubing may be attached, should be within easy reach of each pupil. With pupils facing each other across a working bench of double width, it is possible to place the gas-cocks and the water-cocks so that one of each will accommodate four pupils. Over the benches place narrow shelves to hold the chemical reagents; beneath the benches place shelves or drawers for holding pieces of apparatus, etc. If the building is not connected with a regular water supply, see that water is always at hand in a tank or barrel, or in pails. A small cooking-stove will be a great convenience.

If a room can not be set aside as a laboratory, flat tables may be laid upon the desks, and the reagents, apparatus, etc., kept in a cabinet or cupboard. Of course, a regularly fitted laboratory, with further and better means than those above suggested, is desirable, and *should be provided* when means can be secured for the purpose.

The chief significance of the foregoing is that, as far as possible, each pupil is to perform the experiments for himself, make his own observations, and draw his own conclusions. This is important, whether some of the experiments have been performed by the instructor before the class or not. In every case there must be care that the conclusions arrived at are founded upon actual facts.

See that each pupil has a small note-book, and that he always has it at hand when he is making his experiments. See that the details of all experiments made by him are recorded by him in this book *at the time of the experiment*, not subsequently. In addition to the description of the operation, the record should contain an account of all observed phenomena, and the conclusions drawn from them. The ability to observe accurately and completely, and the ability to draw proper conclusions from observed facts, are the two greatest benefits to be derived from the study of general chemistry.

Make frequent and careful examinations of the pupil's notes, seeking to lead him to accurate observation, to intelligent discrimination between essential and merely incidental conditions and results of an experiment, to correctness of conclusions, and to precision and conciseness of statement.

Do not let your pupils get the idea that they are chemists; do not think that you ought to make chemists of them. After this course has been completed, a course in some good school of applied science will be needed for the pupil who desires to become a chemist.

The author would be glad to receive suggestions from teachers using this book, or to answer any inquiries they may make. He may be addressed at Cleveland, Ohio. He gratefully acknowledges the aid given him by many. Especial mention is due to Professor Albert W. Smith of the Case School of Applied Science; his work shows on almost every page.

TO THE PUPIL.

HAVE a place for everything and, when you are not using it, keep everything in that place. Clean every used utensil or piece of apparatus before you put it away. Cleanliness is a necessity in the chemical laboratory. Habitually label every chemical that you put away or leave for a time.

Before beginning an experiment, look over all your preparations, be sure that everything is ready and within easy reach, or you may suddenly discover a need for another hand. Be sure that all corks and connections are well fitted. Place your materials and apparatus at your left hand, and, when you have used them, lay them down at your right, keeping the middle of your bench clear for operating.

Do not waste even inexpensive material. Be sure that you know why you do a thing before you do it. Always use the simplest form of apparatus. Do not think that you must have everything just as described by the author. If a Florence flask is called for by the text-book and you have not one, you may be able to get along with a bottle.

Make careful notes on all experiments *as they proceed.* For this purpose you should have a note-book with substantial covers. Begin the account of each experiment with a brief statement of the object of the experiment; i.e., what you desire to prove or to illustrate by it. Then give a description of the process followed and of the apparatus used (a sketch is desirable), and record all observations. In conclusion, clearly state the inferences that you draw from what you have observed. Do not depend upon your memory to write up your notes after the experiment is finished. Some of your results thus recorded may subsequently be found to be incorrect. That is to be expected, and a repetition of the experiment will often be necessary. When you find that one of your results is wrong, mark it "Wrong," or "N.G." Do not be discouraged, but try to do better the next time.

Ever keep in mind the fact that an experiment is *intended to teach something*, and that it can not serve its purpose unless it is accompanied by careful observation of the effects produced, and by equally careful study of the relations borne by these effects to the conditions of the experiment.

Take an early opportunity for a careful reading of the Appendix to this book, so that you may be able to refer to it subsequently when you need help that it may give. The density (i.e., specific gravity) of all gases is referred to hydrogen as the standard. All temperatures are recorded in centigrade degrees.

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SCHOOL CHEMISTRY.

CHAPTER I.

THE DOMAIN OF CHEMISTRY.

"Read Nature in the language of experiment."

Experiment 1. — Provide a small quantity of loaf sugar. Before going further be sure of your ability to recognize sugar by its appearance and its taste. If necessary to the development of such ability, use a magnifying glass for inspection, and dissolve some of the sugar in your mouth. Break the sugar lumps into small pieces, and experimentally determine whether the material that you are handling is still sugar. With mortar and pestle (see Appendix, § 12), pulverize the small pieces, and experimentally find out whether the powder is still sugar. In a beaker (see Appendix, § 8), dissolve 50 grams of this powder in 20 cubic centimeters (see Appendix, § 6) of hot water. When the liquid has cooled, set the beaker on a porcelain platter or a tin tray, add a little strong sulphuric acid to the syrup, and stir the two liquids together. The contents of the beaker will become hot, and, instead of the mixed liquids, we shall have a bulky, black, porous mass that has little resemblance to sugar or to sulphuric acid. In fact, the sugar has been changed to something that is not sugar; its identity has been destroyed. This experiment illustrates several fundamental facts that we shall now consider.

1. Matter and Energy. — In the experiment above described we were dealing with things that occupied space and had weight. *Anything that thus "takes up room" and has weight is matter.* The different kinds of matter are called substances, as water, sugar, sulphuric acid, coal, silver, etc. That which brings about change in the position, condition, or nature of matter is called energy. One agent that we call gravitation causes a body, i.e., a definite portion of matter, to fall to the earth; gravitation is a form of energy. Another agent that we call heat causes ice to melt, and works many other changes; heat is a form of energy. Another agent that we call chemism causes iron to rust and, in the above experiment, changed sugar into something that is not sugar. In the study that we are now beginning, we shall have much to do with this agent. Chemism is a form of energy. Energy is the general name for all the agents that effect such changes. In other words, *energy is the power of doing work.*

Chemical Changes.

Experiment 2. — With a pair of pincers, hold a piece of magnesium ribbon in a flame over a piece of black paper. The metal burns with a brilliant flame and loses its identity as magnesium. Instead of a metal, we have on the paper a white, brittle solid or powder. In this powder the most powerful microscope will reveal not the slightest appearance of magnesium. Not heat nor cold nor magnetism nor motion nor mechanical division of any kind will reproduce it. A chemical change has taken place, whereby the magnesium combined with oxygen derived from the air to produce magnesium oxide or magnesium rust. The process is similar to the rusting of any metal, except that it is extremely rapid. In this experiment, as in Experiment 1, another distinguishing characteristic of a chemical change may be observed. Heat was evolved. Every chemical change is accompanied by an evolution or an absorption of heat, or by its equivalent of electricity.

Experiment 3. — Place about half a gram of tin-foil or turnings in a test-tube and cover it with about 10 cu. cm. of a mixture of equal parts of water and strong nitric acid. Care should be taken in handling this acid, as it is extremely corrosive.[1] Fold a strip of

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[1] If such an acid comes into contact with the skin or clothing, the part affected should be promptly treated with dilute ammonia-water, and thoroughly rinsed with water.

paper two or three times upon itself and wrap it around the test-tube near its mouth to serve as a holder, or thus use a strip of asbestos paper. Gently warm the tube until all the metal has been changed, taking care not to breathe the gas evolved. Keep the acid nearly boiling for some time after the action is over, then allow the white solid to settle, carefully pour the acid into a porcelain dish, and evaporate it to dryness over a gas-flame. There will be little or no residue, showing that the tin has been converted into the white solid left in the tube. This is tin oxide or tin rust, and may be collected for further examination and preservation by washing it upon a filter-paper until it is free from acid. This is ascertained by testing the wash-water with blue litmus-paper, which is reddened by all acids. In this experiment the tin has entirely lost its identity, the white tin oxide possessing none of the characteristic properties of tin. There is no simply mechanical means by which the tin can be recovered. Hence we conclude that a chemical change has taken place.

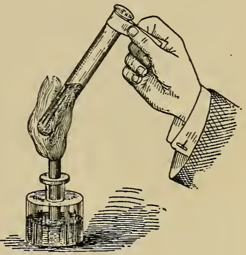
Fig. 1.

2. Changes in Matter. — From the foregoing experiments it appears that matter may be subjected to two kinds of change. In one of these, the substance does not lose its identity. In the other, the substance does lose its identity; it becomes something else from which the original substance can not be recovered by purely mechanical means. Changes of this second kind usually involve an intimate contact of two or more substances, although sometimes only one is sensibly apparent.

(*a*) Crushing, cutting, grinding, heating, cooling, magnetizing, and mixing with other substances are familiar examples of the first class of changes. The substance does not lose its identity, but may be restored, by merely mechanical means, to its first condition. Even when substances are melted or vaporized by heat, or are liquefied or solidified by cold, they are restored to their original state and full identity when the original temperature is resumed. Changes of this kind are *physical* or *mechanical changes*.

(*b*) When a metal rusts, when a body is charred or burned by acid or by fire, when an acid comes into contact with lime, soda, or any alkali, or in any one of many other cases, at least one substance is formed with properties different from those of the materials used. From this product, the original can not be recovered by mechanical means. The rust may be rubbed from the metal, but it is very different from the metal, and the compound formed by the acid and the soda is neither acid nor soda. Changes in which a substance thus loses its identity are called *chemical changes*.

3. What is a Molecule?—If any body of matter is broken or cut in two, both parts are still of the same substance. As in Experiment 1, the dividing process may be many times repeated without changing the identity of the substance; each bit of the sugar powder was as truly sugar as was the original lump. The question may arise whether such division without loss of identity can go on indefinitely. From the time of the great Greek philosophers this has been a disputed question. The prevailing chemical theory is that such a division can not go on indefinitely. Ultimately a portion is reached which, it is assumed, can not be again divided without destroying the identity of the substance. This particle, which is much smaller than the smallest that the best microscope can reveal, is called a molecule.

(*a*) Heat is a kind of energy resulting from motion, but this motion is wholly invisible. The motion pertains to parts so minute and within limits so narrow that we can not detect the absence of any part from its original place. "A molecule may, therefore, be defined as a small mass of matter, the parts of which do not part company during the excursions which the molecule makes when the body to which it belongs is hot."

(*b*) The molecules of any given substance are held to be exactly alike, but different from the molecules of any other substance. For example, one copper molecule is exactly like every other copper molecule, but different from every molecule of any substance that is not copper. The nature of the substance, therefore, depends upon the nature of its molecule. See § 4 (*a*).

(*c*) Any change, then, that does not affect the composition of the molecule is a physical change, because it produces no change in the identity of the substance; any change that does affect the composition of the molecule is a chemical change.

(*d*) Division of the molecule implies the existence of a smaller portion of matter than a molecule. These smaller particles into which molecules are divided by chemical changes have been given a special name.

4. What is an Atom? — The constituent parts of a molecule are called atoms. Nearly every molecule consists of two or more atoms; some molecules are very complex. As we shall see, the water molecule consists of two atoms of hydrogen and one of oxygen (H_2O); the sugar molecule consists of twelve carbon atoms, twenty-two hydrogen atoms, and eleven oxygen atoms, — forty-five in all ($C_{12}H_{22}O_{11}$). In Experiment 1, the sulphuric acid broke up the sugar molecule by abstracting its hydrogen and oxygen atoms and leaving carbon atoms that made up the residual charcoal. According to the generally accepted theory, *an atom is one of the component parts of a molecule, and is indivisible by chemical means.*

(*a*) In the preceding paragraph it is stated that the nature of the molecule determines the nature of the substance. It should be understood that the nature of the molecule is affected not only by the kind and the number of its constituent atoms, but also by the way in which those atoms are grouped or linked to form the molecule.

5. Elementary and Compound Substances. — *Any substance that can not be separated, by any known means, into* *two or more essentially different kinds of matter, is called an element. Any substance that can be thus separated is called a compound.* Compounds consist of two or more elements in chemical combination. The atoms of any given element are of the same kind; those of a compound are of two or more kinds. There are as many kinds of atoms as there are elements. Nearly four score elements have been already recognized (see Appendix, § 1). Some of these are very abundant and widely distributed; others have been found only in such minute quantities that their properties have not been satisfactorily determined. Other elements will doubtless be discovered, and it is possible that some substances now considered elementary will be found to be compound. In fact, nearly every improvement in our methods of examination leads to the detection of elements previously unknown. Silver and gold are elements; wood and water are compounds.

(*a*) The elements are sometimes classified as metals and non-metals, but the classification has lost much of its earlier importance. Iron, copper, gold, and silver are metals, and the properties familiarly associated with them are sufficiently definitive of the word metal as it will be used in this book. Of the groups into which compounds are divided, the most important three are acids, bases, and salts. These groups will be considered in a later chapter.

6. Atomic Attraction. — The attraction existing between atoms pertains chiefly to chemistry. *Atomic attraction is called chemism or chemical energy.*

Chemical Energy.

Experiment 4. — Pulverize *separately* a teaspoonful each of loaf sugar and potassium chlorate (chlorate of potash) and mix them together upon a porcelain plate. Dip a glass rod (see Appendix, § 5, *a*) into strong sulphuric acid and hold the rod in a horizontal position over the mixture and close to it but so as not to touch it. Notice that there is no peculiar action visible. Now hold the rod in a vertical position, so that a drop of acid will fall upon the mixture. The mixture is immediately ignited.

Experiment 5. — Into a mortar, put a bit of potassium chlorate *not larger than a grain of wheat*, and cover it with powdered sulphur. Notice that there is no peculiar action visible. Now rub them together vigorously with the pestle. A sharp explosion or a succession of minute explosions will take place.

CAUTION. — Phosphorus should not be handled with naked, dry fingers. It ignites easily by friction or slight elevation of temperature. Phosphorus burns are serious. Under water, it may be handled and even cut with safety. When taken directly in the fingers, the fingers should be wet. "Better be careful than sorry."

Experiment 6. — Cover a bit of phosphorus, *the size of a pin-head*, with pulverized potassium chlorate and wrap the materials in a bit of soft paper, so as to form a minute torpedo. The phosphorus and the particles of potassium chlorate lie close together, but no action takes place. Now place the torpedo on a small anvil or other smooth, hard surface and force the phosphorus and potassium chlorate closer together by a blow with a hammer. A violent explosion takes place.

7. Limitation of Chemical Energy. — The foregoing experiments illustrate the fact that *atomic attraction is effective at insensible distances only.* In only a few cases is it possible by mechanical means to bring solid particles sufficiently near each other for the desired chemical action. The necessary freedom of molecular motion is generally secured by solution, fusion, or vaporization of one or more of the materials used. Hence solvents and heat are important agents in the chemical laboratory.

(*a*) A body is dissolved or "in solution" when it is so finely divided and its particles are so completely dispersed through the water or other solvent that they can neither be seen nor separated from the liquid by filtering.

Chemical Action.

Experiment 7. — Rub together in a mortar 4 grams of sodium sulphate crystals and 2 grams of potassium carbonate. The two solids form a liquid. Repeat the experiment with ice and salt.

Experiment 8. — Saturate 4 cu. cm. of water with calcium chloride. Add slowly 0.5 cu. cm. of sulphuric acid. The two transparent liquids form a white, opaque solid.

Experiment 9. — Moisten the inner surface of a beaker, or of a clear tumbler, with strong ammonia-water, and place a few drops of the liquid in the glass. Cover it with a glass plate (or a piece of writing paper). Moisten the inner surface of a similar clear glass vessel with hydrochloric (muriatic) acid. Invert the second vessel over the first, mouth to mouth, so that the contents of the two vessels shall be separated only by the plate. Each vessel is filled with an invisible gas. Now remove the plate. The invisible gases diffuse into each other and form a dense cloud that slowly settles in the form of a white powder.

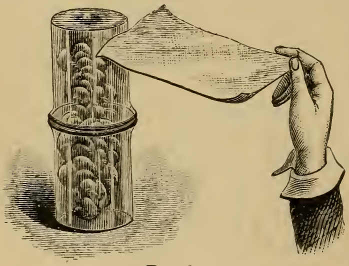

FIG. 2.

Experiment 10. — In a conical test-glass, or in a test-tube, dissolve a few crystals (0.5 of a gram) of silver nitrate in 10 cu. cm. of water. In a second test-glass, place a similar solution of lead nitrate; in a third, a solution of mercuric chloride (corrosive sublimate); in a fourth, 10 cu. cm. of chlorine-water (see Experiment 88), to which a few drops of a freshly prepared dilute solution of starch have been added. Each solution will be as clear as water. To each, add a few drops of the colorless solution of potassium iodide, and notice the colors produced, yellow, orange, scarlet, and blue.

Experiment 11. — Into a glass tube 2 cm. in diameter, and 15 or 20 cm. in length, having one end closed and rounded like a test-tube, place 20 milligrams of freshly burned charcoal. Draw the upper part of the tube out to a narrow neck. Fill the tube with dry oxygen and seal the tube by fusing the neck. Weigh the tube and its contents very carefully. By gradually heating the rounded end of the tube, the charcoal may be ignited and, with sufficient care, entirely burned without breaking the tube. When the charcoal has disappeared, weigh the tube and its contents again. The chemical changes that led to the disappearance of the charcoal have caused no change in the weight of the materials used (see Appendix, § 5, *c* and *d*).

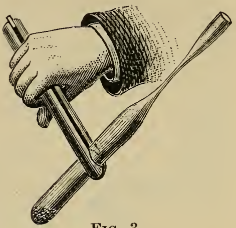

FIG. 3.

8. Conservation of Mass and Energy. — From the preceding paragraphs we learn that atomic attraction is a very powerful agent, but that it acts only upon the minutest divisions of matter and at distances too small to be perceptible. The resulting action leads to a change of identity and to a general change of properties excepting weight. This exception is the direct result of the indestructibility of matter. Every atom of matter has a certain definite weight, and as, in these changes, the atoms are merely rearranged, the sum total of the weights of these atoms must remain unchanged. This is called the law of the persistence or of the conservation of mass. As will be seen from the next paragraph, chemical action takes place between definite quantities of matter only. The law of the conservation of mass finds a parallel in the law of the conservation of energy, — one of the most important generalizations of modern science. The various kinds of energy may be transformed from one to another, but the total energy is not thereby increased or diminished.

Constituents Free or Combined.

Experiment 12. — Fine iron-filings and powdered sulphur may be mixed in any proportion. From such a mixture the iron may be removed by a magnet; the sulphur may be removed by solution in carbon disulphide, filtration, and subsequent evaporation of the filtrate. The iron is still iron, the sulphur is still sulphur. In the mixture the free iron or sulphur particles may be detected with a microscope. Now mix thoroughly 4 grams of the powdered sulphur with 7 grams of the iron-filings, and place the mixture in an ignition-tube (see Appendix, § 5, *a*) about 12 cm. long. By wooden nippers, hold the tube over the gas- or the alcohol-lamp, as shown in the figure. Part of the mixture may be similarly heated in the bowl of a common clay pipe instead of the ignition-tube. The sulphur melts and combines with the iron to form a sulphide of iron. There is no longer anything to be attracted by a magnet, or to be dissolved by carbon disulphide. The microscope reveals no particle of either constituent of the mixture. The ferrous sulphide, which contains the iron and the sulphur, differs from both in appearance and properties. It always consists of 7 parts of iron to 4 parts of sulphur by weight (or 56 : 32), however or wherever obtained.

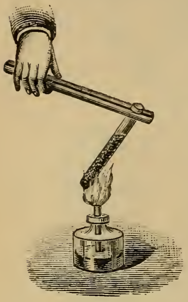

FIG. 4.

9. Mixtures and Compounds. — Mixtures of two or more substances may be formed by mingling them in all conceivable proportions, but a compound formed by chemical action consists of certain invariable proportions of its constituents. Thus, oxygen and hydrogen may be mixed in any desired proportion, but they will unite to form water only in the ratio of eight parts to one by weight, or one part to two by volume. In a mixture, the constituents are said to be free; in a compound, they are said to be combined or in combination.

(*a*) Gunpowder is composed of charcoal, sulphur, and potassium nitrate (niter or saltpeter) mechanically mixed. The potassium nitrate may be washed out by water, and, by evaporating the water, may be secured in the solid form. The sulphur may then be removed from the mixture, as in Experiment 12. The charcoal will be left alone. The constituents of gunpowder could not be thus separated if they were in chemical union. When gunpowder is ignited, the constituents *combine* to form enormous volumes of gaseous products.

10. Chemistry Defined.—*Chemistry is the branch of physical science that deals with changes in the identity of substances, and, hence, with all changes within the molecule.* It treats of the laws, causes, and effects of elemental combination.

11. Atomic Symbols. — Chemists have a short-hand way of writing the names of the substances with which they deal. In chemical notation, each element is represented by the initial letter of its Latin name. When the names of two or more elements begin with the same letter, the initial letter is followed by the first distinctive letter of the name. Thus, C stands for carbon, Ca for calcium, and Cl for chlorine. This use of the initial letters of Latin names secures uniformity among chemists of all countries. In only a few cases do the Latin and the English initials differ. The symbols of all the elements may be found in the list on the third page of the cover of this book. These symbols are frequently used to represent their respective substances in general. Thus, for the sake of brevity, we may write "a liter of O," but in the symbols (i.e., formulas) of compound bodies, and in equations representing chemical reactions (§ 141), the symbol of an element represents a single atom. To represent several atoms, we use figures placed at the right of the symbol and a little below it. Thus, C_2 means two atoms of carbon.

12. Molecular Formulas. — The symbol of a molecule is formed by writing together the symbols of its constituent atoms, indicating the number of each kind, as just stated. A molecule of water consists of three atoms, two of hydrogen and one of oxygen; hence, its symbol is H_2O. Like the atomic symbols of the elements, these symbols of the molecules of compound substances are used to represent their respective substances. Thus, we sometimes speak of a liter of H_2O, but in the equations representing reactions, each of these symbols represents a single molecule. To represent several molecules, we place the proper figure before the symbol. Thus, $3H_2O$ represents three molecules of water. The symbol of a molecule is often called its formula. Chemical notation is the written language of the science.

13. Nomenclature of the Elements. — The nomenclature of chemistry is the result of an attempt to indicate the composition of a substance by its name. The names of the elements were generally chosen arbitrarily, although some of them allude to some prominent property, as chlorine from the Greek *chloros*, signifying green. Chemical nomenclature is the spoken language of the science.

14. Nomenclature of Binary Compounds. — The names of binary compounds (those containing only two elements) have the characteristic termination *-id* or *-ide*. Compounds of single elements with oxygen are called *oxides*, similar compounds with chlorine are called *chlorides*, those with sulphur are called *sulphides*, etc. Thus, we have lead oxide, silver chloride, and hydrogen sulphide. When any two elements unite in more than one proportion, one or both of the words constituting the name are modified, as in hydrogen peroxide, carbon disulphide, mercurous chloride, and mercuric chloride.

NOTE. — In an attempt to simplify the spelling of chemical names, many chemists write chlorin, instead of chlorine; chlorid instead of chloride; oxid, sulphid, etc. It is not yet apparent whether the attempt is to end in success or failure. In either event, no ambiguity will annoy the student of this book.

15. Nomenclature of Ternary Compounds. — The most important compounds containing three or more elements are the acids (see § 89). Most of these consist of hydrogen and oxygen united to a third, or characteristic, element that gives its name to the acid. The terminations *-ic* and *-ous* are used with the name of the characteristic element to indicate a greater or less amount of oxygen in the acid. Thus we have:

Nitr*ic* acid	HNO_3	Sulphur*ic* acid	H_2SO_4
Nitr*ous* acid	HNO_2	Sulphur*ous* acid . . .	H_2SO_3

At least a part of the hydrogen of an acid may be replaced with different metallic elements, giving us the large and important class of compounds called salts (see § 91). The generic name of the salt is formed by changing the *-ic* termination of the name of the acid to *-ate*, or by similarly changing *-ous* to *-ite*. Thus, phosphor*ic* acid furnishes phosph*ates*, while phosphor*ous* acid furnishes phosph*ites*. The specific name of the salt is derived from that of the element used to replace the hydrogen of the acid. Thus we have:

Nitr*ic* acid	HNO_3	Potassium nitr*ate* . . .	KNO_3
Nitr*ous* acid	HNO_2	Potassium nitr*ite* . . .	KNO_2
Sulphur*ic* acid	H_2SO_4	Potassium sulph*ate* . .	K_2SO_4
Sulphur*ous* acid . . .	H_2SO_3	Potassium sulph*ite* . .	K_2SO_3

(*a*) Some chemists prefer to modify the name of the replacing element, making it an adjective, e.g., potassic nitrate. In the case of English words that can not be adapted to such adjective forms, the Latin word is used; e.g., plumbic nitrate for lead nitrate. In some cases old forms are still frequently used; e.g., chlorate of potash for potassium chlorate. In some cases, a strict adherence to systematic chemical nomenclature would lead to the use of inconvenient names, as potassium-aluminum sulphate for common alum.

CHAPTER II.

WATER AND ITS CONSTITUENTS.

I. ANALYSIS OF WATER.

Experiment 13. — The apparatus represented in Fig. 5 consists of a vessel containing water (to which a little acid has been added to increase its conductivity) in which are immersed two platinum strips, the electrodes of a galvanic battery. Glass tubes containing acidulated water are inverted over the platinum electrodes. A battery of one or two good storage cells or of three or four Grove cells will answer very well for our present purpose. When the circuit is closed, bubbles will be noticed rising in the glass tubes and gradually displacing the water therefrom. Gas will accumulate about twice as rapidly in one tube as in the other.

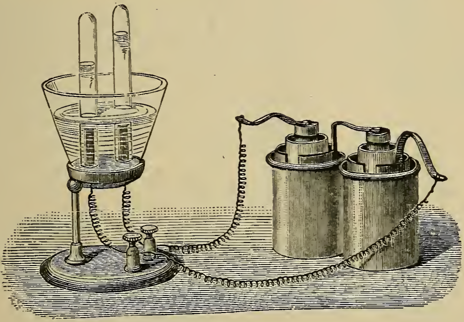

FIG. 5.

16. The First Question. — One of the most familiar substances in nature is water. Perhaps we do not know of what it is made, or whether it is an element or a compound. By the time the water has been displaced from one of the tubes, we shall, perhaps, be wondering what is in the tube. This question, "*What is it?*" is continually recurring to the chemist. Lift the tube carefully, holding it mouth downward, and cover its mouth with the thumb. It looks like air; *is* it air? To obtain our answer, we must, as usual, make an experiment.

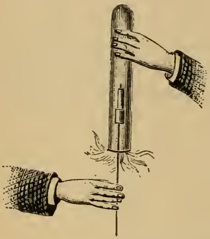

FIG. 6.

Experiment 14. — Light a taper or a dry splinter of wood, and thrust it into the tube. The taper-flame will be extinguished and the gas will burn at the mouth of the tube. Notice the appearance of the flame. The taper may be withdrawn and relighted at the mouth of the tube and the experiment repeated. We have received the answer to our experimental inquiry. It is not air. It is a gas lighter than air and inflammable. It has been named hydrogen.

17. What is in the other tube? — By this time the other tube is probably full of gas. If so, break the electric circuit and remove the tube, closing its mouth as before. Is it air? Is it hydrogen?

Experiment 15. — To put these questions in proper form, light the taper and let it burn until a spark will remain upon the wick when the flame is blown out. Thrust the glowing taper (or a glowing splinter) into the tube. The taper is rekindled and burns with unusual vigor and brilliancy. The answer is as prompt and unmistakable as before. It is not air; it is not hydrogen. It is a gas that supports combustion much more vigorously than air does. It is called oxygen.

18. Analysis and Synthesis. — By chemical analysis, we mean the breaking up of a compound into its constituent parts (see Experiment 29); by chemical synthesis, we mean the union of two or more substances to form one, different from any of its constituents (see Experiment 39). Synthesis may be used to prove the results of analysis.

19. The Synthesis of Water. — So far, we have seen that water is composed of oxygen and hydrogen, there being twice as great a volume of the latter as of the former. If we desire to know whether water has any other constituent, or suspect that these gases came from the small quantity of acid used to increase the electric conductivity of the water, it would be natural to try to unite these gases and to see what the product is. For such an experiment we are not quite ready. By the analysis of something we have secured separated oxygen and hydrogen; for their synthesis, it is desirable that we know more about them.

II. HYDROGEN.

Symbol, H; density, 1; atomic weight, 1; valence, 1.

20. Occurrence. — Free hydrogen occurs in nature as a small constituent of natural gas, of some volcanic gases, and of the gases of some coal mines. It is known to exist in some meteorites, in the nebulæ, and in other stellar bodies. It is a small but constant constituent of our atmosphere. In combination, it is almost everywhere, being found in water, in petroleum, and in all animal and vegetable substances.

21. The Apparatus. — Provide a good bottle, about twenty centimeters (8 in.) high, and having a mouth about two and five-tenths centimeters (1 in.) in diameter. See that the edges of the bottle are smooth. To the mouth of this bottle fit a fine-grained cork or a rubber stopper pierced with two holes. Furnish it with a funnel-tube, *a*, and a delivery-tube, *b* (see Appendix, § 5, *b*). The funnel-tube should be of such a length that, when the cork is in its place, the tube will reach within one centimeter (½ in.) of the bottom of the bottle. In all cases the sharp edges of glass tubing should be rounded in the gas-flame, to prevent its cutting the stopper or the rubber tubing and thus causing the apparatus to leak. To the delivery-tube, *b*, connect a piece of glass tubing, *d*, bent near each end. The connection may be made by a short piece of snugly fitting rubber tubing, *c*. If desirable, *c* and *d* may be replaced by a piece of rubber tubing of suitable length. The lower end of *d* terminates beneath the inverted saucer or tin plate, *e*, placed in the pan, *f*. The saucer has a notch in its edge for the admission of *d*, and a hole in the middle of its bottom; this hole should be a little larger than the delivery-tube. Into the pan, pour enough water to cover the saucer. Fill a bottle, *g*, with water and invert it over the hole in the bottom of *e*. Atmospheric pressure will keep the water in *g*.

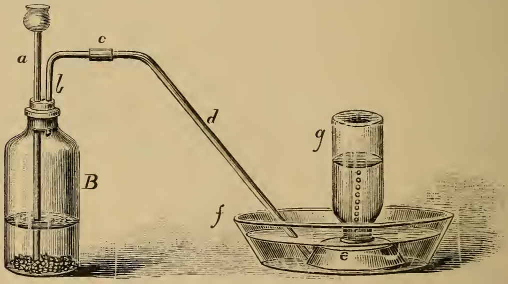

Fig. 7.

22. The Preparation. — Melt about 125 grams (4 oz.) of zinc in a clay crucible or an iron ladle, and slowly pour it, while very hot, into a pail or a tub of water, from a height of several feet. Put twenty-five or thirty grams (1 oz.) of this granulated zinc or of clippings of ordinary sheet zinc into the gas-bottle, *B*, pour in water until the bottle is about a quarter full, and replace the cork. *Be sure that all of the joints about the mouth of the bottle are tight.* To test this, place the delivery-tube between the lips and force air into the bottle until water rises in the funnel-tube and nearly fills it. Place the end of the tongue against the end of the delivery-tube to prevent the escape of air from the bottle. If the water retains its elevation in *a*, the joints are tight. If the water falls in *a* to the level of that in *B*, the apparatus leaks and must be put into satisfactory condition before going on. Pour dilute sulphuric or hydrochloric acid through the funnel-tube, *a*, in small quantities, not more than a thimbleful at a time. Gas will be generated with lively effervescence in *B* and bubble up in *g*, displacing the water therefrom. This method of collecting a gas, by the displacement of water, is called "collecting over water."

23. The Collection. — The gas first delivered will be mixed with the air that was in the apparatus at the beginning of the experiment. This should be thrown away, as *it is dangerously explosive.* When a quantity of gas about equal to the contents of the gas-bottle has thus been allowed to escape, fill a test-tube or a small wide-mouthed bottle with the gas, remove it from the water-pan, being careful to hold it mouth downward, and bring a lighted match or other flame to the mouth. If the gas burns with a puff, or a slight explosion, it is not yet free from air. In this way continue to test the gas until a sample burns quietly at the mouth of the tube and within it. Keep the end of the delivery-tube, *d*, under water until you are sure that the hydrogen is unmixed with air. Do not, at any time, bring a flame into contact with any considerable quantity of hydrogen until you have established its non-explosive character by testing a small quantity as just described. For such tests, bottles are not so good as test-tubes or cylinders as they confine the gas more and thus increase the danger in case of an explosion. Add acid through the funnel-tube from time to time, as may be necessary to keep up a brisk effervescence in the gas-bottle. Fill several bottles with the unmixed gas, slipping the mouth of each, as it is filled, into a saucer containing enough water to seal the mouth of the bottle and thus to prevent the escape of the hydrogen. If you have used the pneumatic trough (see Appendix, § 13) instead of the water-pan, the bottles may be left upon the shelf of the trough, which should be a little below the surface of the water. At your earliest convenience, fill one of the gas-holders (see Appendix, § 14) with hydrogen. At the end of the experiment, pour off some of the clear liquid from the gas-bottle, and evaporate it in a porcelain dish over a lamp until a solid begins to separate. Then allow the liquid to cool and examine the crystals that form.

24. The Reaction.—The hydrogen just prepared resulted from the action of the zinc upon the acid, water being used to dissolve the solid compound thus formed. Resulting from this action we have the hydrogen gas and a chemical compound called zinc chloride if hydrochloric acid was used, or zinc sulphate if sulphuric acid was used. This compound remains dissolved in the water of the gas-bottle. The zinc chloride or sulphate is obtained by evaporating the solution. Hydrochloric acid is composed of hydrogen and chlorine; its molecular formula is HCl. The zinc chloride is composed of zinc and chlorine and is represented by $ZnCl_2$. The changes that took place in the bottle may be represented by the following equation (see § 141):

$$Zn + 2HCl = ZnCl_2 + H_2 + \text{heat}.$$

The free zinc united with the chlorine of the acid to form the zinc chloride, thus setting free the hydrogen of the acid. As hydrogen is a gas, it bubbled through the water causing the effervescence. As zinc chloride is a soluble solid, it was dissolved by the water. From the clashing together of atoms in this reaction, much heat was developed. At the close of the experiment, small black particles are sometimes to be seen floating in the solution in the gas-bottle. These are bits of carbon that were present, as impurities, in the zinc.

Physical Properties of Hydrogen.

Experiment 16. — Instead of "collecting over water," collect the gas by "upward displacement," as follows: Bring the delivery-tube, *d*, of the gas-bottle (Fig. 7) or of the gas-holder into a vertical position. Hold over it a test-tube, or a small bottle, and cause the hydrogen to flow rapidly through the tube, *d*. In a few moments the air will be driven from the test-tube and replaced with hydrogen. That this gas is not mixed with air (after allowing the hydrogen to flow a sufficient length of time) may be shown by testing it in the manner described in § 23. What does this experiment teach?

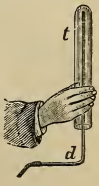

FIG. 8.

Experiment 17. — Refill the bottle with hydrogen, cover the mouth, turn the bottle right side up, remove the cover, and quickly apply a flame. How does the hydrogen flame differ from those previously seen? Why?

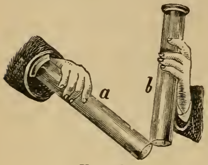

FIG. 9.

Experiment 18. — Take two cylinders or large test-tubes of equal size. Fill one of them, *a*, with hydrogen. Bring the mouth of *a* to that of *b*, gradually turn *a* from its inverted position, until it is upright below *b*. Place *a* upon a table and, in half a minute, test the two tubes with a flame. If the experiment has been neatly performed, it will be found that the hydrogen was poured upward from *a* to *b*. This "upward decantation" is possible because of the extreme levity of this gas as compared with the surrounding air.

Experiment 19. — Equipoise two beakers. Fill the inverted beaker with hydrogen by upward decantation. The equilibrium will be destroyed, and the glass containing hydrogen will rise.

FIG. 10.

Experiment 20. — To the flexible rubber delivery-tube of a gas-holder containing hydrogen, attach the stem of an ordinary clay pipe, or of a small glass funnel. With the gas flowing slowly (the flow being controlled by the stop-cock), dip the pipe into a dish of soap-suds, and, when a film is formed over the mouth of the pipe, turn its mouth upward and open the stop-cock wider. The bubble will soon break away from the pipe and rise like a balloon.

NOTE. — The last experiment will be more satisfactory if the soapsuds is prepared by making a strong solution of white castile soap in warm soft water that has been recently boiled, and adding half its volume of glycerin. Shake the mixture thoroughly, and it is ready for use.

Experiment 21. — Over a vertical tube delivering hydrogen, hold a sheet of gold-leaf or of unglazed paper. The gas will pass through the gold or the paper, and may be lighted on the upper side of the sheet.

Experiment 22. — The remarkably rapid diffusion of hydrogen may be shown by closing one end of a glass tube 3 or 4 cm. in diameter and about 30 cm. long, with a plug of plaster of Paris 1 or 2 cm. thick, filling it with hydrogen by upward displacement and placing the mouth of the tube in a tumbler of water. The outward diffusion of the gas through the porous septum reduces the pressure on the water in the tube, which is then forced upward by atmospheric pressure. An argand lamp chimney answers well for the experiment. The plug may be inserted by spreading a stiff paste of the plaster and water in a layer of the desired thickness upon a piece of writing-paper and pressing one end of the chimney down into it. In an hour or two the plaster will have set. The paper may then be easily removed and the plaster outside the tube broken off. Allow it to dry over night before using. In filling the tube with gas, hold it so that the septum will be covered with the fleshy part of the hand to prevent premature diffusion. The water may be colored with cochineal or indigo or ink.

Experiment 23. — To show the effect of hydrogen upon sounds produced in it, fill a large bell-glass with the gas, suspend it mouth downward, and strike a bell in it. Instead of the bell, one of the small squeaking toys well known to children may be sounded in the hydrogen.

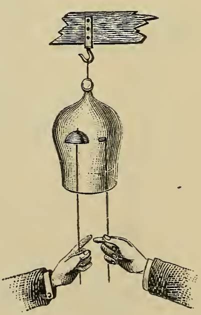

FIG. 11.

25. Physical Properties. — Hydrogen is a transparent, colorless, tasteless, odorless gas, as may be seen by direct inspection. Excepting possibly ethereon,[1] it is the lightest known substance. One liter of it weighs almost exactly 0.09 grams. It has been liquefied and solidified by subjecting it to a very great pressure at a very low temperature. Liquid hydrogen boils (i.e., changes to a gas) at − 240°, and is one of the lightest liquids, its density being only 0.07. Because of its extreme lightness, the gas diffuses very rapidly and has a peculiar effect upon sounds produced in it. It is only sparingly soluble in water.

(*a*) Hydrogen is about $14\frac{1}{2}$ times as light as air, and about 11,000 times as light as water.

(*b*) That hydrogen is not very soluble in water is shown by the fact that it may be collected over water. But the metal palladium absorbs or "occludes" several hundred times its volume of hydrogen, forming what seems to be an alloy. For this reason, and because of its chemical properties, hydrogen may be considered the vapor of a highly volatile metal.

Chemical Properties of Hydrogen.

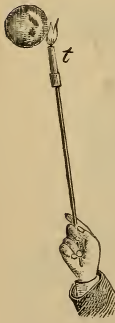

Fig. 12.

Experiment 24. — Repeat Experiment 14, and describe the phenomena fully. What two chemical properties of hydrogen does this experiment illustrate?

Fig. 13.

Experiment 25. — Repeat Experiment 20, and, while the bubble is in the air, touch it quickly with a lighted taper. Be sure to see all that the experiment shows, and then tell what you see.

Experiment 26. — For the bent delivery-tube of the gas-bottle, substitute a straight one having the upper part drawn out to form a jet. After

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[1] Certain physical facts point to the existence of an element at least a thousand times as light as hydrogen. It has been provisionally named "ethereon," but its existence has not yet been definitely proved.

the hydrogen has been escaping for some time, test small quantities of it until you are sure that it is unmixed with air. Then wrap a towel several times around the bottle (as an added precaution) and apply flame to the jet. Hold a small coil of fine wire in the upper part of the flame. Describe fully the flame of this "Philosopher's candle."

Experiment 27. — Over the flame of the "Philosopher's candle" hold a clear, dry, cold tumbler. In a few moments the clear glass will become dimmed with a sort of dew, evidently caused by the condensation of some vapor formed by the burning of hydrogen in air.

Experiment 28. — Pass hydrogen through a tube filled with granular calcium chloride to remove all moisture, and then through a tube terminating in a jet. After tests have shown that unmixed hydrogen is passing, ignite the gas at the jet. Over the jet place a bell-glass that is kept cool by a cloth wet with cold water. A liquid will collect on the inner surface of the cold glass; after a time it may be made to run into a cup below. This liquid may be shown to be pure water.

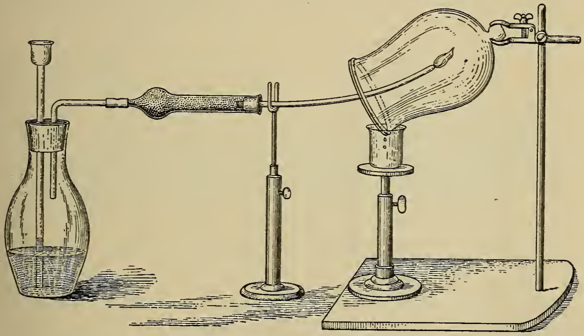


FIG. 14.

26. Chemical Properties. — Hydrogen is combustible at about 500°, i.e., it combines chemically with the oxygen of the air at that temperature. Its flame is pale but intensely hot. The burning of one gram of hydrogen yields more than 34,000 calories, it having the greatest heating power of any known substance. Whenever burned, either in the free state or in combination with other elements (e.g., alcohol or petroleum), the product of its combustion is water. It does not support ordinary combustion or respiration. When immersed in it, a lighted taper is extinguished and an animal is suffocated, in both cases because of the absence of oxygen. It forms an explosive mixture with air or oxygen.

NOTE. — In the periodic system of the chemical elements (§ 148, *b*), hydrogen falls in Group 1, the other members of which are considered in Chapter XI.

27. Uses. — On account of its lightness, hydrogen has been used for the inflation of balloons. On account of the intense heat produced by its combustion, it is used for melting platinum and other refractory substances, and in producing the calcium light (see Experiment 46). It is useful in reducing metallic oxides, the metals thus formed being remarkably free from impurities.

28. Tests. — Hydrogen is easily identified by its physical properties, especially its lightness, its ready inflammability, and the extinction of a flame placed in it.

III. OXYGEN.

Symbol, O; density, 16; atomic weight, 16; valence, 2.

29. Occurrence. — Of all the elements, oxygen is the most abundant and the most widely diffused. One-fifth of the air, by weight, is free oxygen, and eight-ninths of water, by weight, is combined oxygen. It has been estimated that fully two-thirds of the accessible world is oxygen.

Preparation of Oxygen.

Experiment 29. — Place about 10 grams of mercuric oxide in an ignition-tube, fit it with a perforated cork carrying a delivery-tube, and support it in any convenient way. Heat it gently with a gas- or a lamp-flame, and collect the evolved gas in bottles over water. When no more gas comes over, remove the delivery-tube from the water and then remove the lamp. When the ignition-tube has cooled, examine the material left on its walls. A molecule of mercuric oxide (HgO) is composed of one atom of mercury and one of oxygen. When heat is applied, these atoms separate from each other and reunite with atoms of their own kind to produce metallic mercury and oxygen gas. Compare the metal thus obtained with some from the laboratory collection and see if they are alike. Also see that the gas has the properties of one of those obtained in Experiment 13.

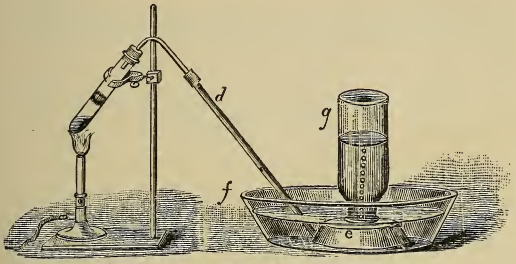


FIG. 15.

CAUTION. — Commercial manganese dioxide is sometimes adulterated with carbon. When such a mixture is heated with potassium chlorate, it gives rise to dangerous explosions. Hence, a new or doubtful sample may well be tested on a small scale by heating it with potassium chlorate in a test-tube.

Experiment 30. — Pulverize five grams of clean potassium chlorate ($KClO_3$) and mix it thoroughly with an equal weight of black oxide of manganese (manganese dioxide, MnO_2) that has been previously heated to redness and allowed to cool. Place the mixture in an ignition-tube, or a piece of gas-pipe, of such size that the tube will be not more than a third full. Keep the mixture four or five inches from the ends of the tube by plugs of asbestos or of glass wool. Close the ends of the tube with corks, one of which carries a delivery-tube. Support the ignition-tube in a slanting position and apply heat. The part of the mixture near the delivery-tube should be heated first and the heat so regulated that the evolution of gas is nearly uniform. Collect the gas over water in bottles of about 250 cu. cm. capacity. The first bottleful of the gas may well be rejected as impure. Remove the end of the delivery-tube from the water, or, better still, break the connection before removing the lamps. Why?

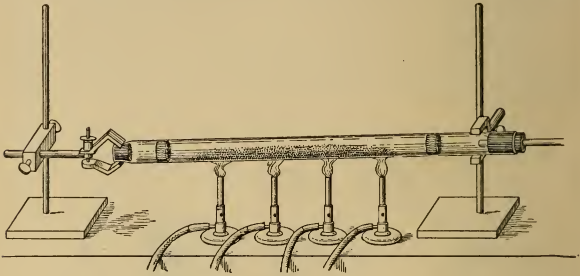


FIG. 16.

As soon as it is convenient, fill one of the larger gas-holders with oxygen. For this purpose it will be better to use larger quantities of the materials. A retort made of large gas-pipe and expressly constructed for the purpose is desirable in every laboratory (see Appendix, § 21).

30. Preparation. — Oxygen was produced in Experiment 13, and it is often prepared in large quantities by this method; small quantities are most conveniently prepared by Priestly's method, as in Experiment 29. The best method of making considerable quantities of oxygen for laboratory experiments, and the method by which it is usually prepared for commercial purposes, is by heating potassium chlorate as in Experiment 30. If the temperature is high enough, manganese dioxide can be reduced to a lower oxide of manganese, with the evolution of oxygen.

When barium peroxide (BaO_2) is heated to 700° under diminished pressure it is reduced to barium oxide (BaO); i.e., it gives up part of its oxygen. When heated in air under an increased pressure, this barium oxide takes up oxygen from the air, and is thus changed back to the peroxide, which may be thus used repeatedly. By continuing such a process, oxygen is sometimes prepared for commercial purposes.

Oxygen may be prepared without the use of heat by the action of dilute hydrochloric acid on a mixture of barium peroxide and manganese dioxide. For this purpose, mix fifty grams of barium peroxide and twenty-five grams of manganese dioxide. Place this mixture in a flask similar to that shown in Fig. 7, slowly add the dilute acid, and collect the gas over water. Small quantities of oxygen may be quickly prepared without the use of heat by the action of water on sodium peroxide. For this purpose, a dropping tube will be found convenient.

As will soon appear, air is a mechanical mixture of two gases, oxygen and nitrogen, and may be liquefied by high pressure at a low temperature. As liquid nitrogen boils at a lower temperature than oxygen does, when the liquefied air is allowed to evaporate, the nitrogen passes off in the first portion and leaves nearly pure oxygen behind. This process is also used on the commercial scale.

31. The Reactions. — In the preparation of oxygen from mercuric oxide, the latter is decomposed into its constituent elements:

$$2HgO + \text{heat} = 2Hg + O_2.$$

At the end of the process described in the preparation of oxygen from potassium chlorate, the ignition-tube contained manganese dioxide and potassium chloride (KCl). This chloride is easily soluble in water; the dioxide is not. After the tube has cooled, all of the manganese dioxide may be recovered unchanged by agitating the solid residue from the tube with water, and filtering. The dioxide suffered no permanent chemical change and was used only because, in some way for which no satisfactory explanation has yet been given, it caused the chlorate to decompose more quietly and at a lower temperature. This effect, produced by what seems to be the mere presence of a substance, has been called catalysis.

$$2KClO_3 + 2MnO_2 + \text{heat} = 2KCl + 2MnO_2 + 3O_2,$$

or

$$2KClO_3 + \text{heat} = 2KCl + 3O_2.$$

In the preparation of oxygen by decomposing manganese dioxide at a high temperature, the changes may be represented thus:

$$3MnO_2 + \text{heat} = Mn_3O_4 + O_2.$$

In the preparation of oxygen by heating barium peroxide, the chemical reactions may be represented thus:

$2BaO_2$ (under reduced atmospheric pressure) + heat (dull red) = $2BaO + O_2$.

$2BaO$ (in air under increased pressure) + O_2 + heat = $2BaO_2$.

Note. — The relations that exist between chemical action and heat have been recognized in the equations given in § 24 and § 31, and elsewhere in this book. As a full consideration of thermochemical phenomena would lead beyond the proper limits of an elementary course, no attempt will be made in these pages to do more than occasionally to call attention to them. See § 145.

32. Physical Properties. — Oxygen is a transparent, colorless, tasteless, odorless gas, not to be distinguished by its appearance from hydrogen or from ordinary air. One liter of it (under ordinary conditions of temperature and atmospheric pressure) weighs 1.4291 grams. As it is about one-tenth heavier than air, it may be collected by downward displacement, but it is more satisfactorily collected over water. It is sparingly soluble in water. Like hydrogen, it may be liquefied by subjecting it to high pressure and low temperature. Liquid oxygen has a light blue color and, under ordinary atmospheric pressure, boils at – 184°.

Chemical Properties of Oxygen.

NOTE. — The bottles containing the oxygen for the experiments immediately following should be prepared by grinding their lips flat with emery powder, as described in Appendix, § 5, *h*. Have ready several greased glass plates with which to close the mouths of the bottles thus prepared. During the combustions, it will be well to keep the mouths of the bottles covered loosely, as with cardboard.

Experiment 31. — Repeat Experiment 15, holding the bottle right side up, and allow the taper to burn until the flame dies out. Remove the taper and cover the mouth of the bottle. Label the bottle "No. 1."

Experiment 32. — Into a second bottle of the gas, thrust a splinter of dry wood having a glowing spark at its end. When aflame, withdraw it, blow out the flame, and repeat until the gas fails to rekindle the splinter. This is one of the best tests for oxygen. Cover the mouth of the bottle. Label this bottle "No. 2."

FIG. 17.

Experiment 33. — Place a lighted candle on a stand between two boys, *A* and *B*. Let *B* fill his mouth with oxygen from the gasholder. *A* may blow out the flame, leaving a glowing wick; *B* may then puff oxygen upon the wick and relight it. Repeat the experiment until the mouthful of oxygen is exhausted. *B* need not inhale the oxygen, but if a little does get into his lungs it will do no harm.

Note. — If convenient, perform the next five experiments in a darkened room.

Experiment 34. — Around a bit of charcoal, wind one end of a fine wire, to form a handle. Have ready a bottle containing a liter or more of oxygen. Ignite the charcoal at the lamp and thrust it into the bottle. Brilliant combustion will take place and continue until all of the charcoal, or all of the oxygen, is consumed. Cover the bottle as before, and label it "No. 3."


Fig. 18.

Experiment 35. — Place a bit of sulphur (brimstone) the size of a pea into a deflagration spoon (see Appendix, § 19) and hold it in the lamp-flame. It will melt and then take fire. While burning, thrust it into a good-sized jar of oxygen. It will burn with a beautiful blue flame and much more brilliantly than it did in the air. At the end of the experiment, cover the jar and label it "No. 4."

Experiment 36. — A larger glass vessel is desirable for this experiment. A good-sized bell-glass, such as is used in air-pump experiments, or a globe, such as is used for keeping gold-fish, will answer well. In the middle of a large plate or tray containing water 4 or 5 cm. deep, place a metal support rising several centimeters above the surface of the water. From a stick of phosphorus, cut, *under water*, a piece the size of a large pea, dry it thoroughly between pieces of blotting- or filter-paper, place it upon the support in the tray, ignite it with a hot wire, and quickly invert over it the vessel of oxygen. The combustion is exceedingly energetic and brilliant. The metal support for the phosphorus may be protected from combustion by coating its upper surface with lime, chalk, or plaster of Paris. At first, part of the gas may bubble out at the mouth of the vessel, but as the dense fumes formed by the burning of the phosphorus are absorbed, water will rise within the vessel. Then pour more water into the tray, if necessary to preserve the seal, and label the globe "No. 5."

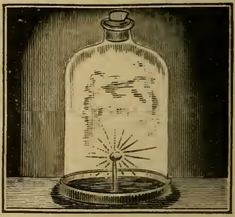


Fig. 19.

Experiment 37. — Form a spiral of fine iron wire (piano-forte wire is preferable, but a single strand of ordinary wire picture-cord will do well) by winding the wire upon a lead pencil or a piece of glass tubing; wind some waxed thread upon the lower end of the wire, or dip the end of the wire into melted sulphur so that a small sulphur bead shall adhere to the wire. At the bottom of a vessel containing two or three liters of oxygen place a layer of water or of sand. Ignite the thread or sulphur and quickly place the wire in the oxygen. The burning wax, or sulphur, heats the end of the wire to redness. The wire then burns with beautiful scintillations. The experiment may be made more brilliant by using a coiled watch-spring instead of the iron wire. The watch-spring, which may be had gratis of almost any jeweler, is to be softened by heating it to redness and allowing it to cool slowly; it may then easily be coiled. Wind the lower end of the spring with twine and dip it into melted sulphur, to prepare the kindling material. The kindling matter should be no larger in quantity than is necessary to heat the wire or spring to the necessary temperature; any excess interferes with the success of the experiment, by consuming the free oxygen and forming undesirable compounds in the jar. The melted metal globules sometimes fuse their way into or through the bottom of the jar, when the water or the sand is not provided to prevent such a result.

Fig. 20.

Experiment 38. — Blow a jet of oxygen into the flame of an alcohol-lamp. In the flame thus produced hold a piece of watch-spring or of steel wire. It will burn with brilliant scintillations.

Experiment 39. — Into bottle No. 1, put a piece of moistened blue litmus-paper; it will be reddened. Now pour in a little clear lime-water (slacked lime dissolved in water; see Experiment 56), cover the mouth of the bottle tightly with the palm of the hand and shake the bottle vigorously; a partial vacuum will be formed and the clear lime-water will become turbid and yield a white precipitate. *The reddening of the blue litmus-paper shows the presence of an acid.* The colorless gas formed by the burning of the taper in oxygen has united with the water to form an acid. What is this colorless gas? The turbidity of the lime-water and the precipitate show that it is carbon dioxide (CO_2), sometimes called carbonic anhydride, or carbonic acid gas. The carbon of the taper united with the oxygen.

$$C + O_2 = CO_2.$$

Experiment 40. — Try the contents of jars 2 and 3 with a lighted taper. The flame is extinguished as promptly as it would be by water. Numerous gases act in this way. We have seen that hydrogen extinguishes flame; but this gas is not kindled as we know that hydrogen would be. Try the contents of the jars with moistened blue litmus-paper. The paper is reddened. Have you any idea of what the gas is? Try the gas with clear lime-water. We have the turbidity, etc., as before. What do you now think the gas is? The dry wood burned in No. 2 was largely carbon, and the charcoal burned in No. 3 was nearly pure carbon. In either case,

$$C + O_2 = CO_2.$$

Experiment 41. — Test the contents of jar No. 4 with a lighted taper. The flame is promptly extinguished as before. Test with the moistened blue litmus-paper. The paper is reddened as before. What does this reddening show? Does the jar contain hydrogen? Does it contain oxygen? Do you *think* that it contains carbon dioxide? Why? Test with clear lime-water. *Does* it contain carbon dioxide? How was this gas formed? Was any carbon used in its production? The gas is sulphur dioxide (SO_2) sometimes called sulphurous anhydride.

$$S + O_2 = SO_2.$$

Note. — If we turn to jar No. 5 we shall find that the phosphoric oxide (P_2O_5) formed by the combustion of the phosphorus was dissolved in the water. If this water is tested with blue litmus-paper it will be found to have acid properties. We have thus formed oxides of carbon, of sulphur and of phosphorus, and seen that these oxides unite with water to form acids. If the litmus-paper used in testing these gases had been dry instead of wet it would not have been reddened. The oxide of iron (Fe_3O_4) formed in Experiment 37 is solid and insoluble in water.

33. Chemical Properties. — As illustrated in the preceding experiments, oxygen gas is chiefly marked by great chemical activity. In each case, the substance ignited in the oxygen united with it chemically, forming a compound called an oxide. Thus, an oxide is the product of the chemical union of oxygen with another element. Oxygen enters into combination with all the elements except fluorine, helium, and argon.

Oxygen unites directly with most substances with sufficient energy to produce light and heat. In the ordinary use of the term, combustion is chemical union with oxygen with such attending phenomena.

Liquid oxygen has a chemical activity even more vigorous than that of the gas, and has been used with oxidizable substances as an explosive. For instance, felt and similar substances, when moistened with liquid oxygen or liquid air, explode violently upon ignition. Such explosives have the advantage of becoming safe upon the evaporation of the liquid.

Note. — In the periodic system of the chemical elements (§ 148, *b*), oxygen falls in Group 6, the other members of which are considered in Chapter XVI.

34. Uses. — Oxygen is used in countless ways in the laboratories of nature and of man. It is essential to the processes of animal respiration, ordinary combustion, fermentation, and decay. It is used in the arts to increase the intensity of combustion for purposes of heat and light. If nearly pure oxygen could be made so cheaply that it might be used for the combustion of coal in furnaces, and for other chemical operations, such use would result in the material cheapening of many industrial processes. Because of its relation to respiration and combustion, oxygen is probably more commonly and constantly used than any other substance, certainly more than any other element. Its great importance in these connections will be more fully explained in the chapter on the atmosphere.

(*a*) When oxygen is needed in considerable quantities, it may be bought under high pressure in steel cylinders in which it may be kept indefinitely, and from which it may be drawn out as required.

Tests for Oxygen.

Experiment 42. — Into a large test-tube filled, over water, with nitric oxide (NO, see § 70) pass a small quantity of oxygen. The two colorless gases combine eagerly, forming dense red fumes that are rapidly dissolved in the water.

Experiment 43. — Dissolve a piece of potassium hydroxide (caustic potash, KOH) the size of a pea, in 10 cu. cm. of water and pour the solution into a long test-tube filled with oxygen. Add a few flakes of pyrogallic acid. Close the mouth of the tube with the thumb and shake the contents. The liquid will be blackened. Place the mouth of the tube under water and remove the thumb. Water will rise in the tube to fill the partial vacuum formed by the absorption of the oxygen in the tube by the liquid mixture.

35. Tests. — Free oxygen, not much diluted with other gases, is most easily tested by plunging into it a glowing splinter, as in Experiment 31. The only other gas that will thus rekindle the splinter is nitrous oxide (laughing gas, N_2O). This test, though generally enough, is not conclusive except in the known absence of nitrous oxide. When oxygen is mixed with nitric oxide (NO), the two colorless gases unite at ordinary temperatures to form a reddish brown gas, nitrogen peroxide (NO_2). Another test for oxygen is its action on an alkaline solution of potassium pyrogallate, with which it unites chemically to produce the brown compound with which fingers are often stained in photographic work. This test is commonly used to determine the amount of oxygen present in a mixture of gases containing it.

Ozone.

Experiment 44. — Prepare a cylinder of phosphorus three or four centimeters long, by scraping its surface clean under water. (Remember the caution preceding Experiment 5.) Place the phosphorus in a clean bottle of one or two liters capacity, and pour in enough water to half cover the cylinder. Close the mouth of the bottle with a plate of glass or a loose stopper, and set the bottle in a warm place (20° or 30°). In 10 or 15 minutes, notice the fog above the phosphorus. Allow the bottle to remain for several hours. The feeble, chlorine-like odor of ozone will be discernible. A still more convenient method is to place a few drops of ether in a tall beaker, and to stir the quickly formed vapor with a hot glass rod.

Experiment 45. — Prepare two slips of white paper by dipping them into a solution of starch and potassium iodide (see Experiment 102). Thrust one of these into a bottle of oxygen; no change will be noticed. Thrust the other test-paper into a bottle or beaker containing ozone; the white paper will be promptly colored blue. The energetic ozone displaces the iodine.

$$2\,KI + O_3 = K_2O + O_2 + I_2.$$

The free iodine colors the starch blue. See Experiment 132.

36. Ozone. — In addition to the ordinary form of oxygen, which contains two atoms in each molecule, a remarkable variety is known in which there are three atoms to each molecule. *This condensed and more active form of oxygen is called ozone.* In changing oxygen to ozone there is a volumetric condensation of one-third. Ozone is formed at the + electrode in the electrolysis of water; by the discharge from an electric machine through air or oxygen; or by the slow oxidation of phosphorus in moist air, etc. It is best prepared by electric apparatus devised for that purpose.

37. Properties of Ozone. — Ozone is one of the most powerful oxidizing agents known. It is probably present in pure country and sea air, and is noticeably absent in the atmosphere of large cities, where its oxidizing influence upon organic and other deleterious matter results in partial disinfection and its own transformation into oxygen and oxygen compounds. It has a highly penetrating odor. It is so energetically oxidizing that, if breathed continuously, it produces a corroding action on the throat and lungs. Unlike ordinary oxygen, ozone, especially when moist, oxidizes strongly at ordinary temperatures. For this reason, it is one of the most valuable disinfectants and purifiers.

Ozone may be detected by its odor in the air near a dynamo or an electric motor that is sparking, as in starting a loaded electric car. In its oxidizing action, its volume is supposed to undergo no change, the third atom of the ozone molecule (O_3) entering into combination and leaving the two atoms of the ordinary oxygen molecule (O_2). It is changed by heat into ordinary oxygen, with increase of volume.

38. Allotropism. — Although ozone manifests characteristics decidedly different from those of ordinary oxygen, its fundamental, chemical identity with oxygen is unquestionable. For example, the potassium oxide (K_2O) that it formed by displacing the iodine of the potassium iodide, in Experiment 45, is identical with the potassium oxide formed in any other way. *This capability of exist-*

ing in different physical forms with chemical identity undestroyed is called allotropism or allotropy. Ozone is an allotropic modification of oxygen.

EXERCISES.

1. How may Nature be questioned?
2. Judging only from the names, which is the richer in oxygen, phosphorous acid or phosphoric acid?
3. Suppose that the hydrogen of sulphuric acid is replaced with potassium; give the name of the resultant compound and of the class to which it belongs.
4. How many kinds of atoms are there in calcium oxide? In calcium carbonate?
5. State a characteristic difference between chemical energy and gravitation.
6. What is the chemical difference between sheet zinc and granulated zinc?
7. How is a gas collected over water?
8. What property of hydrogen enables us to transfer it from one vessel to another by upward decantation?
9. How may hydrogen be freed from moisture?
10. What is the chemical difference between O_2 and O_3?

IV. COMPOUNDS OF HYDROGEN AND OXYGEN.

39. Combustion of Hydrogen. — When hydrogen is heated to the temperature of about 500°, in the presence of free oxygen, the two elements enter into chemical union, forming water (H_2O). This was shown in a general way in Experiment 28. *Whatever the conditions under which hydrogen is burned in oxygen or in air, the sole product is water.* This is true, even in the combustion of a hydrogen compound.

$$2H_2 + O_2 = 2H_2O.$$

As oxygen is sixteen times as heavy as hydrogen, the gravimetric composition of water is eight parts of oxygen to one of hydrogen. See § 141 (*c*).

40. The Compound Blowpipe. — The compound or oxyhydrogen blowpipe consists of a double tube, one inside the other. The interior tube is connected by rubber tubing with the oxygen gas-holder; the outer tube, with the hydrogen gas-holder. Hydrogen is first turned on and ignited at *a*. Oxygen is then turned on until the flame is reduced to a fine pencil. The pressure at the gas-holders should be steady, the amount thereof being easily determined by trial.

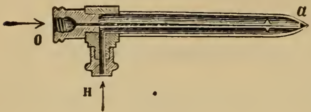


FIG. 21.

The Combustion of Hydrogen.

Experiment 46. — Hold bits of iron and of copper wires, watch-springs, strips of zinc, etc., in the flame of the compound blowpipe. They will be readily dissipated with characteristic luminous effects. A fine wire of platinum, an exceedingly refractory metal, is readily melted, and silver can be thus distilled. A piece of lime or of chalk, freshly scraped to a point and held in the flame, is heated to such a high degree of incandescence that it produces a light of remarkable intensity. This is essentially the Drummond or calcium light.

Experiment 47. — Over the jet, *a*, of the compound blowpipe, slip a piece of rubber tubing. With both gases flowing, dip the tubing into a metallic dish full of soap-suds until a mass of foam has formed. Close the stop-cocks at the gas-holders or at the blowpipe, remove the tubing from the soap-suds, and then touch the foam with a flame carried at the end of a stick about a meter in length. A violent explosion will take place. (See note following Experiment 20.)

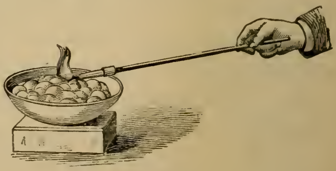


FIG. 22.

NOTE. — If you have no compound blowpipe, introduce one volume of oxygen and two of hydrogen into a gas-bag or a small gas-holder (see Appendix, § 14). The gases will soon become thoroughly mixed by diffusion, when they may be passed into the soap-suds through the rubber tubing. Remember that this mixture is *dangerously explosive; be sure that there is no possibility of flame coming into contact with the contents of the gas-bag or of the connected tubing.* The explosion just described was free from danger, because the restraining wall of the explosive mixture was only a thin film of water, the flying fragments of which could do no harm. If the contents of your gas-holder should explode, the flying fragments would probably do serious damage. It is advisable to throw away the mixed gases that may remain at the close of the experiments with them. Any attempt to burn these gases previously mixed, even as they issue from the jet of the compound blowpipe, will result in an explosion.

Experiment 48. — Repeat Experiment 26, using the mixed gases instead of hydrogen, and guarding carefully against an accidental explosion. The bubble, or a mass of bubbles dipped from the dish shown in Fig. 22, may be safely exploded while resting in the palm of the hand.

Experiment 49. — Support a wide tube of clear glass in a vertical position. A bottomless bottle, the neck of a broken retort, or a lamp-chimney will answer well. Through the perforated cork that closes the upper end, pass a stream of hydrogen from the gas-holder. When the air has been driven out of the bottle, apply a flame at the lower end and regulate the flow so that the gas burns slowly at the opening. From another gas-holder pass a current of oxygen through a piece of glass tubing drawn out to form a small jet. As the jet passes through the burning gas, the oxygen takes fire and burns in an atmosphere of hydrogen.

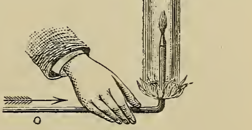


FIG. 23.

41. The Eudiometer. — The eudiometer is an instrument for determining the proportions in which gases unite. It consists of a strong glass tube with two platinum wires fused into the sides near the closed end. The wires nearly touch within the tube. One of the most common forms consists of a U-tube with the closed arm, *b*, graduated to cubic centimeters.

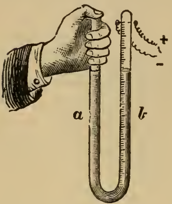


FIG. 24.

Volumetric Composition of Water.

Experiment 50. — Fill the eudiometer with water and hold it with the open arm, *a*, horizontal, under water and under the closed arm, *b*. By means of a rubber tube carrying a short piece of glass tubing drawn out to a fine jet, pass about 20 cu. cm. of pure oxygen from the gas-holder into *b*. Be sure that the air had been previously driven out of the delivery-tube; make the measurement with the eudiometer erect and the water standing at the same level in both branches. Water may be removed from *a*, if necessary to this end, by means of a pipette (see Appendix, § 6). Now introduce about 50 cu. cm. of pure hydrogen into *b*, and note the exact amount of gas therein as before. It may prove difficult to introduce exactly 20 and 50 cu. cm. A little variation matters not, *provided* that you measure accurately the amounts actually introduced, and that the volume of the hydrogen is more than twice that of the oxygen. Suppose that the first measurement shows 21 cu. cm. of oxygen, and that the second shows 75 cu. cm. of mixed gases. Then you have introduced 54 cu. cm. of hydrogen. Close the open end firmly with the thumb, leaving a cushion of air between it and the surface of the water, as shown in Fig. 24. Produce an electric spark between the ends of the platinum wires in the mixed gases. The spark produces combination between the oxygen and part of the hydrogen. On removing the thumb and bringing the liquid surfaces to the same level, it will be found that there are only 12 cu. cm. of gas in *b*. By filling *a* with water and closing it with the thumb, the gas may be easily passed from *b* into *a*, and thence, under water, to a convenient vessel for testing. It will be found to be hydrogen. The 21 cu. cm. of oxygen has united with 42 cu. cm. of hydrogen to form a minute quantity of water, leaving the 12 cu. cm. of hydrogen because there was no oxygen with which it could unite.

42. Volumetric Composition of Water. — If in the preceding experiment the eudiometer had been kept at a temperature above 100°, and the gases confined by mercury instead of water, *b* would have contained forty-two cubic centimeters of steam and twelve cubic centimeters of hydrogen. The volume of steam would be the same as that of the hydrogen that entered into its composition. The combination was accompanied by a diminution of volume equal to that of the oxygen entering into chemical union. In other words, three volumes shrink to two volumes in the process of combination. Representing equal volumes of the gases by equal squares, the volumetric composition of water and the condensation just mentioned may be represented to the eye as follows:

$$\boxed{\begin{matrix}\mathrm{H}\\1\end{matrix}} + \boxed{\begin{matrix}\mathrm{H}\\1\end{matrix}} + \boxed{\begin{matrix}\mathrm{O}\\16\end{matrix}} = \boxed{\quad\begin{matrix}\mathrm{H_2O}\\18\end{matrix}\quad}$$

Water Tests.

Experiment 51. — Provide three samples of water; one of clean, fresh rain-water, one from the city or household supply, and one that is known to be contaminated. Put a portion of each sample into separate test-tubes that are clean, add to each a few drops of nitric acid and then a few drops of a solution of silver nitrate. Compare the quantities of precipitate formed in the several tubes. This is a test for chlorides, and is used here because animal refuse is always accompanied by salt, which is a chloride.

In like manner, place about 100 cu. cm. of each of the sample waters in clean test-tubes. To each, add, drop by drop, a dilute solution of potassium permanganate, shaking the tube after the addition of each drop. Count the drops added until a faint pink color remains after a few minutes. The permanganate is destroyed by animal or vegetable matter in solution. The number of drops required to produce a permanent pink color is a rough measure of the degree of contamination.

In separate porcelain dishes, on a steam bath (a beaker containing boiling water will answer), evaporate to dryness about 100 cu. cm. of each of the sample waters. When the residue is quite dry, carefully heat each dish over a gas- or an alcohol-flame until the residue begins to char. Observe the odor evolved. The residue from a pure water will be white, and will not evolve a disagreeable odor on charring.

43. Contaminated Waters. — Like oxygen, water is essential to the existence of animal life. It is universally present in the air, in the ground, and in animal and vegetable tissues. As it occurs in nature, it is never pure, fresh rain-water approaching most nearly to purity. Clearness alone does not indicate purity, as the most common impurities are held in solution. These dissolved impurities are commonly mineral salts, but they may consist of animal and vegetable substances.

The mineral substances in solution are smallest in natural waters derived from springs in regions of granite rocks, and highest in waters from limestone formations. When water is used in boilers for steam making, these mineral salts separate as the water is evaporated, and either form a muddy sediment in the boiler or adhere firmly to the flues and walls of the boiler, forming boiler-scale. See § 184.

Because of the animal and vegetable substances dissolved in it, water may become one of the most dangerous carriers of contagious diseases. The germs that cause these diseases feed on these dissolved substances and, under favorable conditions of temperature, multiply with great rapidity. For this reason epidemics of typhoid and similar diseases are often spread by the use of contaminated drinking water. When, for any reason, water is suspected of contamination with animal refuse, or, better still, until it has been proved free from all such contamination, it should not be used for drinking unless it has been boiled a quarter of an hour or more. The organisms that cause these diseases are killed by the temperature of boiling water, so that, unless subsequently contaminated, boiled water is free from this danger.

It may often be ascertained whether waters contain animal contamination by the fact that such waters give a white cloudy precipitate with a solution of silver nitrate, decolorize a dilute solution of potassium permanganate, and, when evaporated to dryness, leave a residue that blackens and emits a disagreeable odor when heated with a flame.

(*a*) The most perfect purification of water is secured by distillation. This process is largely used at sea, but it is not easily available for domestic purposes. The "flat" or vapid taste of boiled or distilled water may be removed by passing the water through a filter thus exclusively employed. Filtration affords a valuable but not complete protection against bacterial diseases, and the process is largely employed for both individual and public water-supply.

(*b*) Many natural waters act upon the lead of pipes through which they are conveyed, forming poisonous compounds. Lead pipes used for such purposes should be tin-lined.

44. Hydrogen Dioxide. — Hydrogen dioxide (H_2O_2) is generally prepared by the action of dilute sulphuric acid on barium dioxide:

$$Ba_2O + H_2SO_4 = BaSO_4 + H_2O_2.$$

It is a syrupy, colorless liquid and, when rapidly heated, separates into water and oxygen with almost explosive violence and the liberation of heat. It may be considered as composed of two groups of OH; thus, (HO)–(OH). This atomic group, OH, is called hydroxyl. Hydrogen dioxide is sometimes called free hydroxyl. It is used as an oxidizing agent, as a disinfectant and germicide, and for bleaching hair.

EXERCISES.

1. What is the difference between a chemical and a physical change? Make your answer as explicit as you can, and illustrate it.

2. (*a*) Describe briefly the common method for the preparation of oxygen, omitting no essential. (*b*) Tell what you can of hydrogen and its preparation.

3. (*a*) Give the symbol and chemical properties of oxygen. (*b*) What is meant by oxidation?

4. (*a*) What is an element? (*b*) How many are known? (*c*) What gases enter into the composition of water? (*d*) Prove your answer in two ways, one method being the reverse of the other. (*e*) What name do you give to each method?

5. When a current of steam is passed through an iron tube nearly filled with bright iron-turnings or filings, the tube being placed across a furnace and its middle portion heated to redness, large quantities of a combustible gas that may be collected over water are delivered from the tube. (*a*) What do you suppose the gas to be? Why? (*b*) Will the iron-turnings in the tube weigh more or less at the end of the experiment than they did at the beginning? Why?

6. How many hydrogen oxides are known? Name them. Define chemistry.

7. What is the distinction between a mixture and a compound?

8. (*a*) If 240 cu. cm. of hydrogen and 120 cu. cm. of oxygen are made to combine, what will be the name of the product? (*b*) If the experiment is performed in a vessel having a temperature above that of boiling water, what will be the name and volume of the product?

9. If 300 cu. cm. of steam are condensed to water and the water is decomposed, what will be the volume and composition of the product?

10. (*a*) What weight of hydrogen is there in 8064 grams of water? (*b*) What volume of hydrogen?

11. Describe the potassium permanganate test for the purity of water.

12. How could you tell oxygen from hydrogen?

13. State the principal difference between ordinary oxygen and its allotropic modification.

CHAPTER III.

AIR AND ITS CONSTITUENTS.

I. AIR.

45. Occurrence. — The earth is surrounded by an atmosphere of air extending to a height variously estimated at from fifty to two hundred miles.

Composition of the Air.

Experiment 52. — Repeat Experiments 42 and 43, using common air instead of oxygen. These tests show the presence of free oxygen in the air.

Experiment 53. — Provide a cork about 5 cm. in diameter and 2 cm. in thickness. Cover one side with a thin layer of plaster of Paris mixed with water. The paste may be raised near the edge of the cork so as to produce a concave surface. Dry the cork thoroughly and you have a convenient capsule for floating upon water. For a single experiment, the cork may be covered with dry powdered chalk or lime. Notice the "Caution" on page 15. Upon this capsule, place a piece of phosphorus *that has been dried* by wrapping it in blotting- or filter-paper. Float the capsule upon water in a pan, ignite the phosphorus with a hot wire, and cover it with a bell-glass or other wide-mouthed vessel. The water in the pan should seal the mouth of the bell-glass so as to exclude the external air. While the phosphorus is burning, hold the bell-glass down with the hand. The phosphorus combines

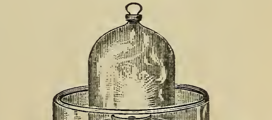


Fig. 25.

with the oxygen of the air, forming dense fumes of phosphoric oxide (P_2O_5). These fumes are soon absorbed by the water, which rises in the bell-glass to occupy the space vacated by the oxygen. As the water rises in the bell-glass, pour water into the pan as may be necessary to preserve the seal. If any phosphorus remains at the end of the experiment, be sure that it is burned up.

Experiment 54. — When the fumes of P_2O_5 have been absorbed, slip a glass plate under the mouth of the bell-glass and place it mouth upward, without admitting any air. If the bell-glass is capped, as shown in Fig. 25, it need not be removed from the water-pan; water should be poured into the pan until the liquid outside the receiver is at the same level as that inside. Test the gaseous contents with a lighted taper. The flame is extinguished, but the gas does not burn. It is neither oxygen nor hydrogen. It is nitrogen, an element that we shall study in the next section, and was left behind when the oxygen of the air united with the phosphorus.

Experiment 55. — To show approximately the quantitative composition of the atmosphere, pour into a graduated tube 10 cu. cm. of a solution of 3 grams of potassium hydroxide (caustic potash) in 1 gram of pyrogallic acid. Close the tube air-tight with a rubber stopper, and note the volume of the air in the tube. Shake the tube gently for about five minutes, and then remove the stopper under water. Carefully raise the tube, keeping its mouth under water, until the water inside and outside the tube are at the same level. The free oxygen in the confined air has been absorbed by the pyrogallate solution. The residual gas is nitrogen. Its volume is about four-fifths that of the air confined at the beginning of the experiment.

46. Composition of Air. — Air is composed chiefly of oxygen and nitrogen. Very careful determinations show its percentage composition to be about as follows:

	By Volume.	*By Weight.*
Oxygen	21	23
Nitrogen	79	77
	100	100

This composition of the air is nearly but not quite constant at different times and places. The air also contains small quantities of carbon dioxide, more or less watery vapor, and traces of ammonia, hydrogen, sulphur gases, nitrogen acids, and several elementary gases of which not much is known. See § 58.

47. Physical Properties. — The air, when pure, is transparent, colorless, tasteless, and odorless. It is 14.45 times as heavy as hydrogen. It may be liquefied by intense pressure at a very low temperature. The liquid air may even be frozen. As the boiling point of nitrogen (− 194°) is lower than that of oxygen (− 183°), the nitrogen volatilizes first when the liquid is slowly warmed, leaving nearly pure oxygen behind. Liquid air has large commercial and industrial possibilities.

48. Chemical Properties. — The chemical properties of air are those of its several constituents. Its oxygen supports combustion, the energy of the combustion being checked by the diluting nitrogen. Its nitrogen manifests all the properties of nitrogen. Its watery vapor condenses when the temperature falls, just as any other watery vapor would do. Hence, we have dew and frost. When a stream of air is passed through lime-water, its carbon dioxide renders the clear liquid turbid, just as carbon dioxide always does.

49. Air is a Mixture. — The first sentence in the preceding paragraph intimates that the constituents of our atmosphere are not chemically united but merely mixed; that each of them is free. This fact is shown by the following additional considerations:

(*a*) When the constituents are mixed in the proper proportions they form air, but there is no change of volume or manifestation of heat, light, or electricity.

(*b*) The composition of air is slightly variable.

(*c*) Each gas dissolves in water independently of the other. When water is boiled, it loses the gases it held in solution. Of these gases, 32 parts in 100 are oxygen and 68 parts are nitrogen. The water absorbed oxygen just as if there was no nitrogen present; it absorbed nitrogen just as if no oxygen was present. This increased richness in oxygen is of vital importance to fishes. If the constituent gases were chemically united, they would be absorbed by water in the proportion stated in § 46.

(*d*) The gases do not unite in any simple ratio of their atomic weights. As will be seen subsequently, this is a very important consideration.

50. Oxidation.—Combustion is the rapid union of other substances with oxygen. When the fire burns, oxygen from the air is uniting with the coal or other fuel to produce carbon dioxide and water. All decay of vegetable and animal substances is a similar but much slower process, so slow that the heat produced is not noticed. In general, decay is brought about by the action of bacterial organisms. When such substances are perfectly sterilized, they remain intact as long as kept sterile. The rusting of metals is also a process of oxidation, the rust being an oxide of the metal.

(*a*) Since all ordinary combustion takes place in air, which furnishes the necessary supply of oxygen, it is customary to speak of oxygen as a supporter of combustion, and the hydrogen or other substance that thus unites with the oxygen as a combustible.

A Product of Animal Respiration.

Experiment 56.—Put a piece of fresh lime about the size of a hen's egg into a pitcher and upon it pour a small teacupful of water. When the lime has crumbled, pour a pint or so of water into the pitcher and stir the contents thoroughly. Let the turbid mixture stand until it settles, and then half fill a clear tumbler with the clear liquid. Fill the lungs with air. Slowly breathe through a tube so that air from your lungs bubbles up through the lime-water in the tumbler. The clear water quickly becomes turbid, as in Experiment 39, showing that carbon dioxide is one of the products of animal respiration.

FIG. 26.

51. Relation to Animal Life. — Animals must have free oxygen in order to live; plants give off oxygen in their process of breathing. Animals having lungs absorb the oxygen directly from the air, while those having gills take up by this means the oxygen that the water has dissolved. The oxygen is taken through the lungs or gills into the red blood-corpuscles and carried by the blood to all parts of the body. In the minute capillary blood-vessels the oxygen and the constituents of the digested food unite, just as the fuel burns in the fire. The two processes differ chiefly in rapidity of combustion. In both cases the object is the same, to produce heat. The heat so produced by the burning of the food maintains the body's warmth. The chemical products are also the same, consisting mainly of water and carbon dioxide which are exhaled by the breath. Some of the tissues of animals are being continually burned up by oxygen. Unless the loss is made good by proper food, emaciation and death follow. If by any means the supply of oxygen is cut off, as by choking or drowning, this chemical action is arrested and the victim dies by suffocation.

EXERCISES.

1. Show that the terms addition and subtraction might be applied to the processes involved in Experiment 53.

2. Is phosphoric oxide soluble in water? How did you ascertain the fact?

3. How can you ascertain whether the atmosphere of the schoolroom is contaminated with carbon dioxide or not? If you found that it was thus contaminated, what would you suppose to be the most probable source of the contamination?

4. What is proved by the fact that the composition of our atmosphere is variable?

5. State the difference in the source of the supply of oxygen for living fishes and for animals that live on the land.

6. Is it proper to speak of a molecule of air? Why?

II. NITROGEN.

Symbol, N; density, 14; atomic weight, 14; valence, 1 to 5.

52. Occurrence. — Nitrogen is widely diffused in nature. It is found free in some of the nebulæ and in the earth's atmosphere. In combination, it exists in a number of minerals, as the sodium and potassium nitrates (niter) of Peru and India, and in ammonia and nitric acid in the atmosphere and natural waters. It also forms an essential part of most animal and vegetable substances.

53. Preparation. — The usual way of preparing nitrogen is to burn out, with phosphorus, the oxygen from a portion of air confined over water, as shown in Experiment 53. Instead of the burning phosphorus, a jet of burning hydrogen may be used. The nitrogen thus prepared is not perfectly pure, but nearly enough so for ordinary purposes.

(*a*) Any method of getting the oxygen of the air to enter into combination and to form a compound that is easily removed from the residual nitrogen will answer. Thus, if a slow stream of air is passed over bright copper-turnings heated to redness in a glass tube, the oxygen will unite with the copper, leaving the nitrogen to be collected over water.

(*b*) Pure nitrogen may be obtained by chemical processes, such as heating ammonium nitrite, which decomposes into water and nitrogen, as follows:

$$(NH_4)NO_2 + \text{heat} = 2H_2O + N_2.$$

54. Physical Properties. — Nitrogen is a transparent, colorless, tasteless, odorless gas. It is a little lighter than air or oxygen, and fourteen times as heavy as hydrogen, a liter weighing 1.2544 grams. It is very slightly soluble in water.

Relation to Combustion.

Experiment 57. — Fill a bell-glass with oxygen, and a stoppered bell-glass of the same size with nitrogen. Cover their mouths with glass plates and bring them mouth to mouth. Remove the stopper and the glass plates and introduce a lighted taper having a long wick (or a pine splinter). As the taper passes through the nitrogen, the flame is extinguished; if the wick is still glowing, it will be rekindled in the oxygen. By moving the taper up and down from one gas to the other, it may be rekindled repeatedly before the gases become mixed by diffusion.

FIG. 27.

55. Chemical Properties. — The leading characteristic of nitrogen is its inertness. Its properties are chiefly negative. It enters into direct combination with but few elements. It is not easily burned nor is it a supporter of combustion. It may be burned to its oxide by passing an electric spark through a mixture of oxygen and nitrogen. It is not poisonous; we are continually breathing large quantities of it, and it is an essential constituent of food. When breathed pure it kills by suffocation, by cutting off the necessary supply of oxygen, just as hydrogen or water does. Its compounds are generally unstable and energetic. Some of them are decomposed by being lightly brushed with a feather or by a heavy step on the floor.

NOTE. — In the periodic system of the chemical elements (§ 148, *b*), nitrogen falls in Group 5, the other members of which are considered in Chapter XV.

56. Uses. — The chief use of nitrogen is to dilute the oxygen of the air, and thus to prevent disastrous chemical activity, especially in the processes of respiration and combustion.

57. Tests. — Nitrogen may be recognized by its physical properties and its refusal to give any reaction with any known chemical test, except its combustion by the electric spark and the fact that it is absorbed by heated magnesium, to form a nitride of magnesium.

58. Minor Constituents of Air. — Argon, helium, krypton, neon, and xenon are constituents of the atmosphere existing only in small proportions, and distinguished by being chemically even more inert than nitrogen, which they so closely resemble in their properties that they were only recently discovered. As yet, no method has been found whereby they can be made to unite with any other element, and they are as yet unknown in combination. They were first separated from the air by burning the nitrogen by the passage of an electric spark. The residue, consisting mainly of argon, was at first supposed to be a single element. However, through liquefying it by intense cold and high pressure, and fractionally distilling the liquid, these five elements have been isolated. They differ in their densities, boiling-points, and spectra.

EXERCISES.

1. What is meant by allotropism? Analysis? Synthesis?
2. What is the difference between an elementary and a compound molecule?
3. Why does the burning of alcohol (C_2H_6O) yield steam?
4. Why does the gas-bottle become heated in the preparation of hydrogen?
5. Explain the statement that food is a fuel.
6. Is hydrogen poisonous? Can you live long in an atmosphere of hydrogen? Why?
7. Is oxygen poisonous? Can you live long in an atmosphere of oxygen? Why?
8. Why is the word oxygen a misnomer?
9. Is the ordinary method of preparing oxygen analytic or synthetic?
10. What is the chief characteristic of oxygen?
11. Why is the inner rather than the outer tube of the compound blowpipe used for oxygen?
12. Name five constituents of ordinary air.
13. State three or more reasons for holding that the air is a mixture.
14. What is the weight of 1 cu. m. of nitrogen? Of oxygen?
15. State the composition of an explosive mixture of gases.

CHAPTER IV.

SOME NITROGEN COMPOUNDS.

I. AMMONIA.

59. Occurrence. — Ammonia (NH_3) exists in small quantities in the air, whence it is brought down to the earth by rain and dew. It is formed by the putrefaction of animal and vegetable matter. The ammonia of commerce is chiefly obtained from ammoniacal salts made in the purification of illuminating-gas, from the by-product of coke ovens, and from furnaces in which iron ore is smelted with bituminous coal. It was discovered long ago by distilling horn, and so was called hartshorn, a name that is still sometimes used.

Preparation of Ammonia.

Experiment 58. — In a mortar, or in the palm of the hand, rub together equal weights of pulverized ammonium chloride (sal-ammoniac, NH_4Cl) and quicklime (CaO). Notice the smell before and after rubbing.

$$2NH_4Cl + CaO = CaCl_2 + H_2O + 2NH_3.$$

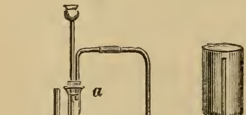


FIG. 28.

Experiment 59. — Into a half-liter flask, pour about 200 cu. cm. of strong ammonia-water (ammonium hydroxide, NH_4OH). Close the flask, *a*, with a cork carrying a funnel-tube and a delivery-tube. The delivery-tube should pass to the bottom of a tall drying-bottle, *b*, containing about a liter of quicklime broken into small pieces. Gently heat the liquid in *a*, and ammonia (which is a gas) will be given off. After passing through *b*, it may be collected by upward displacement or over mercury. If collected over mercury, the funnel-tube in *a* must have a considerable length.

Experiment 60. — Mix 25 or 30 grams of pulverized ammonium chloride with 50 to 60 grams of freshly slacked lime ($CaO + H_2O = CaO_2H_2$), that has been allowed to cool. Place the mixture in a half-liter flask and add enough water to cause it to aggregate in lumps when stirred with a rod. When the mixture is gently heated, ammonia is produced.

$$2NH_4Cl + Ca(OH)_2 = CaCl_2 + 2H_2O + 2NH_3.$$

The gas, after being dried, may be collected in bottles by upward displacement and the bottles corked. This is the most common way of preparing ammonia in the laboratory.

Experiment 61. — From the flask of Experiment 60, pass the gas through a series of Woulffe bottles, partly filled with water. The delivery-tube of one bottle dips into the water in the next. A safety-tube, *s* (open at both ends), passes through the cork in the middle neck of each bottle. The delivery-tube of the generating flask should not dip into the water of the first bottle. This precaution prevents the possibility of water being forced back into the heated flask and breaking it. It is well to keep the Woulffe bottles in vessels containing cold water, as heat is evolved in the condensation of the ammonia. At the end of the experiment, put the ammonia-water just prepared into convenient bottles, cork the bottles tightly, and save the liquid for future use. See Appendix, § 7.

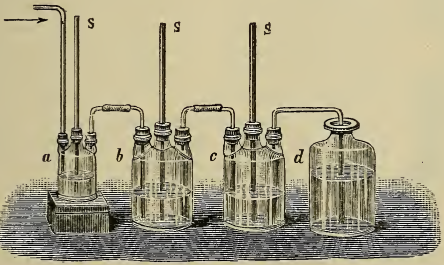


FIG. 29.

60. Preparation. — Anhydrous ammonia is made from gas-house liquor and other sources by distillation, and by cooling and compressing the distillate until it liquefies. For aqua ammonia (ammonia-water), which is a solution of the gas in water, the distilled gas is absorbed in cold water; by heating this solution the gas may be recovered. Ammonia may be made by heating an ammoniacal salt, like ammonium chloride, with a strong base, like lime, or by absorbing free nitrogen by red-hot metallic magnesium and treating the resulting nitride of magnesium with water.

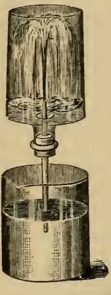


FIG. 30.

Physical Properties of Ammonia.

Experiment 62. — Fill a liter bottle, *a*, with ammonia by upward displacement. By holding at the mouth of the inverted bottle a moistened strip of turmeric-paper or of red litmus-paper, the experimenter will be able to tell when the bottle is filled; the turmeric will turn brown or the litmus blue. Close the bottle with a cork (a rubber stopper is preferable), through which passes a small glass tube. Place the end of this tube in water colored with red litmus solution. The water will, in a moment, rush into the bottle with violence, changing from red to blue as it enters.

61. Physical Properties. — Ammonia is a colorless, irrespirable gas, and has a pungent odor. It is much lighter than air, only eight and a half times as heavy as hydrogen. It liquefies under a pressure of six and a half atmospheres at 10°, four and a half atmospheres at 0°, or one atmosphere at − 40°. The liquid solidifies at − 85°. Under ordinary conditions, the liquid rapidly evaporates, producing intense cold. This forms the basis of Carré's refrigeration process and of ice manufacture.

Chemical Properties of Ammonia.

Experiment 63. — From the drying-bottle of Experiment 59, lead the delivery-tube, *d*, through a narrow glass cylinder to its upper end. As the ammonia issues at *a*, try to light it; it will refuse to burn. Through the flexible tube, *b*, pass a current of oxygen into the cylinder. The jet of ammonia, being now surrounded by an atmosphere of oxygen, may be lighted; it will burn with a yellowish flame.

$$2NH_3 + 3O_2 = 6H_2O + N_2.$$

Experiment 64. — Pass a stream of oxygen from the gas-holder through a strong aqueous solution of ammonia in a flask. Heat the flask, and bring a flame into contact with the mixed gases as they issue from the neck of the flask. They will burn with a large yellow flame.

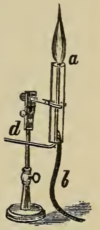


FIG. 31.

Experiment 65. — Upon a piece of broadcloth or of dark-colored calico, let fall a few drops of dilute sulphuric acid. The acid will produce red spots. Apply ammonia-water to the spots and they will disappear. This is a familiar experiment in most laboratories.

62. Chemical Properties. — Ammonia and its water solution have strong alkaline properties, neutralizing acids and restoring vegetable colors changed by acids. The gas is combustible only when mixed with oxygen, this reaction burning only the hydrogen and setting free the nitrogen. Ammonia has a strong attraction for water and is remarkably soluble in it. One volume of water absorbs 803 volumes of the gas at 14°, or 1146 volumes at 0°, the gas entering into chemical combination with water as follows:

$$NH_3 + H_2O = NH_4OH.$$

This saturated solution (aqua ammonia fortior) has a density of .85, and contains about thirty-five per cent of the gas. A weaker solution (aqua ammonia, ammonia-water), containing ten per cent or less of the gas, is more commonly sold.

(*a*) When ammonia is dissolved in water, the reaction liberates a large quantity of heat (see § 145); of course, a like quantity of heat is absorbed when the gas is prepared from its solution as described in the preceding paragraph.

(*b*) As will be explained in a later paragraph, the atomic group, NH_4, is called ammonium. The product of the reaction above written, NH_4OH, is sometimes called ammonium hydroxide, just as though the ammonium had united directly with hydroxyl. Ammonia unites additively with acids (for example, hydrochloric acid, HCl) thus:

$$NH_3 + HCl = NH_3HCl.$$

The effect is the same as if an ammonium group, NH_4, had replaced the hydrogen of the acid, and the formula for the product is so written, NH_4Cl. (See Experiment 58.) The name of the product, ammonium chloride, as well as the formula, suggests that the ammonium group may thus replace a single atom of hydrogen in an acid. This suggestion is given more color by the fact that when the hydroxide and the acid react, the equation is

$$NH_4OH + HCl = NH_4Cl + H_2O.$$

In similar manner, ammonium nitrate (NH_4NO_3) is formed from nitric acid (HNO_3).

63. Volumetric Composition. — When ammonia gas is decomposed, its volume is doubled, two volumes of the compound yielding four volumes of its elementary constituents. Of these, three volumes are hydrogen and one volume is nitrogen. In other words, the compound yields one and a half times its volume of hydrogen, and half its volume of nitrogen. Of course, there is no change in weight, the constituents consisting of three parts of hydrogen to fourteen parts of nitrogen. This may be represented to the eye as follows:

$$\boxed{\begin{matrix}H\\1\end{matrix}} + \boxed{\begin{matrix}H\\1\end{matrix}} + \boxed{\begin{matrix}H\\1\end{matrix}} + \boxed{\begin{matrix}N\\14\end{matrix}} = \boxed{\begin{matrix}HN_3\\17\end{matrix}}$$

(*a*) Suppose 100 cu. cm. of ammonia to be confined over mercury in an eudiometer. By producing electric sparks in it, the gas is decomposed, and increases its volume to 200 cu. cm. Add, say 100 cu. cm. of oxygen, and produce a spark in the mixed gases. There is a shrinkage of 225 cu. cm., the gases now measuring 75 cu. cm. The shrinkage was due, of course, to the formation of water. Hence, two-thirds of the 225 cu. cm., or 150 cu. cm., was hydrogen, and the other 75 cu. cm. was oxygen. But, as we introduced 100 cu. cm. of oxygen, and only 75 cu. cm. of it has combined, the other 25 cu. cm. must be in the eudiometer as part of the residual 75 cu. cm. Consequently, we have left 50 cu. cm. of nitrogen, and 25 cu. cm. of oxygen. The 50 cu. cm. of nitrogen and the 150 cu. cm. of hydrogen came from the 100 cu. cm. of ammonia.

64. Uses. — Ammonia-water is used in the laboratory for many purposes, in the household for softening "hard" water and for cleansing purposes, and in many industrial processes. It is largely used in the preparation of sodium carbonate, in the production of aniline colors, and in the manufacture of indigo. Liquid ammonia is used in the freezing of artificial ice. The salts of ammonia are largely used as constituents of commercial fertilizers, this being the principal use of ammonia.

65. Tests. — The tests for ammonia are its pungent odor, its turning moistened red litmus-paper blue, and the fumes of the ammonium chloride it produces with hydrochloric acid as in Experiment 9. Ammonia may be set free from its compounds by heating them with potassium hydroxide, and then detected as above indicated.

EXERCISES.

1. (*a*) What weight of hydrogen is contained in 17 grams of NH_3? (*b*) What volume of hydrogen?

2. (*a*) What volume of hydrogen can be produced by the decomposition of 2 liters of NH_3? (*b*) What weight of hydrogen?

3. (*a*) What weight of hydrogen can be united with 28 grams of nitrogen to form ammonia? (*b*) What volume of hydrogen?

4. (*a*) What weight of nitrogen can be united with 9 grams of hydrogen to form NH_3? (*b*) What will be the weight of the product?

5. (*a*) If 100 cu. cm. of ammonia are decomposed in an eudiometer, 100 cu. cm. of oxygen added, and an electric spark passed through the mixed gases, what gases will remain? (*b*) What will be the volume of each?

6. Why were the safety tubes used in Experiment 61?

7. What is the difference between ammonia-water and liquid ammonia? State one use of each.

8. Explain the formation of boiler-scale.

9. State two uses of free hydroxyl.

10. Describe an experiment for showing approximately the volumetric composition of atmospheric air.

11. Describe the electrolysis of water. Make a sketch of the apparatus used in the process.

12. What is the lightest gas that you have studied? The heaviest?

II. NITROGEN OXIDES.

66. Nitrogen Oxides. — Nitrogen combines with oxygen in five different ratios to form five different chemical compounds or oxides.

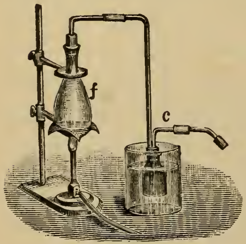


Fig. 32.

Preparation of Laughing-gas.

Experiment 66.—Into a small Florence flask place a tablespoonful of ammonium nitrate. Heat gently and carefully over the sand-bath or a piece of wire gauze, and collect the gas over warm water. Remove the delivery-tube from the water before the gas stops flowing.

67. Nitrogen Monoxide. — Nitrogen monoxide (nitrogen protoxide, nitrous oxide, laughing-gas, N_2O) is prepared by decomposing ammonium nitrate by heat.

$$NH_4NO_3 + \text{heat} = N_2O + 2H_2O.$$

(*a*) To show that water is produced, interpose between the Florence flask and the water-pan, a condensing bottle placed in iced water, as shown at *c* in Fig. 32. Test the liquid that collects in this bottle by dropping a small piece of potassium into it. The flask would break before all of the NH_4NO_3 was decomposed, but by heating a small quantity of the nitrate upon platinum foil, it will be seen that no residue is left. When needed in large quantities, the gas under pressure in steel cylinders may be bought of dealers in dental supplies.

Properties of Laughing-gas.

Experiment 67.—Repeat Experiments 31, 34, and 35, using N_2O instead of oxygen. (These are simply combustions in oxygen, the binary gas being decomposed into its elements.)

68. Properties.—Nitrogen monoxide is a colorless, sweet-tasting gas, and a good supporter of combustion. When a substance is burned in the monoxide, free nitrogen is formed. At the temperature of ignition, the oxygen is more strongly attracted by the combustible substance than is the nitrogen with which it was united. When pure nitrogen monoxide is mixed with one-fourth its volume of oxygen, it may be safely inhaled, producing the effects that have secured for it the name of *laughing-gas*. If its inhalation is continued, it acts as an anæsthetic. It should not be thus inhaled except under the direction of a competent medical attendant.

69. Volumetric Composition.—The composition of nitrogen monoxide is strictly analogous to that of steam, two volumes of nitrogen uniting with one of oxygen to form two of this compound.

$$\boxed{\begin{matrix}N\\14\end{matrix}} + \boxed{\begin{matrix}N\\14\end{matrix}} + \boxed{\begin{matrix}O\\16\end{matrix}} = \boxed{\begin{matrix}N_2O\\44\end{matrix}}$$

When decomposed by electric sparks, it yields one and a half times its own volume of mixed gases, as represented by the typical squares.

Nitric Oxide.

Experiment 68. — Partly fill the gas-bottle with small lumps of ferrous sulphate (blue vitriol, copperas) and pour in enough water to seal the funnel-tube. Add strong nitric acid in small quantities. Collect the gas over water, rejecting as impure the part first collected.

70. Nitric Oxide. — Nitric oxide (nitrosyl, NO) may be prepared as in the preceding experiment, or by the action of dilute nitric acid upon copper clippings, turnings, or filings. The apparatus is arranged as shown in Fig. 7. The generating bottle is, at first, filled with red fumes (§ 74) but the gas collected over water is colorless. In this reaction the nitric acid (HNO_3) gives up a part of its oxygen to the copper to form copper oxide, nitric oxide, and water.

$$3Cu + 2HNO_3 = 3CuO + 2NO + H_2O.$$

The copper oxide thus formed unites with some of the excess of acid used to form copper nitrate, the solution of which gives the blue color noticed.

$$CuO + 2HNO_3 = Cu(NO_3)_2 + H_2O.$$

These changes actually occur in one reaction which may be written thus:

$$3Cu + 8HNO_3 = 2NO + 3Cu(NO_3)_2 + 4H_2O.$$

The blue solution of copper nitrate should be properly labeled and saved for future use.

(*a*) As we shall soon see, nitric acid is composed of nitrogen pentoxide (N_2O_5) and water. Similarly, one of the proximate constituents of ferrous sulphate is ferrous oxide (FeO). In the preparation of nitric oxide as already indicated, the copper of the ferrous sulphate reduces the N_2O_5 to NO. In thus taking oxygen from the pentoxide the copper is oxidized to CuO, and the FeO is changed to a higher oxide of iron, namely ferric oxide (Fe_2O_3).

Properties of Nitric Oxide.

NOTE. — In the next three experiments, keep (as far as possible) the nitric oxide from contact with the air.

Experiment 69. — Into a bottle of NO, lower a burning splinter, a burning candle, or sulphur burning in a deflagration-spoon (see Appendix, § 18). It will not burn in the gas.

Experiment 70. — Into a bottle of NO, lower a deflagration-spoon containing a bit of vigorously burning phosphorus, the size of a pea. It will continue to burn with great brilliancy.

Experiment 71. — In a jar of NO, place a few drops of carbon disulphide. Close the bottle for a few minutes to allow the liquid to evaporate and its vapor to mix with the oxide. In a dark room, bring a lighted taper to the open mouth of the jar. The mixture burns with a vivid light rich in actinic rays.

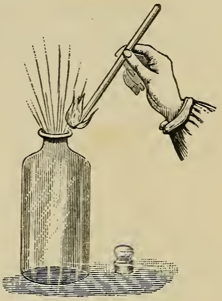


FIG. 33.

71. Properties. — The leading property of this colorless gas is its strong attraction for oxygen. Its relation to combustion is peculiar. Ordinary combustibles will not burn in it at all; phosphorus may be melted in the gas without kindling, but when well aflame it burns in it with great energy. The gas is only slightly soluble in water, but dissolves readily in a solution of ferrous sulphate. It may be condensed to a colorless liquid. The experiments already given show that, while the oxygen of nitric oxide is held so loosely that it may be extracted from the nitrogen by certain substances, it is held more firmly than is the oxygen of nitrous oxide.

72. Volumetric Composition.—This is the first compound that we have studied, the gaseous constituents of which unite without condensation. One volume of oxygen unites with one volume of nitrogen to form two volumes of nitric oxide.

$$\boxed{\begin{matrix}\mathrm{N}\\ 14\end{matrix}} + \boxed{\begin{matrix}\mathrm{O}\\ 16\end{matrix}} = \boxed{\begin{matrix}\quad\mathrm{NO}\quad\\ 30\end{matrix}}$$

73. Nitrogen Trioxide.—This is a dark-blue, unstable liquid, sometimes called nitrous anhydride (N_2O_3). It begins to decompose at a temperature of $-21°$ below zero, and at a temperature of 3.5° it rapidly separates into nitrogen monoxide and nitric oxide. For this reason, it does not exist in the gaseous state. It unites with cold water to form nitrous acid.

$$N_2O_3 + H_2O = 2HNO_2.$$

(*a*) Nitrogen trioxide is sometimes called nitrogen sesquioxide because the number of its oxygen atoms is one and a half times the number of its nitrogen atoms, the Latin prefix, *sesqui*, signifying one and a half.

Nitrogen Peroxide.

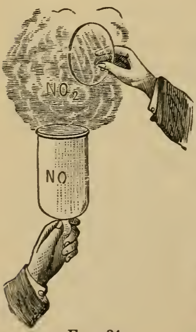


Fig. 34.

Experiment 72.—Into a jar of nitrosyl, standing over water, pass a stream of oxygen from the gas-holder. After the red fumes that are promptly formed have been dissolved by the water, repeat the experiment several times, noticing the phenomena carefully. Ascertain the nature of the solution by testing it with litmus-paper.

Experiment 73.—Fill a large bell-glass with nitric oxide at the water-bath. Cover the mouth under water with a glass plate, invert the bell-glass and remove the plate. The nitric oxide absorbs oxygen from the air and forms a cloud of the now familiar red fumes.

74. Nitrogen Peroxide. — Nitrogen peroxide (nitryl, NO_2) is the brownish red gas that is best prepared by bringing together two volumes of nitric oxide and one volume of oxygen, both constituents being perfectly dry. It is an energetic oxidizing agent. It may be liquefied and solidified. In the presence of water it forms acid compounds, probably a mixture of nitric and nitrous acids.

(*a*) In the solid and liquid conditions, this oxide seems to have the formula N_2O_4, whence the name sometimes used, nitrogen tetroxide. In other words, the solid and the liquid oxide are polymeric with the dark-colored gas. See § 252 (*a*).

75. Volumetric Composition. — The composition of nitrogen peroxide may be represented as follows:

$$\boxed{\begin{matrix}\mathrm{N}\\14\end{matrix}} + \boxed{\begin{matrix}\mathrm{O}\\16\end{matrix}} + \boxed{\begin{matrix}\mathrm{O}\\16\end{matrix}} = \boxed{\begin{matrix}\mathrm{NO_2}\\46\end{matrix}}$$

(*a*) If we modify Experiment 72 by adding one volume of pure oxygen to two volumes of pure nitric oxide in a graduated tube over mercury, we may notice that the three volumes of gas are condensed into two volumes of nitrogen peroxide.

$$\boxed{\mathrm{NO}} + \boxed{\mathrm{NO}} + \boxed{\mathrm{O_2}} = \boxed{2\,\mathrm{NO_2}}$$

76. Nitrogen Pentoxide. — Nitrogen pentoxide (nitric anhydride, N_2O_5) is a crystalline white compound, so unstable that it spontaneously decomposes in a sealed tube into oxygen and nitrogen peroxide. It is particularly interesting on account of its relation to nitric acid.

$$N_2O_5 + H_2O = 2HNO_3.$$

NOTE. — For definitions of hypothesis, theory, and law, see Avery's School Physics, § 10.

77. Law of Definite Proportions. — The truth stated in § 9 has been verified by numberless analyses and may be formulated as follows: *Any given chemical compound always contains the same elements in the same relative quantities.*

(*a*) Identity of properties implies identity of composition, but we shall find that identity of composition does not necessarily carry with it identity of properties.

78. Law of Multiple Proportions. — *If two substances combine to form more than one compound, and the quantity of one constituent is kept constant, the varying quantities of the other constituent are in the ratio of small whole numbers.*

(*a*) This important principle was discovered in 1808 by John Dalton. To account for it he proposed the atomic theory (§ 132). It is best illustrated by the nitrogen oxides just studied.

Names.	Symbols.	By Gravimetric Analysis.				By Volumetric Analysis.			
		Actual.		Ratio.		Actual.		Ratio.	
		Weight of Nitrogen.	Weight of Oxygen.	Weight of Nitrogen.	Weight of Oxygen.	Volumes of Nitrogen.	Volumes of Oxygen.	Volumes of Nitrogen.	Volumes of Oxygen.
Nitrogen monoxide	N_2O	28 :	16	1¾ :	1	2 :	1	2 :	1
Nitric oxide	NO	14 :	16	1¾ :	2	1 :	1	2 :	2
Nitrogen trioxide	N_2O_3	28 :	48	1¾ :	3	2 :	3	2 :	3
Nitrogen peroxide	NO_2	14 :	32	1¾ :	4	1 :	2	2 :	4
Nitrogen pentoxide	N_2O_5	28 :	80	1¾ :	5	2 :	5	2 :	5

Attention is called to the consecutive numbers 1, 2, 3, 4, and 5, in the columns headed "Ratio."

(*b*) This law necessarily results from the definition of an atom (§ 4). Since the atoms can not be divided, the elements can combine only atom by atom and, consequently, either in the ratio of their atomic weights or some simple multiple of that ratio.

EXERCISES.

1. Is the air a mixture or a compound? Why?

2. State the points of resemblance and difference between oxygen and nitrogen.

3. (*a*) Is the process of preparing oxygen analytic or synthetic? (*b*) Of preparing NO_2? (*c*) N_2O?

4. How could you prove the presence of oxygen in air?

5. If two liters of nitrogen and one of oxygen are combined, what will be the name and volume of the product?

6. (*a*) How is ammonia-water prepared? (*b*) How is liquid ammonia prepared? (*c*) What will result from the decomposition of a liter of laughing-gas into its constituent elements? (*d*) Write the reaction for the preparation of ammonia.

7. When nitrous oxide is mixed with hydrogen and the mixture exploded, nitrogen and a compound vapor are formed. Write the reaction.

8. Name the products formed by the decomposition of ammonium nitrate by heat.

9. One cubic centimeter of ice-cold water will absorb more than a liter of one of the gases that you have studied. How may you prepare and test that gas without any laboratory apparatus?

10. How would you guard against personal injury in the cutting and handling of phosphorus?

11. Give the reason for the caution in the Note preceding Experiment 69.

12. Determine experimentally the action of nitric oxide and of nitrogen peroxide upon blue litmus-paper.

III. NITROGEN ACIDS, ETC.

79. Nitric Acid. — The most important of the nitrogen acids is nitric acid (aqua fortis, HNO_3). Its chief sources are potassium nitrate (saltpeter or niter) which is obtained in abundance in India, and sodium nitrate (Chile saltpeter or soda niter), which is found as an efflorescence on the soil of a sterile region in Chile and Peru, and exported in large quantities from those countries. At present, it is made almost exclusively from Chile saltpeter.

Preparation of Nitric Acid.

Experiment 74.—Into a quarter-liter retort, *a*, having a glass stopper, put 50 grams of pulverized potassium nitrate (KNO_3), or 40 grams of pulverized sodium nitrate ($NaNO_3$), and 35 cu. cm. of strong sulphuric acid (H_2SO_4). The materials should be introduced through the tubulure, *s*, and care taken that none falls into the neck of the retort. It is well to use a paper funnel for the nitrate and a funnel-tube for the acid. Replace the stopper and place the retort upon sand in a shallow sheet-iron or pressed-tin pan, supported by a ring of the retort-stand over the lamp, or upon wire gauze, as shown in the figure. The use of the sand-bath or the gauze lessens the danger of breaking the retort. Place the neck of the retort loosely in the mouth of a Florence flask, *r*, or other convenient receiver, kept cool by water. It is well to cover the receiver with cloth or bibulous paper; the water may be brought by a rubber tube siphon from a pail of water sufficiently elevated. As the retort is heated, the nitrate liquefies, reddish fumes appear, and HNO_3 condenses in the neck of the retort and in the receiver. The fumes in the retort will soon disappear; continue the distillation until they reappear.

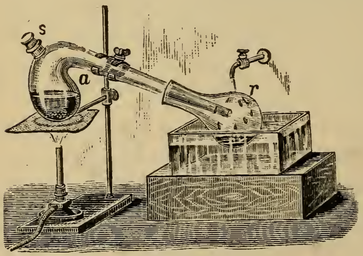


FIG. 35.

$$KNO_3 + H_2SO_4 = KHSO_4 + HNO_3.$$

Transfer the acid to a glass stoppered bottle and save it for future use. After the retort has become thoroughly cool, the solid residue, potassium-hydrogen sulphate, should be dissolved by heating with water and then removed.

80. Preparation. — Nitric acid may be made by the combination of nitrogen pentoxide and water, but it is generally prepared from a nitrate by distillation with sulphuric acid (H_2SO_4).

(*a*) In the arts, the retort is made of cast-iron and the distillate is condensed in earthenware receivers. A higher temperature and frequently only half as much H_2SO_4 are used.

$$2KNO_3 + H_2SO_4 = K_2SO_4 + 2HNO_3,$$

$$2NaNO_3 + H_2SO_4 = Na_2SO_4 + 2HNO_3.$$

81. Physical Properties. — Nitric acid is a fuming liquid, colorless when nearly pure, but generally slightly tinted with the fumes seen in the retort during its preparation. It has a density of 1.52, freezes at $-47°$, and boils with partial decomposition at 86°. On standing, it decomposes slowly, with formation of nitrogen peroxide, which dissolves in the acid and gives it a brownish color. It may be mixed with water in all proportions, the aqua fortis of commerce usually containing sixty-eight per cent of nitric acid.

Chemical Properties of Nitric Acid.

Experiment 75. — Pulverize and heat a few grams of charcoal. Upon the heated charcoal, pour a little strong HNO_3. The charcoal will be rapidly oxidized to combustion.

Experiment 76. — From the end of a meter-stick drop a thin slice of phosphorus into strong HNO_3. The phosphorus will be oxidized with violent combustion.

Experiment 77. — Into dilute HNO_3 dip a skein of white sewing-silk. In a few minutes, remove the silk and wash it thoroughly with water. The silk will be permanently colored yellow.

Experiment 78. — Get a sheet of "Dutch leaf" from a sign painter; put it into a test-tube, and pour upon it a small quantity of HNO_3. The metal will be instantly dissolved.

Experiment 79. — Cover a smooth piece of brass or of copper with a film of beeswax. With a sharp instrument, write your name upon the metal, being sure to cut through the wax. Cover the writing with strong HNO_3. In a few moments the name will appear in a tracery of minute bubbles. A few moments later, wash the acid away with water, and remove the wax. The autograph will be etched upon the metal.

Experiment 80. — Into a test-tube, put a brass pin and cover it with HNO_3. Red fumes will appear, and the liquid will be colored blue by the copper nitrate formed. Brass is an alloy that contains copper.

82. Chemical Properties. — Nitric acid is a powerful oxidizing agent, and one of the most corrosive known substances. It colors nitrogenous animal substances (e.g., silk, skin, and parchment) yellow, and converts many non-nitrogenous substances (e.g., cotton and glycerin) into violently explosive compounds. It dissolves all of the common metals, except gold and platinum, forming nitrates. Its oxidizing power is due to the ease with which it is decomposed, giving up part of its oxygen and forming nitrogen oxides, that contain a smaller proportion of oxygen.

83. Uses. — Nitric acid is largely used in the laboratory and in the arts, in the manufacture of guncotton, nitroglycerin, etc., and in the preparation of aqua regia (§ 119). Engravers use it for etching on copper and steel. Nitric acid or nitrates constitute the foundation of almost all high explosives.

(*a*) Gunpowder is made by mixing potassium nitrate with sulphur and charcoal. When it is ignited, the oxygen of the niter combines with the sulphur and charcoal, producing instantly large volumes of gases.

(*b*) Guncotton, largely used for filling torpedoes and as a basis for making blasting gelatine, is made by immersing purified cotton in a mixture of strong nitric and sulphuric acids. After a proper length of time, the cotton is carefully washed to free it from every trace of acid and dried. The product burns quietly when ignited but explodes violently by concussion.

(*c*) Nitroglycerin, the most important of modern explosives, is made by slowly running a small stream of glycerin into a mixture of strong nitric and sulphuric acids, keeping the mixture cool. The product, an oily liquid, is carefully washed free from acid, since the smallest quantity left may cause it to heat and explode. Like guncotton, nitroglycerin may be burned quietly by ignition, but is exploded by shock. In the pure state it is unsafe to transport.

(*d*) Dynamite is made by mixing nitroglycerin with enough of some inert substance like wood-pulp or soft earth to give it the consistency of a solid. While it may be exploded by detonation, it is less susceptible to the small shocks incident to transportation.

(*e*) Guncotton and nitroglycerin are incorporated with each other by mixing with a mutual solvent, to produce the various kinds of blasting gelatin, and smokeless powder.

Tests for Nitric Acid.

Experiment 81. — Into a narrow test-tube place about 1 cu. cm. of concentrated sulphuric acid. Incline the test-tube and upon the acid pour carefully, so that they do not mix, a like quantity of a strong solution of ferrous sulphate (green vitriol) to which has been added a single drop of dilute nitric acid. A brown ring will form at the line of contact of the two liquids. This ring is due to the formation of a brown compound of the ferrous sulphate with the nitrogen peroxide set free from the HNO_3, and is one of the most delicate tests for the presence of a nitrate.

Experiment 82. — Into a test-tube put a few cubic centimeters of a dilute solution of indigo. Add HNO_3 until the blue solution is bleached. The acid oxidizes the blue indigo to a colorless compound.

84. Tests. — In testing for nitric acid, first try blue litmus-paper. If this test-paper is not reddened when dipped into the liquid in question, the liquid is not an acid. If it is reddened, the liquid is an acid. As the nitrates are all easily soluble, tests for nitric acid yield no precipitates. Free nitric acid may be detected by its bleaching an indigo solution, or by its forming red fumes when added to copper bits or filings. Nitrates show the same effects when heated with sulphuric acid, because of the nitric acid thus set free. The nitrates also deflagrate when thrown upon burning charcoal.

Nitrates.

Experiment 83. — In a small evaporating dish (see Appendix, § 20), place a few cubic centimeters of HNO_3 and add an equal bulk of water. In another vessel, place a small quantity of diluted ammonia-water. Into the first liquid, dip a strip of blue litmus-paper. The change of color shows an acid. Dip this litmus-paper (now red) into the other liquid. The restoration of the blue color shows the presence of an alkali. To the first liquid add the second, in small quantities at first, and finally drop by drop. Stir the mixture continually with a glass rod, and test with blue litmus-paper after each addition of ammonia-water. At last, it will be found that the mixture will neither redden blue litmus-paper nor restore red litmus-paper to its original blue. It has neither an acid nor an alkaline reaction. The acid has been "neutralized" by the alkali, and we have a solution of a neutral salt. Without boiling the liquid, evaporate it until, when the glass rod is removed, the adhering liquid becomes almost solid upon cooling. Crystals will now form upon the cooling of the liquid; these crystals are to be carefully drained and dried. They are ammonium nitrate (NH_4NO_3).

85. Nitrates. — Compounds formed by replacing the hydrogen of nitric acid by ammonium (NH_4) or by a metal are called nitrates. They have neither an acid nor an alkaline reaction; that is, they produce no change in vegetable colors, such as litmus. In nature, they are produced by the decay of the nitrogen-containing compounds of animal and vegetable tissues — the final product of their oxidation. This decay and oxidation are caused by the growth of nitrifying bacteria. The nitrates are among the most important plant foods, and are largely used as components of commercial fertilizers.

(*a*) Nitrates are also produced in the soil from the free nitrogen of the air by the action of certain bacterial organisms that grow most freely around the roots of leguminous plants, such as peas, clover, and vetch. The cultivation of these crops, therefore, increases the nitrate contents of the soil, and makes it more fertile for the growth of other crops that require much nitrogen. Plants are unable to assimilate directly the free nitrogen of the air. Many ways have been attempted to convert atmospheric nitrogen into nitrogen compounds of economic value, but none of them have yet been commercially successful.

(*b*) The fact that air and nitrifying bacteria rapidly convert animal and vegetable substances into nitrates and carbon dioxide is utilized in the disposal of the sewage of cities by the systems of intermittent or aërated filtration. The sewage is spread on large sand-filters at the proper temperature for the growth of the nitrifying bacteria, and given free access of air. Under these conditions, the water is rapidly purified and fitted for return to the natural water courses.

86. Nitrous Acid. — Nitrous acid (HNO_2) does not exist free. When a nitrite is decomposed by a strong acid, a mixture of nitrogen oxides, instead of nitrous acid, is produced. The nitrite may be prepared by reducing a nitrate. Thus, if 20 or 30 grams of potassium nitrate are melted and thoroughly stirred with about twice that quantity of metallic lead, the nitrate will be reduced to potassium nitrite.

$$KNO_3 + Pb = KNO_2 + PbO.$$

When a solution of this nitrite is decomposed by an acid, analogy would suggest such a reaction as the following:

$$2KNO_2 + H_2SO_4 = K_2SO_4 + 2HNO_2.$$

As a matter of fact, instead of nitrous acid, the substance formed is nitrogen trioxide, which is nitrous acid less the elements of water.

$$2HNO_2 = N_2O_3 + H_2O.$$

The oxide is so unstable that it quickly breaks up, forming other nitrogen oxides. The phenomenon may be attributed to the fact that the attraction of. hydrogen for oxygen is greater than the forces that tend toward the equilibrium of the nitrous acid molecule.

(*a*) Many compounds that contain oxygen and hydrogen show this tendency to decompose with the formation of water. This is what would naturally take place when the attraction between the oxygen and the hydrogen atoms is greater than the forces that are at work in the molecule to keep its constituents in equilibrium. Many compounds that do not thus break up at ordinary temperatures do so when heated. (See § 67). As we shall soon see, nitrogen trioxide is one of a class of compounds called anhydrides.

87. Hyponitrous Acid. — This acid (HNO) does not exist in the free state, but the corresponding salt, potassium hyponitrite (KNO), is known. We may *imagine* this reaction:

$$N_2O + H_2O = 2HNO.$$

EXERCISES.

1. Describe the laboratory preparation of nitric acid.
2. Is nitric acid a stable compound or is it easily decomposed? Illustrate.
3. How would you etch your name on the blade of a hand-saw?
4. What is the difference between nitroglycerin and dynamite?

5. What is the most common test for an acid?

6. I have a liquid that reddens blue litmus-paper, and that gives off reddish-brown fumes when I drop a few copper cartridge-shells into it. Write the molecular formula for the acid.

7. In what way do certain bacteria contribute to plant life?

8. Show that nitrogen trioxide is a dehydrated acid.

9. Name three physical and two chemical properties of oxygen.

10. (*a*) If 180 cu. cm. of ammonia are decomposed by electric sparks, what will be the volume of each of the resultant gases? (*b*) If, then, 130 cu. cm. of oxygen are introduced and another electric spark is produced in the containing vessel, the temperature being 16°, what will be the volume of the remaining gaseous contents of the vessel?

11. (*a*) If a mixture of 50 cu. cm. of hydrogen and 50 cu. cm. of oxygen is exploded in an eudiometer, what will be the name and volume of the remaining gas? (*b*) What precaution must be taken in measuring the gases?

12. Explain why, in Experiment 26, it is safe to remove the towel from the bottle after the gas has been ignited.

CHAPTER V.

ACIDS, BASES, AND SALTS.

88. Three Important Groups. — The last chapter introduced to us a member of each of three large and important classes of chemical compounds. Nitric acid represents a group having certain properties in common and called acids; ammonia represents another group called bases; the union of an acid and a base, as shown in Experiment 83, produces a member of a third group called salts.

89. Acids. — All acids contain hydrogen; the rule does not work both ways. The hydrogen of an acid is easily replaceable by a metal. This property distinguishes acids from all other chemical substances.

(*a*) Another property of most acids is a sour taste. Any substance that has a sour taste is an acid or contains an acid as one of its constituents. Thus lemons and oranges contain citric acid, apples and many other fruits contain malic acid, and vinegar owes its sour taste to acetic acid.

(*b*) Next to the taste, the simplest test for an acid is its action upon vegetable colors. Nearly all acids change litmus from blue to red and produce analogous changes in many other vegetable colors. Any substance that reddens blue litmus is an acid or contains an acid.

90. Bases. — Substances of this class have the common property of uniting with an acid in such a way as to destroy its typically acid properties. A part of the base replaces the hydrogen of the acid and thus forms a compound that is not sour and does not change litmus or other vegetable colors. All bases contain oxygen; many of them also contain hydrogen, an atom of each being united to form a group of hydroxyl (OH); there is always another constituent, generally a metal. For example, lime (CaO) and sodium hydroxide ($NaOH$) are bases.

(*a*) An alkali is a base that is soluble in water, combines with fats to form soaps, has a caustic action on animal and vegetable tissue, turns reddened litmus back to blue, and changes turmeric from yellow to brown. The most common alkalis are the hydroxides (§ 96) of sodium, potassium, calcium, and ammonium. As distinguished from the fixed alkalis, ammonia is called the volatile alkali.

(*b*) When the base and the acid are brought into sufficiently intimate contact, as when a solution of one is mixed with a solution of the other, the hydrogen atoms in the acid molecules combine with the hydroxyl of the basic molecules to form water. The remaining atoms or the radicals with which the acid hydrogen and the basic hydroxyl were united, also unite to form a compound called a salt. As in most bases the hydroxyl is united with an atom of a metal, most salts contain a metallic element. To this general rule ammonia and ammonium salts are exceptions, the group of atoms NH_4 (i.e., the radical ammonium) acting the part of a metallic atom.

(*c*) Acids and bases, then, have each the power of destroying the properties that are typical of the other. This process is called neutralizing; the two bodies are said to neutralize each other; when the resulting product has no power to change the color of either blue or red litmus, it is said to be neutral.

Salts.

Experiment 84. — Dissolve 5 grams of caustic soda (sodium hydroxide, sodium hydrate, $NaOH$) in 50 cu. cm. of water. Slowly add dilute hydrochloric acid (HCl), frequently testing the solution with blue litmus-paper until a final drop turns the paper slightly red. If too much acid has been added by mistake, make the solution again alkaline with the soda, and repeat the neutralization with the acid until the test-paper is only very faintly reddened. Then evaporate the solution on a water-bath until the residue is dry. Taste the resulting solid and determine its reaction with litmus.

91. Salts. — In the above experiment, the caustic soda, an alkaline base, reacted with the hydrochloric acid as follows:

$$NaOH + HCl = NaCl + H_2O.$$

The hydrogen and the sodium changed places. The product of such a reaction between an acid and a base, in which one or more of the hydrogen atoms of the acid have been replaced by metallic atoms or basic radicals, or in which the hydrogen atoms of the base are more or less replaced by non-metallic atoms or acid radicals, is called a salt.

(*a*) A salt may be formed —

(1) By replacing one or more of the hydrogen atoms of an acid with electropositive (metallic) atoms or radicals. Compare HNO_3 and KNO_3.

(2) By replacing one or more of the hydrogen atoms of a base with electronegative (non-metallic) atoms or compound radicals. Compare KOH and $K(NO_2)O$ or KNO_3.

(3) By the direct union of an anhydride (see § 95) and a basic oxide. Thus, calcium sulphate results from the direct union of sulphuric anhydride and calcium oxide (quicklime): $SO_3 + CaO = CaSO_4$.

NOTE. — Of these three views of the formation of a salt, the first is the one most frequently taken, but occasionally the other two are convenient. An acid is sometimes called a "hydrogen salt"; e.g., hydrogen nitrate (HNO_3).

92. Classification of Salts. — Salts may be normal (or neutral), double, acid, or basic.

(*a*) A normal salt is one that contains neither basic nor acid hydrogen (see § 94). All of the basic hydrogen of the acid, or acid hydrogen of the base from which it was formed has been replaced as stated in the last paragraph. K_2SO_4 and $CuSO_4$ are normal salts.

(*b*) A double salt is one in which hydrogen of the acid from which it was formed has been replaced by metallic (or positive) atoms of different kinds. For example, common alum, $Al_2K_2(SO_4)_4$, is a double salt.

(*c*) An acid or hydrogen salt is one that contains basic hydrogen (see § 94). As only part of the replaceable hydrogen of the acid has been replaced, the salt, in most cases, still acts like an acid, reddening blue litmus. The potassium-hydrogen sulphate, $KHSO_4$, mentioned in Experiment 74, is an acid or hydrogen salt.

(*d*) A basic salt is one that contains acid hydrogen. Only part of the hydrogen of the base from which it was formed has been replaced, on account of which, in many cases, it still acts like a base, turning reddened litmus to blue. For example, lead hydroxide is a base with the symbol, PbH_2O_2 or H_2PbO_2. Replacing half of this hydrogen with the acid radical, NO_2, we have $H(NO_2)PbO_2$, the symbol for lead hydronitrate, a basic salt.

(*e*) A binary acid will yield a binary salt when its hydrogen is replaced. Thus, HCl yields NaCl.

93. The Nomenclature of Acids. — Acids take their names from their non-metallic radicals, such as chlorine and sulphur (see § 15). A few acids contain no oxygen. The names of these begin with the prefix *hydro-*, and end with the suffix *-ic*, as hydrochloric acid (HCl), the most important of this class. If only two ternary acids of a non-metallic element are known, the one in which the molecule contains the greater number of oxygen atoms takes the termination *-ic*; the other takes the termination *-ous*. Sometimes the radical forms three or even four ternary acids. The acid in which the molecule contains a number of oxygen atoms greater than that of the *-ic* acid takes the prefix *per-*; the one in which the number is less than that of the *-ous* acid takes the prefix, *hypo-*. The use of these prefixes and suffixes will be made clear by a study of the following examples:

$HClO_4$	*per*chlor*ic* acid		
$HClO_3$	chlor*ic* acid	H_2SO_4	sulphur*ic* acid
$HClO_2$	chlor*ous* acid	H_2SO_3	sulphur*ous* acid
$HClO$	*hypo*chlor*ous* acid	H_2SO_2	*hypo*sulphur*ous* acid

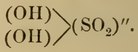
This system of nomenclature was introduced by Lavoisier.

94. Basicity of Acids. — The hydrogen of an acid that may be readily replaced by a metal is called basic hydrogen. If the acid molecule has one atom of basic hydrogen, the acid is called a monobasic acid. If it has two such atoms, the acid is called a dibasic or bibasic acid; if three, it is tribasic; if four, it is tetrabasic.

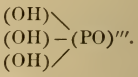
(*a*) The basicity of an acid molecule depends upon the number of its directly exchangeable hydrogen atoms and may generally be represented by the number of hydroxyl groups it contains. For example:

HNO_3 is a monobasic acid . . . . . . $(OH)-(NO_2)'$.

H_2SO_4 is a dibasic acid . . . .



H_3PO_4 is a tribasic acid . . . .



Be it remembered, however, that the basicity of an acid molecule depends, not upon the total number of its hydrogen atoms, but upon the number of them that may be directly exchanged for metallic atoms. H_3PO_4 is called tribasic, not because it has three hydrogen atoms, but because it may form three distinct salts with one metal.

95. Anhydrides. — An oxide of a non-metallic (or electronegative) element which, with the elements of water, may form an acid, is called an anhydride. Nitrogen trioxide and nitrogen pentoxide, and sulphurous and sulphuric oxides are anhydrides. They unite directly with water to form the corresponding acids, thus:

$$N_2O_3 + H_2O = 2HNO_2 \text{ (nitr\textit{ous} acid),}$$

$$N_2O_5 + H_2O = 2HNO_3 \text{ (nitr\textit{ic} acid),}$$

$$SO_2 + H_2O = H_2SO_3 \text{ (sulphur\textit{ous} acid),}$$

$$SO_3 + H_2O = H_2SO_4 \text{ (sulphur\textit{ic} acid).}$$

96. Nomenclature of Bases. — The bases that contain hydrogen are often called hydroxides or hydrates, distinguished by the names of the metals that they severally contain, as sodium hydroxide ($NaOH$), potassium hydroxide (KOH), and calcium hydroxide [$Ca(OH)_2$]. They may be regarded as hydroxyl compounds, or as water in which half of the hydrogen has been replaced by a metal. Many of them may be made by simply bringing the metal into contact with water, as, when sodium is thrown upon water, hydrogen is evolved from the water, and sodium hydroxide (sodium hydrate or caustic soda) is formed, thus:

$$Na_2 + 2H_2O = 2NaOH + H_2.$$

97. Nomenclature of Salts. — The names of the salts of any acid are derived from the name of that acid and qualified by the name of the metallic atoms that they contain, as explained in § 15. Thus we have

Sodium hypochlorite ($NaClO$) from hypochlorous acid.
Sodium chlorite ($NaClO_2$) from chlorous acid.
Potassium chlorate ($KClO_3$) from chloric acid.
Potassium perchlorate ($KClO_4$) from perchloric acid.

The names of the salts derived from binary acids, like hydrochloric acid (HCl), are exceptions. Following the general rule of binary compounds, they end in *-ide*, like sodium chloride ($NaCl$).

EXERCISES.

1. (*a*) What is the difference between an atom and a molecule? (*b*) Between a physical and a chemical property? (*c*) Define and illustrate base, acid, salt. (*d*) State the differences between an *-ic*, an *-ous*, and an *-ate* compound.

2. (*a*) Why is sulphurous acid said to be dibasic? (*b*) What is the difference between an acid sulphite and a normal sulphite? (*c*) Between an acid sulphite and a hydrogen sulphite?

3. Is every alkali a base? Is every base an alkali?

4. Why are there no acid nitrates?

5. Name the acid and the base, the reaction of which yields the salt with which you are the most familiar.

6. What is the common name of hydroxyl hydride?

7. Write the molecular formulas for hydrochloric and hypochlorous acids.

8. When mercuric oxide (HgO) is heated, it decomposes. Write the reaction. (Owing to the high price of mercuric oxide, this reaction is seldom employed.)

9. State the composition of water, both volumetric and gravimetric.

10. What word describes the hydrogen in an acid salt? In a basic salt?

CHAPTER VI.

VALENCE, RATIONAL SYMBOLS, RADICALS.

98. Valence. — The valence of an element is its relative combining capacity measured by that of hydrogen as the unit; in other words, it indicates the number of hydrogen atoms with which an atom of the element can unite, or the number of hydrogen atoms that it can replace. Thus,

In hydrochloric acid (HCl), the valence of chlorine is 1.
In water (H_2O), the valence of oxygen is 2.
In ammonia (H_3N), the valence of nitrogen is 3.
In marsh-gas (H_4C), the valence of carbon is 4.

Similarly, one atom of potassium (K) can replace one atom of hydrogen in a molecule of nitric acid (HNO_3) yielding a molecule of potassium nitrate (KNO_3), while one atom of calcium (Ca) can replace two atoms of hydrogen in a molecule of sulphuric acid (H_2SO_4) yielding a molecule of calcium sulphate ($CaSO_4$). One atom of potassium can replace one atom of hydrogen, but no more, its valence is one; one atom of calcium can replace two atoms of hydrogen, but no less, its valence is two.

(*a*) Atoms are classified according to their valence as monads, dyads, triads, tetrads, pentads, hexads, and heptads, from the Greek numerals. They are similarly described by the adjectives univalent, bivalent, trivalent, quadrivalent, quinquivalent, sexivalent, and septivalent, from the Latin numerals. Thus, oxygen is a dyad, or it is bivalent; carbon is a tetrad, or it is quadrivalent.

(*b*) The valence of some elements varies with the natures of the elements with which they are brought into contact. Thus, with hydrogen alone, a nitrogen atom can combine with only three atoms forming a molecule of ammonia (NH_3). In this case, nitrogen acts as a triad. But when ammonia is brought into contact with hydrochloric acid (HCl), the nitrogen atom unites with both the hydrogen and the chlorine to form ammonium chloride (NH_4Cl). In this case, nitrogen acts as a pentad. When atoms of a given element thus act with different valences, they frequently form compounds as dissimilar as atoms of different kinds would do. A change in the valence of an atom implies a change in all its chemical relations. N_2O is as different from N_2O_5 as H_2O is.

(*c*) The valence of an atom is indicated by Roman numerals placed above, or minute marks placed above and at the right of the symbol, as $\overset{\text{IV}}{C}$ or N'''. They should not be confounded with the figures below and at the right of the symbol.

(*d*) Sometimes the words "quantivalence," "equivalence," and even "atomicity" are used in the sense in which we have used the word valence. The word "atomicity" more properly refers to the number of atoms in a molecule.

99. Graphic Symbols of Atoms. — The graphic symbol of an atom represents its valence by lines or bonds extending from the symbol, as follows:

Monad,	*Dyad,*	*Triad,*	*Tetrad,*	*Pentad,*	*Hexad.*
H –	O =	N ≡	C ≣	= P ≡	≡ S ≡

The number of bonds is significant; their direction is not. Thus, the graphic symbol of an atom of oxygen may be written $-O-$, $O=$, $\overset{|}{O}-$, $-\underset{|}{O}$, $O<$, etc.

100. Graphic Symbols of Molecules. — The graphic symbol or formula of a molecule is composed of the graphic symbols of the constituent atoms. It attempts to indicate the constitution of the molecule, not by showing the arrangement of the atoms in space, for we know nothing about that, but by showing that certain atoms are united to certain other atoms. Sometimes these symbols suggest the possible modes of formation and of decomposition of substances; sometimes they are necessary to enable us to distinguish between substances that have the same percentage composition and different properties (see § 252).

(*a*) The graphic symbol of H_2O may be written $H-O-H$; that of H_3N, $H-\overset{\overset{\displaystyle H}{|}}{N}-H$; that of CO_2, $O=C=O$; that of $H\overset{\text{v}}{N}O_3$, $H-O-\overset{\overset{\displaystyle O}{\|}}{N}=O$; and that of $\overset{\text{vi}}{S}O_2$, $O=\underset{\|}{S}=O$. It will be noticed that each atom has the number of bonds that represents its valence. A modification of the graphic symbol, often called the semigraphic symbol, is sometimes conveniently used, as $(HO)-(HO)$, or $Ca\begin{array}{l}\diagup NO_2\\ \diagdown NO_2\end{array}$.

(*b*) Less important than the graphic formula, and yet often convenient, is the typical formula, examples of which are here given:

Free Hydrogen.	*Water.*	*Ammonia.*	*Marsh-gas.*
$\left.\begin{array}{l}H\\H\end{array}\right\}$	$\left.\begin{array}{l}H\\H\end{array}\right\}O$	$\left.\begin{array}{l}H\\H\\H\end{array}\right\}N$	$\left.\begin{array}{l}H\\H\\H\\H\end{array}\right\}C.$

101. Radicals. — An atom or group of atoms that seems to determine the character of a molecule is called a radical. Such an atom is called a simple radical; such a group of atoms is called a compound radical. In the graphic symbols given above, it will be noticed that, in each case but one (SO_2), every atom has its valence fully satisfied; i.e., each bond of each atom is engaged. Such atomic groups are said to be saturated. But the group, $O=\underset{\|}{S}=O$, has two free bonds.

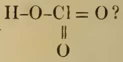
Such an unsaturated group of atoms, assumed to exist in a compound body and to remain intact in many of the chemical *changes that the body undergoes, is called a compound radical. It may enter into combination like a simple atom, always acting with a valence equal to the number of unsatisfied bonds.* See § 94 (*a*).

(*a*) The names of compound radicals generally terminate in *-yl*, as nitrosyl (NO) and nitryl (NO_2). Two of these atomic groups may unite, like two atoms, to form a saturated molecule. If, from H–O–H, we remove one atom of H, we have the compound radical H–O–, called hydroxyl. Two of these univalent groups may unite to form H_2O_2, as follows: (HO)–(HO) or H–O–O–H.

EXERCISES.

1. Considering chlorine to be a monad, write the graphic symbols for Cl_2O, Cl_2O_3, HClO and $HClO_3$.

2. What valence for chlorine is indicated by

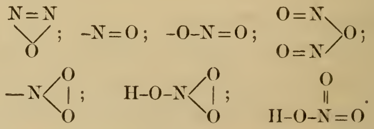


$$\text{H–O–}\underset{\underset{\text{O}}{\|}}{\text{Cl}}\text{ = O ?}$$

3. Write three graphic symbols for SO_2, two of which shall represent it as a compound radical (sulphuryl) and all of which shall represent sulphur as a dyad.

4. Write two graphic symbols for SO_3, one of them representing sulphur as a dyad, the other representing sulphur as a hexad.

5. Name the substances symbolized as follows, indicating the symbols for compound radicals:



State the difference between the indications given by the last two symbols.

6. (*a*) Write the molecular formula for the hydroxide of the monad radical, nitryl. (*b*) For the hydroxide of $(SO_2)''$.

7. Why may not hydrogen dioxide be represented by H–O–H–O?

8. Write the graphic or structural formula for ammonia.

9. Considered as a compound radical, what is the valence of ammonium?

10. Write the full graphic formula for ammonium hydroxide.

CHAPTER VII.

THE HALOGEN GROUP.

I. CHLORINE.

Symbol, Cl.; density, 35.2; atomic weight 35.2; valence, 1, 3, 4, 5, 7.

102. Occurrence. — Chlorine does not occur free in nature, but it is very abundant and widely diffused, being a constituent of common salt (sodium chloride, $NaCl$), and of potassium chloride (KCl). Sea-water may be made to yield about five times its volume of chlorine. The name comes from the Greek *chloros*, meaning green.

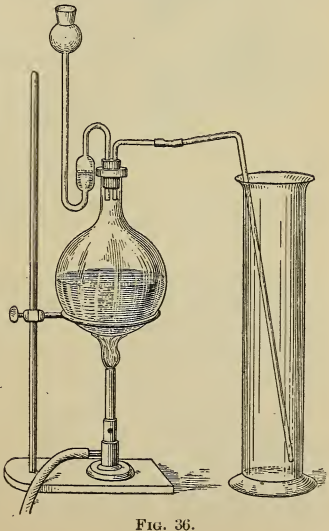


FIG. 36.

Preparation of Chlorine.

Experiment 85. — Into a flask of about 300 cu. cm. capacity put about 30 grams of dry sodium chlorine (common salt, $NaCl$), and add an equal weight of coarse manganese dioxide (MnO_2) and 35 cu. cm. of strong sulphuric acid (H_2SO_4), previously diluted with an equal bulk of water. The stopper of the flask should carry a delivery-tube, passing to the bottom of a tall, dry glass cylinder, and a safety-tube. Shake the flask to mix the materials, place it upon a sand-bath, and heat gently. Chlorine is evolved and is collected in the cylinder by downward displacement. When the cylinder is full, close the mouth with a greased glass plate. The yellowish green color of the gas enables the experimenter to see when the cylinder is full. Be careful not to inhale the gas. Perform all experiments with chlorine in a draught of air or in a ventilating closet.

$$2NaCl + MnO_2 + 3H_2SO_4 = MnSO_4 + 2HNaSO_4 + 2H_2O + Cl_2.$$

When sulphuric acid acts on sodium chloride alone, hydrochloric acid and sodium sulphate are formed.

$$H_2SO_4 + 2NaCl = 2HCl + Na_2SO_4.$$

But when the manganese dioxide is present, some of its oxygen unites with hydrogen from this hydrochloric acid, forming water and setting chlorine free, as indicated above.

Experiment 86.—In apparatus arranged as described in Experiment 85, gently heat 12 grams of manganese dioxide and 25 cu. cm. of hydrochloric acid.

$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2.$$

The gas may be collected, although with loss, over hot water or strong brine. It may be noticed that in Experiment 85, as truly as here, the method of preparing the gas is to oxidize the hydrogen of the hydrochloric acid to water, thus liberating the chlorine of the acid.

Experiment 87.—Put a small bottle containing 15 or 20 grams of bleaching-powder into a glass vessel of several liters capacity. Then, by means of a funnel-tube passing through the pasteboard cover of the large jar, pour dilute sulphuric acid upon the bleaching-powder. Chlorine will be evolved and displace the air from the jar.

103. Preparation.—Chlorine is generally prepared indirectly from common salt. The immediate chemical process is by oxidizing the hydrogen of hydrochloric acid, thus setting free the chlorine. Different agents, generally potassium chlorate or manganese dioxide, are used in such oxidation.

$$KClO_3 + 6HCl = KCl + 3H_2O + 3Cl_2.$$

Chlorine is prepared on the commercial scale as an accompaniment of the Leblanc process for making sodium carbonate.

Physical Properties of Chlorine.

Experiment 88. — Prepare some chlorine-water by passing a current of chlorine through water, in a series of Woulffe bottles, arranged as in Experiment 61, except that the tubes should not dip so deep into the water. The chlorine-water may be preserved for a considerable time by placing it in bottles wrapped in opaque paper and closed with greased stoppers.

Experiment 89. — Into a wide-mouthed bottle filled with chlorine, pour water until the jar is a third full of the liquid. Close the mouth of the bottle with the hand and shake the bottle. The gas will be absorbed, a vacuum formed, and the bottle held against the hand by atmospheric pressure.

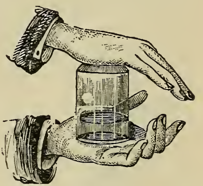


Fig. 37.

104. Physical Properties. — Chlorine is a yellowish green, irrespirable gas with a suffocating odor and astringent taste. Even a very small quantity of it in the air produces violent coughing and irritation of the air passages when it is inhaled. It may be easily liquefied by pressure or cold. If it was not so corrosive, it could be transported and handled commercially in the liquid form. At very low temperatures, it crystallizes to a yellow mass that melts at − 102°. It is largely soluble in water, one volume of which, at 10°, dissolves two and a half volumes of the gas. The solution has most of the properties of the gas, and, when saturated, gives off the gas freely on exposure to the air. One volume of charcoal will absorb two hundred volumes of the gas. Chlorine gas is nearly two and a half times as heavy as air.

Chemical Properties of Chlorine.

Experiment 90. — Fill a tall bottle or cylinder holding 500 cu. cm. or more with chlorine. The gas may well be dried by passing it over calcium chloride, as in Experiment 28, or by passing it over fragments of pumice saturated with sulphuric acid (H_2SO_4), or by allowing the gas to bubble through sulphuric acid. Slowly sift freshly prepared filings of metallic antimony into the bottle. The two elements will combine with the evolution of heat and light. Filings of metallic arsenic or bismuth give similar effects.

Experiment 91. — Place a thin slice of dry phosphorus in a deflagration-spoon and place it in a jar of chlorine. The gas and the solid combine directly with a pale flame.

Experiment 92. — Burn a jet of hydrogen or one of illuminating gas, in an atmosphere of chlorine. Reverse the conditions and burn a jet of chlorine in hydrogen (see Fig. 23). Try to burn a jet of chlorine in oxygen, and a jet of oxygen in chlorine.

Experiment 93. — Pour chlorine-water into a solution of hydrogen sulphide (H_2S, see Experiment 260). The chlorine robs the sulphide of its hydrogen to form hydrochloric acid, while the sulphur is precipitated.

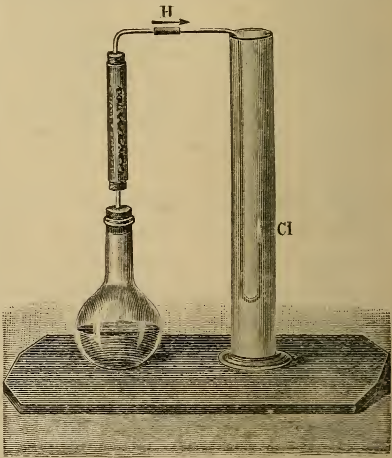


Fig. 38.

Experiment 94. — In a darkened room, mix equal volumes of hydrogen and chlorine, previously prepared in the light. With the mixture, fill three stout soda bottles. Wrap one of the bottles with a towel, remove the cork and apply a flame to the mouth of the bottle. The mixed gases combine with an explosion. The towel will protect the experimenter if the explosion breaks the bottle. Wrap the second bottle with a towel to which a string, several meters long, has been attached. Carry the covered bottle into a sunny place and, by means of the string, remove the towel. The sun's direct rays cause the mixed gases to explode. This experiment succeeds best with a thin glass bulb filled with a gaseous mixture obtained by the electrolysis of hydrochloric acid. Place the third bottle in diffused sunlight. The two gases will unite gradually and quietly. Allow the bottle to remain for future use.

Experiment 95. — Fill five wide-mouthed bottles with dry chlorine and close their mouths with greased glass plates. Heat some oil of turpentine over the water-bath. Fasten a tuft of shredded tissue-paper or of cotton to a wire or splinter, dip it into the hot turpentine, and *quickly* plunge it into the first bottle of chlorine. The paper or cotton will generally take fire and burn with a very dense smoke (Fig. 39). Into the second bottle, thrust a burning dry wood splinter; into the third, thrust a burning piece of paper; into the fourth, a burning wax or tallow taper (Fig. 40); into the fifth, a deflagration-spoon containing burning petroleum. Note the effect in each case.


FIG. 39.


FIG. 40.

NOTE. — The combustibles used in the last experiment contain hydrogen and carbon. This hydrogen combines with the chlorine and sets the carbon free, as smoke.

Experiment 96. — Fill a tall tube with chlorine and invert it over a cup of water. Place the tube in a sunny place. After a few days, test the gaseous contents of the tube for oxygen, and the water for an acid. Seek for the odor of chlorine.

$$H_2O + Cl_2 = 2HCl + O.$$

105. Chemical Properties. — Chlorine is a very energetic chemical agent. It unites directly with all of the common elements except oxygen, nitrogen, and carbon, its attraction for hydrogen being very remarkable.

Bleaching.

Experiment 97. — Pass a current of *dry* chlorine through a bulb- or a U-tube containing a bit of dry calico print. After a few moments, attach a second tube containing a bit of similar calico that has been moistened. Notice that the chlorine passes the dry calico without bleaching it, but that it quickly bleaches the moist calico with which it subsequently comes into contact.

Note. — Pink or blue paper-cambric is desirable for the above experiment. The presence of moisture is necessary to this bleaching action. Dry chlorine seldom acts directly on coloring matters, but oxygen in its "nascent state," or at the instant of its liberation from water, does so act. In this case, the nascent oxygen is the immediate bleaching agent.

Experiment 98. — Nearly fill seven test-tubes with chlorine-water. Into the first, pour a few drops of indigo solution; into the second, litmus solution; into the third, cochineal solution; into the fourth and fifth, aniline dyes of different colors; into the sixth, the colored petal of a flower, and into the seventh put a strip of colored calico or of paper-cambric. The colors will quickly disappear.

Experiment 99. — Dip a piece of colored cambric or of calico into a half liter of water into which 15 grams of bleaching-powder have been stirred. Notice the effect upon the color of the cloth. Then dip the cloth into very dilute hydrochloric or sulphuric acid. Notice the effect on the color of the cloth. Wash the cloth thoroughly in water.

106. Bleaching-powder. — For convenience in transportation, chlorine is absorbed, at the works where it is manufactured, in slightly moistened slacked lime with which it unites chemically, forming calcium hypochlorite ($CaCl_2O_2$) and calcium chloride ($CaCl_2$). From this bleaching-powder, chlorine is easily set free by adding enough acid to combine with the calcium present. The quantity of bleaching-powder made each year is very large and increasing. Its principal use is as a bleaching agent in the manufacture of paper and of cotton goods, and for recovering gold from certain of its ores. It is sometimes called chloride of lime.

(*a*) The chlorine required in the manufacture of bleaching-powder is made by three different processes:

1. The oldest method (now the least used) is that of treating manganese dioxide with hydrochloric acid.
2. Another method is by the electrolysis of some chloride, generally common salt. The electric current breaks up the sodium chloride into sodium and chlorine. The sodium thus freed unites with water, producing hydrogen and sodium hydroxide (caustic soda, $NaOH$). Thus caustic soda is an important product of this process.
3. The method, known from the name of the inventor as the Deacon process, is the one most largely used. It consists in passing air and hydrochloric acid together through a heated chamber containing clay balls saturated with copper sulphate. Under these conditions, the hydrogen of the acid and the oxygen of the air unite and leave the chlorine free.

$$4HCl + O_2 = 2H_2O + 2Cl_2.$$

Uses of Chlorine.

Experiment 100. — Upon a piece of printed paper, write your name in ink. Dip the paper into chlorine-water. The written characters will be bleached out; the printed characters will remain.

Experiment 101. — Repeat Experiment 93, noticing the odor of hydrogen sulphide before the addition of the chlorine-water and its absence after such addition.

107. Uses. — Chlorine is used in the arts as a bleaching and disinfecting agent, its action depending very largely upon its attraction for hydrogen. The non-mineral coloring matters are largely composed of oxygen, hydrogen, nitrogen, and carbon. When such coloring matter is brought into contact with chlorine in the presence of moisture, the chlorine attacks the hydrogen of both, the nascent oxygen thus liberated from the water greatly aiding the chlorine in the decomposition of the coloring substance. Colorless compounds are formed by a process of chlorination and oxidation. Chlorine has little effect upon mineral colors, or free carbon.

Tests for Chlorine.

Experiment 102. — Prepare a quantity of thin starch paste by boiling 30 cu. cm. of water and stirring into it half a gram of starch previously reduced to the consistency of cream by thoroughly mixing with a few drops of cold water. In this paste, dissolve a piece of potassium iodide, half the size of a pea. Into a test-tube, put 10 cu. cm. of water and five or six drops of this mixture of starch and potassium iodide. Shake the tube vigorously for a few seconds and let a few drops of chlorine-water fall into it. Notice the blue color thus formed. The chlorine decomposes the potassium iodide; the free iodine colors the starch.

Experiment 103. — Into the solution of starch and potassium iodide, dip two or three strips of white paper. Hold one of these strips of test-paper in a current of chlorine. The white paper is turned to blue. Remove the stopper from the bottle containing chloride of lime (bleaching-powder) and hold another strip of the test-paper in the atmosphere of chlorine that fills the upper part of the bottle. The paper is instantly colored blue.

Experiment 104. — Place a strip of gold-leaf in saturated chlorine-water. The gold will be dissolved.

108. Tests. — Free chlorine is easily distinguished by its odor; pure chlorine, by its color. Chlorine is also easily detected by its bleaching action upon organic coloring matters, or by its forming a blue color with a mixture of starch and potassium iodide. This last-mentioned reaction is very delicate, but an excess of chlorine removes the color and the same effect is produced by bromine, ozone, and a few other actively oxidizing substances. A cloud of ammonium chloride is formed when chlorine comes into contact with ammonia, and this serves as a delicate test for its presence when hydrochloric acid is known to be absent.

EXERCISES.

1. When chlorine-water is exposed to sunlight, HCl is formed and oxygen is set free. (*a*) Write the reaction. (*b*) What volume of chlorine is necessary thus to set free 20 cu. cm. of oxygen?

2. Chlorine unites with the metals acting as a monad. (*a*) Symbolize the binary compounds of chlorine with the following: Na'; K'; Cu''; Au'''; Ag'; Fe''; Zn''; $(Fe_2)^{v}$. (*b*) Symbolize the nitrates formed by replacing the hydrogen in nitric acid by the several metals just mentioned.

3. About how many liters of chlorine may be obtained from 10 liters of sea-water?

4. May chlorine be collected by upward or by downward displacement? Why?

5. Which is the more largely soluble in water, chlorine or ammonia?

6. With which does chlorine combine the more readily, oxygen or hydrogen? Give a reason for your answer.

7. With which does chlorine combine the more readily, hydrogen or carbon? Describe an experiment that supports your answer.

8. In what proportions do chlorine and nitrogen unite?

9. Of what is the valence of an element a numerical expression?

10. What is the difference between a molecule of Lake Superior copper and a molecule of Montana copper?

II. HYDROCHLORIC ACID.

109. Source. — Hydrochloric acid (hydrogen chloride, HCl) is the only known compound of hydrogen and chlorine. In its preparation, the hydrogen is generally furnished by sulphuric acid (H_2SO_4), and the chlorine by common salt (sodium chloride, $NaCl$), the cheapest and most abundant source of chlorine. The pure acid is a gas, the water solution of which constitutes the muriatic acid of commerce.

(*a*) Hydrochloric acid is found in the exhalations of active volcanoes, especially Vesuvius and Hecla, and in the waters of several South American rivers that have their rise in volcanic regions.

110. Preparation. — Hydrochloric acid is almost always prepared from common salt by distillation with sulphuric acid.

(*a*) Into a liter Florence flask, put 30 grams of $NaCl$ and 30 cu. cm. of concentrated sulphuric acid. Heat the flask gently over the sand-bath and collect the gas by downward displacement in dry jars, as in the preparation of chlorine. By holding a piece of moistened blue litmus-paper at the mouth of the jar, the experimenter can easily tell when the jar is full.

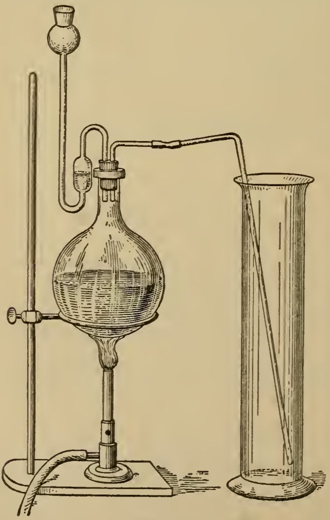


FIG. 41.

$$NaCl + H_2SO_4 = HCl + NaHSO_4.$$

(*b*) At a higher temperature, the same quantity of sulphuric acid would combine with twice as much sodium chloride, yield twice as much hydrochloric acid, and leave sodium sulphate (Na_2SO_4) instead of sodium-hydrogen sulphate ($NaHSO_4$).

$$2NaCl + H_2SO_4 = 2HCl + Na_2SO_4.$$

The greater heat necessary for this latter reaction would be severe upon the apparatus. At the end of the experiment, the $NaHSO_4$ remaining in the flask may be easily removed with warm water.

(*c*) Hydrochloric acid may be prepared by the direct union of equal volumes of its constituents. See Experiment 94.

(*d*) In the arts, the retort used is an iron cylinder, or the retort is replaced by a brick furnace. Sometimes an improved "salt-cake" furnace is used. This consists of two chambers, a kind of muffle, *G*, in which the first reaction takes place, and a reverberatory, *E*, in which may be secured the higher temperature needed for the second reaction. The two chambers may be separated by closing the connecting aperture. The gaseous acid from either chamber may be led off separately and dissolved in water contained in a series of earthenware Woulffe bottles. Very large quantities (thousands of tons weekly) of the acid liquid are made as an incidental product of the manufacture of sodium carbonate.

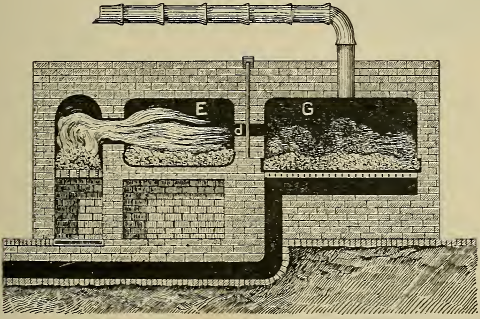


FIG. 42.

(*e*) Dry, gaseous HCl may be obtained by heating the acid liquid and passing the gas given off through a drying-tube or bottle.

Physical Properties of Hydrochloric Acid.

Experiment 105. — Fill a long test-tube with dry hydrochloric acid and invert it over mercury. Thrust a bit of ice into the mouth of the tube. The ice and gas will quickly disappear, the mercury rising in the tube. Explain.

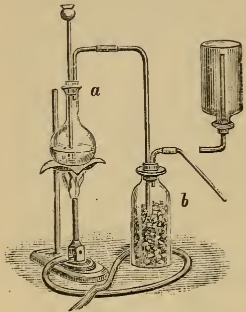


FIG. 43.

Experiment 106. — Fill a bottle with dry HCl. Close the bottle with a cork carrying a glass tube and invert it over water colored with blue litmus. The water will soon enter the bottle with violence, and its color will be changed from blue to red (see Fig. 30).

Experiment 107. — Pass HCl from the generating flask through a series of Woulffe bottles arranged as in Experiment 61, except that the delivery-tube from each bottle should barely dip into the water of the next bottle. It is well to place the Woulffe bottles in water to keep them cool. When the gas ceases to flow, test the contents of each bottle with blue litmus-paper. Bottle the liquid and save it for future use.

111. Physical Properties. — Hydrochloric acid is a colorless gas having an acid taste and pungent odor. It is irrespirable, corrosive, and neither combustible nor a supporter of combustion. It is a little heavier than air, its density being 18.25. It liquefies at ordinary temperatures under a pressure of eighty-six atmospheres. This liquid has a density of 1.27, boils at − 80°, and freezes at − 115.7° to a white, crystalline mass. The gas is remarkably soluble in water, one volume of which, at the ordinary temperature, absorbs about 450 volumes of the gas, or 505 volumes at zero. This saturated solution, the muriatic acid of commerce, fumes strongly in the air because of the strong attraction of the gaseous acid for the moisture of the air. It has a density of 1.21 and readily gives up the acid gas when heated. If pure, it freezes at temperatures below $-40°$ to a butter-like mass having the composition $HCl + 2H_2O$. The commercial acid is yellow from dissolved impurities.

Chemical Properties of Hydrochloric Acid.

Experiment 108. — Nearly fill a test-tube with dilute, commercial HCl and drop into it a few pieces of granulated zinc. The zinc is quickly dissolved. What gas escapes? Write the reaction. Repeat the experiment with as many other metals as you can readily obtain.

Experiment 109. — In a beaker, place several pieces of marble (calcium carbonate, $CaCO_3$), and pour upon them some HCl solution. Write the reaction. Repeat the experiment, using lime (CaO) instead of marble.

112. Chemical Properties. — Hydrochloric acid acts upon many metals and their oxides, forming chlorides, most of which are soluble in water.

(*a*) The liquefied anhydrous HCl does not act upon any of the metals except aluminum.

Composition of Hydrochloric Acid.

Experiment 110. — If the second bottle used in Experiment 94, was strong enough to stand the explosion without breaking, open it with its mouth under mercury. Notice that no mercury enters the bottle and that no gas escapes. Try it with the third bottle used in that experiment. Then test the contents of the bottles with moistened blue litmus-paper. The reddening of the paper shows that we have an acid; it is HCl. We have shown that the volume of the acid is the same as that of the gases that united to form it. How was this shown?

Experiment 111. — Half fill a U- or a V-shaped tube with HCl. Through each of two corks pass a wire attached to a strip of platinum. Insert the corks snugly, push the wires down until the platinum strips are nearly immersed in the acid liquid, and connect the wires with the poles of a galvanic battery. At the end of four or five minutes, remove the cork that carries the negative electrode and apply a lighted match. Hydrogen was present, mixed with the air that was in that arm of the tube at the beginning of the experiment. Remove the other cork and thrust a bit of moistened litmus-paper into that arm of the tube. The bleaching of the paper and the peculiar odor show the presence of chlorine. Of course, delivery-tubes may be provided for the corks and the gases collected separately. See Fig. 5. Exact experiments of this kind are difficult on account of the solubility of chlorine in water, but when made they show that equal volumes of hydrogen and of chlorine are liberated.

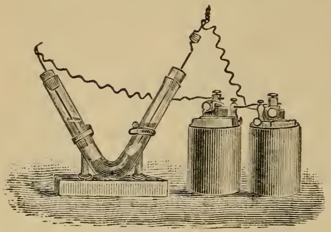


Fig. 44.

Experiment 112. — Fill a small graduated tube with pure, dry, hydrochloric acid gas over mercury contained in a proper trough. Into the tube thus containing the gas, introduce a piece of potassium weighing one or two grams. The metal will take the chlorine from the acid to form solid potassium chloride, leaving the hydrogen free.

$$K_2 + 2HCl = 2KCl + H_2.$$

The volume of the remaining hydrogen ought to be just half the volume originally measured by the acid gas.

Experiment 113. — If a mixture of equal volumes of hydrogen and chlorine confined over mercury is exploded in the manner described in Experiment 50, and the product of the chemical union is allowed to cool to the initial temperature, it will be found that there has been no change of the gaseous volume. The litmus test will show that an acid has been formed. Other tests would show that none of either of the mixed gases has been left free.

113. Volumetric Composition. — In the preparation of hydrochloric acid by the direct union of hydrogen and chlorine, one volume of hydrogen combines with one volume of chlorine to form two volumes of hydrochloric acid gas. The composition may be graphically represented as follows:

$$\boxed{\begin{matrix}\mathrm{H} \\ 1\end{matrix}} + \boxed{\begin{matrix}\mathrm{Cl} \\ 35.2\end{matrix}} = \boxed{\begin{matrix}\mathrm{HCl} \\ 36.2\end{matrix}}$$

The chemical action effects neither a volumetric nor a gravimetric change, but it does effect a thermometric change.

114. Uses. — Hydrochloric acid is used in the manufacture of chlorine, bleaching-powder, ammonium chloride, and many other chlorine compounds. It is of very frequent use in the chemical laboratory and has become almost indispensable in the manufacturing arts. It acts directly upon most of the metals, forming metallic chlorides, e.g., zinc chloride.

Tests for Hydrochloric Acid.

Experiment 114. — Dissolve a few crystals of silver nitrate ($AgNO_3$) in water. Add a few drops of a solution of sodium chloride (common salt, $NaCl$). A white curdy precipitate of silver chloride ($AgCl$) is formed.

Experiment 115. — Wash the $AgCl$ obtained in the last experiment and try to dissolve it in nitric acid. It is insoluble.

Experiment 116. — Wash the $AgCl$ of the last experiment and treat it with strong ammonia-water. It dissolves.

115. Tests. — Hydrochloric acid gas may be detected by its reddening moistened blue litmus-paper and its forming dense fumes of ammonium chloride when brought into contact with ammonia gas (see Experiment 8). Its aqueous solution may be detected by its reddening blue litmus-paper and forming, with a solution of silver nitrate, a white precipitate ($AgCl$) that is soluble in ammonia-water but insoluble in nitric acid. This is a test for all chlorides.

EXERCISES.

1. When ammonium chloride (sal ammoniac, NH_4Cl) is acted upon by sulphuric acid, we have a reaction partly represented as follows:

$$2NH_4Cl + H_2SO_4 = (NH_4)_2SO_4 +$$

See § 141 (*a*). Complete the equation.

2. A strip of paper moistened with a certain solution and exposed to chlorine turns blue. (*a*) What is the solution? (*b*) Explain the reaction. (*c*) What other gas will produce the same change of color?

3. Define and illustrate valence.

4. What is a chemical experiment?

5. Write the chemical formula for the most abundant source of chlorine.

6. How many kinds of atoms are involved in the reaction represented in Exercise 1 above? How many atoms are represented in the first member of the completed equation? In the second member? How many atoms of each kind are represented in the first member? Should the completed equation show the same number of each kind in the second member?

7. In what way does the presence of moisture aid the bleaching action of chlorine?

8. What is litmus-paper and what are its laboratory uses?

9. In what way may hydrochloric acid be prepared from water and chlorine? Write the reaction.

10. Write, in tabular form, the molecular symbols for the oxides, the chlorides, the iodides, the nitrates, and the sulphates of the dyad metals, Zn, Ca, Mg, Cd, and Hg.

III. OTHER CHLORINE COMPOUNDS.

Experiment 117. — Pulverize *separately* 1 gram of sugar and 1 gram of potassium chlorate ($KClO_3$). If they were ground together, there would be danger of an explosion. Mix them intimately upon a piece of paper and, from a glass rod dipped in sulphuric acid (H_2SO_4), let a drop of acid fall upon the mixture. The chlorine tetroxide (Cl_2O_4) thus set free causes an energetic combustion.

Experiment 118. — In a test-glass, place 1 gram of potassium chlorate (not pulverized). Add a few *small* pieces of phosphorus and nearly fill the glass with water. By means of a pipette, bring sulphuric acid into contact with the $KClO_3$. The phosphorus burns under water in the Cl_2O_4 thus set free.

FIG. 45.

116. Chlorine Oxides. — Chlorine does not unite directly with oxygen, but it may be made to do so by indirect means.

(*a*) Five oxides of chlorine are theoretically possible, of which only three have been isolated.

(1) Chlorine monoxide (hypochlorous oxide) . Cl_2O.
(2) Chlorine trioxide (chlorous oxide) . . . Cl_2O_3.
(3) Chlorine tetroxide (chloryl) . . . . Cl_2O_4.
(4) Chlorine pentoxide (chloric oxide) . . . Cl_2O_5.
(5) Chlorine heptoxide (perchloric oxide) . . Cl_2O_7.

(*b*) Chlorine monoxide is an explosive, yellow gas, formed by passing dry chlorine over mercuric oxide:

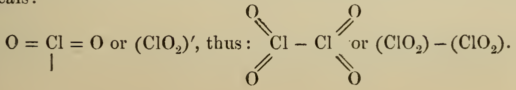
$$2Cl_2 + 2\,HgO = Hg_2OCl_2 + Cl_2O.$$

It liquefies at $-20°$.

Chlorine trioxide is a greenish, yellow, unstable gas, prepared by the reduction of chloric acid, thus:

$$2HClO_3 + N_2O_3 = Cl_2O_3 + 2HNO_3.$$

Chlorine tetroxide is an explosive gas obtained by the action of sulphuric acid upon potassium chlorate. It is sometimes called free chloryl, the molecule being considered as composed of two compound radicals:



$$O = \underset{|}{Cl} = O \text{ or } (ClO_2)', \text{ thus: } \begin{matrix} O & & O \\ \diagdown & & \diagup\!\!\diagup \\ & Cl - Cl & \\ \diagup\!\!\diagup & & \diagdown \\ O & & O \end{matrix} \text{ or } (ClO_2) - (ClO_2).$$

Cl_2O_5 and Cl_2O_7 have not yet been isolated, but their compounds are known.

(*c*) Note the varying valence of the chlorine in these several oxides, and that it is represented by the series of odd numbers, 1, 3, 5, and 7.

117. Chlorine Acids. — From four of these chlorine oxides results a corresponding list of acids and salts. The molecular formulas for the acids may be obtained from those of the corresponding oxides.

(*a*) The addition of H_2O to the formula of the oxide will give double the formula of the acid:

$Cl_2O + H_2O = H_2Cl_2O_2 = 2HClO$, hypochlorous acid.
$Cl_2O_3 + H_2O = H_2Cl_2O_4 = 2HClO_2$, chlorous acid.
$Cl_2O_5 + H_2O = H_2Cl_2O_6 = 2HClO_3$, chloric acid.
$Cl_2O_7 + H_2O = H_2Cl_2O_8 = 2HClO_4$, perchloric acid.

(*b*) The most important of these acids are $HClO$, because of its relation to calcium hypochlorite, and $HClO_3$, because of its relation to potassium chlorate, two salts of commercial importance.

Potassium Chlorate.

Experiment 119. — Repeat Experiment 5.

Experiment 120. — Repeat Experiment 117.

Experiment 121. — Repeat Experiment 3. The mixture may be placed in a paper or a metal cylinder and the experiment made in a dark room with good effect.

Experiment 122. — Place a *pinch* of powdered potassium chlorate and one of flowers of sulphur in a mortar and rub them together with a pestle. A series of explosions will take place. A minute quantity of the same mixture may be exploded by a blow of a hammer.

118. Potassium Chlorate.—Potassium chlorate (chlorate of potash, $KClO_3$) is made by electrolyzing a solution of potassium chloride. It is largely used in the preparation of oxygen, and for other purposes in the laboratory. It is also used in medicine, in calico printing, and in the manufacture of fireworks and friction-matches. It is chiefly valuable as an oxidizing agent.

Aqua Regia.

Experiment 123. — Put a small piece (4 or 5 sq. cm.) of gold-leaf into a test-tube and pour in strong nitric acid until the tube is a third full. Put a similar piece of gold-leaf into another test-tube and pour in a like quantity of hydrochloric acid. Gently heat the contents of each test-tube. If the leaf *is gold-leaf*, neither liquid will dissolve it. Pour the contents of one tube into the other. The gold-leaf will quickly dissolve in the mixed acids.

119. Aqua Regia. — Gold and platinum are insoluble in nitric or in hydrochloric acid, but are easily soluble in a warm mixture of these acids, especially when heated in the mixture. The acids react upon each other, chlorine is set free and, in the "nascent" condition, acts upon the metal or metallic compound more energetically than it would otherwise do.

(*a*) The name "aqua regia" (royal water) was given by the old alchemists because the mixture was able to dissolve gold, the "king of metals."

(*b*) The expression "nascent" state or condition is used to describe the condition of a chemical agent at the moment it is set free from some compound. The most marked effect is greatly increased chemical energy. We shall see other cases in illustration as we proceed.

(*c*) It is probable that "nascent" chlorine is in the atomic condition and ordinary chlorine in the molecular condition. They might be symbolized as follows: Cl and Cl_2; or $Cl -$ and $Cl - Cl$. A certain amount of energy is necessary to separate the atoms of a molecule, so that molecules act less vigorously than atoms do.

EXERCISES.

1. What chlorine oxide has trivalent chlorine?

2. (*a*) Write the graphic symbol for chloric acid. (*b*) What is the valence of the chlorine?

3. (*a*) Write the graphic symbol for $HClO_4$. (*b*) What is the valence of the chlorine?

4. Read aloud the following equation: $KNO_3 + H_2SO_4 = KHSO_4 + HNO_3$.

5. (*a*) If 20 liters of hydrogen are exploded with oxygen, how many liters of oxygen will be required? (*b*) How many liters of dry steam will be produced?

6. (*a*) If 15 liters of hydrogen are mixed with 10 liters of oxygen and the mixture is exploded, how many liters of dry steam will be produced? (*b*) Will any elementary gas remain free? If so, give its name and volume.

7. (*a*) How many grams of hydrogen are there in 36 grams of water? (*b*) How many grams of oxygen? (*c*) How many liters of hydrogen? (*d*) How many liters of oxygen?

8. (*a*) 24 liters of oxygen will yield how many liters of ozone? (*b*) 30 liters of ozone is equal to how many liters of oxygen?

9. Why should Cl – or H – have greater affinity for another element than Cl – Cl or H – H?

10. (*a*) How many kinds of atoms are known? (*b*) How many kinds of molecules?

11. Describe the experiment that may be fairly summarized by the equation given in Exercise 4 above.

12. Nitrohydrochloric acid dissolves platinum. What is the more common name for this acid?

IV. FLUORINE, BROMINE, IODINE, AND MANGANESE.

FLUORINE: symbol, F; atomic weight, 19; valence, 1.

120. Source. — Fluorine occurs in nature as a constituent of fluor-spar (calcium fluoride, CaF_2), and of cryolite (sodium and aluminum fluorides). It has also been found in minute quantities in the teeth, bones, and blood of animals.

(*a*) Fluor-spar is a mineral found somewhat abundantly in nature. Cryolite is found in large quantities only in Greenland.

121. Properties. — Fluorine is a greenish yellow gas, and one of the few elements that form no compound with oxygen; it attacks almost every other known substance. Owing to its intense chemical activity, it is difficult to prepare. Because of its attraction for almost all substances, it can be kept only in vessels made of platinum or of a fluoride. It is liberated by electrolyzing cold, anhydrous hydrofluoric acid to which some sodium fluoride (NaF) has been added. The properties of fluorine are remarkable. In it boron and quartz crystals burn at the ordinary temperature, and organic substances are carbonized or inflamed. It unites with various elements to form fluorides and decomposes water yielding hydrofluoric acid and ozone. Its compounds resemble those of chlorine, bromine, and iodine. It liquefies at −187°. As a liquid, at this temperature it loses most of its chemical activity, and may be kept in glass or metal vessels without change.

Hydrofluoric Acid.

Experiment 124. — Rub a heated piece of glass with beeswax or paraffin. If the glass is hot enough to melt the wax, it may easily have one of its surfaces covered with a thin layer of nearly uniform thickness. Let the glass cool. If the coating is not satisfactorily uniform, it may be improved with a hot spatula-blade. With any pointed instrument, write a name or draw a design, being careful that every stroke cuts through to the glass below. In a small tray made of lead (platinum is better, but a saucer that you are willing to spoil will answer), mix a spoonful of powdered fluor-spar or of cryolite with enough sulphuric acid to make a thin paste. Place the prepared glass (coated side down) over the tray; heat the tray gently (not enough to melt the wax) and set it aside in a warm place for a day. *Do not inhale the acid fumes.* Clean the glass by scraping it and rubbing with turpentine if you used beeswax, or with hot water if you used paraffin. The name or design will be seen etched upon the glass.

Experiment 125. — Upon a pane of glass that will fit the window of your chemical laboratory, or the glass front of one of your laboratory cases, etch the proper designation of the class, the date, and the autographs of the individual members of the class. The "class artist" may add an appropriate border and emblematic designs.

122. Hydrofluoric Acid. — This acid (HF) is distinguished from all other substances by its power of corroding glass. It corresponds closely to the other haloid acids (i.e., HCl, HBr, and HI), but it is more energetic than any of them. It is readily prepared, as above, by distilling some fluoride with sulphuric acid, e.g.,

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF.$$

(*a*) The reaction is closely analogous to that for the distillation of NaCl with H_2SO_4 (§ 110, *a*). The solution of HF is also used for etching glass. The dry acid does not act on glass, but the slightest trace of water renders it capable of doing so. Its aqueous solution is an article of commerce.

BROMINE: symbol, Br; density at 0°, 3.188; atomic weight, 80; valence, 1, 5, 7.

123. Source. — Bromine does not occur free in nature, but is found combined with metals, especially as magnesium bromide, in sea-water and in the water of certain salt-wells and springs.

(*a*) Much of the bromine made in the United States comes from the salt-wells of Ohio, West Virginia, and Michigan. The bittern that remains after the crystallization of the sodium chloride contains magnesium bromide in such quantities that bromine is profitably extracted from it. The bittern is treated with sulphuric acid and potassium chlorate or manganese dioxide in stone retorts and heated with steam, when the free bromine distils into a cold receiver.

$$MgBr_2 + MnO_2 + 2H_2SO_4 = MnSO_4 + MgSO_4 + Br + 2H_2O.$$

The name bromine is derived from the Greek *bromos*, meaning a stench.

Properties of Bromine.

Experiment 126. — Into a flask of two or three liters capacity, put a few drops of bromine, and cover the flask loosely. In a few minutes the jar will be filled with the heavy red vapor of bromine.

Experiment 127. — Into the jar of vaporized bromine, introduce a strip of moistened litmus- or turmeric-paper. It will be bleached.

Experiment 128. — Add a few more drops of bromine, and after it has vaporized, introduce a thin slice of dry phosphorus. It will ignite.

Experiment 129. — Into a tall jar filled with bromine vapor, let fall a few freshly prepared filings of metallic antimony. The result is much like that of Experiment 90.

124. Properties, etc. — Bromine is a dark red liquid of disagreeable odor, very volatile at ordinary temperatures, and extremely corrosive. It is sparingly soluble in water and easily soluble in ether, carbon disulphide, or chloroform. Its vapor has a density of 80, being more than five times as heavy as air. Its chemical properties closely resemble those of chlorine, but it is less active. Its attraction for hydrogen fits it for bleaching and disinfecting uses. Some of the bromides are used in medicine and photography.

(*a*) Bromine forms acids as follows: hydrobromic, HBr; hypobromous, $HBrO$; bromic, $HBrO_3$; perbromic, $HBrO_4$. They closely resemble the corresponding chlorine compounds.

(*b*) Bromine, when swallowed, acts as an irritant poison; when dropped upon the skin it produces a sore that is very difficult to heal. The best antidote for its corrosive action is some substance that takes up oxygen readily, as sulphurous oxide (SO_2), or a sulphite.

IODINE: symbol, I; density, 4.95; atomic weight, 126; valence, 1, 3, 5, 7.

125. Source. — Iodine compounds exist in very minute quantities in the water of the sea and of some saline springs. From sea-water, the iodide is absorbed by certain marine plants. The ashes (kelp) of these seaweeds contain sodium and magnesium iodides. Iodine is obtained by heating the kelp with water, concentrating this solution until most of the less soluble salts are removed, and treating the resulting liquid with sulphuric acid and manganese dioxide. Iodine is set free in the form of a beautiful violet-colored vapor that soon condenses to a solid. At present, the principal source of iodine is the niter beds of Chile and Peru, where it occurs as sodium iodate ($NaIO_3$). After separating the iodate from the nitrate, the iodine is set free by sulphurous acid.

Properties of Iodine.

Experiment 130. — Put about 0.1 of a gram of iodine[1] into a dry test-tube. Heat the test-tube in a flame and notice that the crystals vaporize without visible liquefaction. Notice that the vapor is very heavy as well as very beautiful. If the upper part of the tube is cold, minute iodine crystals will condense there.

Experiment 131. — Prepare some starch paste, as in Experiment 102, and dilute 5 or 6 drops of it with 10 cu. cm. of water. Dissolve a very small piece of iodine in alcohol and add a drop of the alcoholic solution (tincture) to the dilute starch. The starch will be colored blue even when the tincture is very dilute. The blue color will disappear upon heating the solution and reappear upon cooling it.

Experiment 132. — Drop a few crystals of iodine into a large bottle. Dip a strip of white paper into the colorless starch paste and suspend

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[1] In weighing iodine, place it on a small piece of thin paper or glass. Do not let it come into contact with a metal scale-pan.

it in the bottle. The paper may be held in place by the stopper of the bottle. As the iodine sublimes and diffuses through the bottle, it soon comes into contact with the starch and colors the paper blue. Starch will detect the presence of one part of iodine in 300,000 parts of water.

Experiment 133. — Add a few drops of the alcoholic solution prepared in Experiment 131 to 10 cu. cm. of water in a test-tube. Owing to the sparing solubility of iodine in water, most of the iodine will be precipitated. Pour 5 cu. cm. of this aqueous solution into a test-tube, add 8 or 10 drops of carbon disulphide (CS_2), and shake the contents of the tube. On standing for a few moments, the disulphide will settle to the bottom, when it will be seen to be colored purple-red; its color is due to the iodine dissolved in it. Carbon disulphide will detect the presence of one part of iodine in 1,000,000 parts of water.

Experiment 134. — Pour 10 cu. cm. of water into each of three tall test-glasses. Add a few drops of a solution of potassium iodide to each. To the first, add a few drops of a solution of lead acetate (sugar of lead). Brilliant yellow lead iodide is formed. To the second, add a few drops of a solution of mercurous nitrate. Yellowish green mercurous iodide is formed. To the third, add a few drops of a solution of mercuric chloride (corrosive sublimate). Scarlet mercuric iodide is formed.

126. Properties, etc. — Iodine is a blue-black, crystalline solid having a metallic luster. Its vapor is very heavy, having a density of about 126. Iodine is very sparingly soluble in water but readily dissolves in alcohol, ether, chloroform, carbon disulphide, or aqueous solutions of the metallic iodides. The chemical activity of this element is less than that of bromine. Iodine is used in medicine, photography, and the manufacture of aniline-green. The blue color it forms with starch, its beautifully colored vapor, and the purple-red color it forms with carbon disulphide form delicate tests for free iodine.

(*a*) Iodine forms acids as follows: hydriodic, HI; iodic acid, HIO_3; periodic acid, H_5IO_6. They closely resemble the corresponding chlorine and bromine compounds.

127. The Halogen Group. — Fluorine, chlorine, bromine, and iodine constitute a remarkable natural group. They exhibit a marked gradation in properties and close analogies in their elementary condition and in their corresponding compounds (see § 148).

(*a*) Concerning their gradation of properties:

1. At the ordinary temperature, fluorine is a gas; chlorine is a gas; bromine is a liquid, and iodine is a solid.

2. Liquid chlorine is transparent; bromine is but slightly so; iodine is opaque.

3. Chlorine has a density of 35.2; bromine vapor, 80; iodine vapor, 126.

4. Fluorine has an atomic weight of 19; chlorine, 35.2; bromine, 80; iodine, 126.

5. Generally speaking, their chemical activities are graded in the inverse order, being greatest in the case of fluorine, less in chlorine; still less in bromine, and least in iodine. (In the case of such natural groups the chemical activities frequently vary inversely as the atomic weights.) The atomic weight of bromine is nearly the arithmetical mean of those of chlorine and iodine; in general chemical deportment, bromine stands midway between the other two elements.

(*b*) Concerning their analogies:

1. Their binary compounds with potassium and sodium resemble common salt. Hence, these compounds are called haloid salts and these elements, halogens (Greek, *halos*, salt and *gennao*, I produce).

2. Each of them combines with hydrogen, volume to volume and without condensation, to form the haloid acids.

3. These acids have a great attraction for water. Their aqueous solutions have the same chemical properties as the acids.

(*c*) Recapitulation:

	Fl	Cl	Br	I
Atomic weight .	19	35.2	79.96	126.85
Fusing-point . .		– 102°	– 72°	+ 114°
Boiling-point . .	– 187°	– 33°	+ 60°	+ 184°
Density	1.14	1.47	3.18	4.96
Color	greenish yellow	yellowish green	brown	black

MANGANESE: symbol, Mn; density, 7.2; atomic weight, 55; valence, 2, 3, 4, 6, 7.

128. Manganese. — The principal source of manganese is the dioxide (MnO_2) which is found in nature as the mineral pyrolusite. Among the other manganese ores are braunite (Mn_2O_3) and hausmanite (Mn_3O_4). The metal is seldom prepared, but may be obtained by heating one of the oxides with carbon at an intense white heat for several hours, and in other ways. It is very hard and brittle, easily soluble in dilute acids, and decomposes warm water with the evolution of hydrogen. When pure, it is almost as infusible as platinum and oxidizes easily in the air. It is best kept in petroleum. It is feebly magnetic and forms a beautiful alloy with copper. The metal is used as an alloy of iron in the manufacture of steel.

NOTE. — Manganese has certain properties that ally it to chromium, iron, nickel, cobalt, and copper, so that these six metals are sometimes grouped as a family. Their atomic weights lie nearly together, and they all belong to the fourth series in the periodic system (§ 148, *b*). Because of other characteristics, manganese is here grouped with the halogens.

Manganese Oxide.

Experiment 135. — Put a small quantity of manganese dioxide into an ignition-tube and add enough sulphuric acid to wet it thoroughly. Support the tube in a slanting position and heat it gently. Collect the gas, and find out what it is.

129. Oxides. — At least five distinct manganese oxides are known:

(*a*) Manganese monoxide (manganous oxide, MnO) is powerfully basic.

(*b*) Red oxide of manganese (mangano-manganic oxide, Mn_3O_4) may be considered a compound of MnO and Mn_2O_3. It is analogous to magnetic iron ore.

(*c*) Manganese sesquioxide (manganic oxide, Mn_2O_3) is the mineral braunite. It is isomorphous with Al_2O_3 and Fe_2O_3. The corresponding hydroxide [$Mn_2O_2(OH)_2$] is found in nature as manganite, or gray manganese ore.

(*d*) Manganese dioxide (manganese peroxide, black oxide of manganese, MnO_2) is the most important manganese ore. It is used in preparing oxygen and chlorine, and in coloring and decolorizing glass. At a bright red heat, it gives up oxygen and is reduced to Mn_3O_4. In the preparation of chlorine from hydrochloric acid and manganese dioxide (see Experiment 86), large quantities of the practically worthless manganous chloride are produced. The Weldon process for the utilization of this product is, in effect, a regeneration of the MnO_2. When a solution of the manganous chloride is treated with lime, the following reaction takes place:

$$MnCl_2 + Ca(OH)_2 = Mn(OH)_2 + CaCl_2.$$

When this manganous hydroxide is mixed with lime, and treated with steam and air, one of the following reactions takes place:

$$Mn(OH)_2 + Ca(OH)_2 + O = CaMnO_3 + 2H_2O; \text{ or}$$

$$2Mn(OH)_2 + Ca(OH)_2 + O_2 = CaMn_2O_5 + 3H_2O.$$

These calcium compounds may be regarded as mixtures of lime and manganese dioxide.

$$CaMnO_3 = CaO,\ MnO_2.$$

$$CaMn_2O_5 = CaO,\ 2MnO_2.$$

The treatment of either of them with hydrochloric acid yields chlorine.

(*e*) Manganic anhydride (MnO_3) and manganic acid (H_2MnO_4) have not yet been isolated, but several manganates (e.g., K_2MnO_4) are well known.

(*f*) Manganese heptoxide (Mn_2O_7) is an anhydride, yielding permanganic acid ($HMnO_4$) when brought into contact with water.

Manganese Salts.

Experiment 136. — Dissolve 0.5 of a gram of oxalic acid ($C_2H_2O_4$) crystals in 50 cu. cm. of water; add 5 cu. cm. of sulphuric acid; warm to about 60°. To this colorless solution, add, drop by drop, a solution of potassium permanganate ($KMnO_4$). The $KMnO_4$ gives up oxygen and converts the $C_2H_2O_4$ to H_2O and CO_2, and is reduced to $MnSO_4$ and K_2SO_4, in which process, its rich color is destroyed. If an excess of the potassium permanganate is added, it will not be decolorized.

Experiment 137. — Repeat the last experiment, using ferrous sulphate ($FeSO_4$) instead of $C_2H_2O_4$. The $KMnO_4$ oxidizes the ferrous to ferric sulphate.

NOTE. — Knowing the reactions for these experiments and the quantity of $KMnO_4$ used before the decoloration ceases, the quantity of oxidizable matter ($C_2H_2O_4$ or $FeSO_4$) present is easily calculated (quantitative analysis).

Experiment 138. — Mix some $KMnO_4$ and barium dioxide (BaO_2) in a mortar. Transfer the mixture to a flask and moisten it with sulphuric acid. A starch and potassium iodide test-paper held at the mouth of the flask will be colored blue. Explain the discoloration.

130. Manganese Salts. — A few years ago, the manganates and permanganates were found only in the laboratory where they were used as oxidizing agents. They are now manufactured on the large scale for use as disinfectants.

EXERCISES.

1. Give two of the most marked physical properties of hydrogen, and two of its distinctive chemical properties.
2. What is a triad? A pentad? A quadrivalent atom? A bivalent compound radical? Illustrate each.
3. By passing the vapor of iodine with hydrogen over platinum sponge heated to redness, a strongly acid gas is synthetically formed. What is its name, its molecular weight, and its density?
4. A large jar, about a quarter full of bleaching-powder had been standing for some time until the upper part contained a gas given off by the chloride. Into this gas, a moistened slip of paper was thrust. The paper was instantly colored deep blue. What was the gas and with what was the test-paper moistened? Explain the phenomenon.
5. What analogies exist between members of the halogen group?
6. Symbolize the chlorides, bromides, iodides, chlorates, bromates, and iodates of the following: K', Na', Ag', Cu'', Zn'', Au''', Pt^{iv}.
7. How is tincture of iodine prepared?
8. How many products of the combustion of hydrogen in air can you name?

9. Name and symbolize a gaseous compound that is most conveniently prepared by the action of strong sulphuric acid upon common salt.

10. Describe in two words a chemical reaction that results only in the synthesis of water.

11. You have had an experiment involving the process of sublimation. Describe the experiment.

12. Pyrolusite may be reduced to Mn_3O_4 by intense heat. Write the reaction.

13. Write a graphic formula for K_2MnO_4.

14. Write two graphic formulas for $KMnO_4$.

15. Write a graphic formula for manganese sesquioxide, representing the metal as a dyad.

16. Write a graphic formula for $Mn''O_3$.

CHAPTER VIII.

ATOMIC AND MOLECULAR WEIGHTS, ETC.

131. Combining Weights of Elements. — A study of the figures that represent the quantitative composition of chemical compounds shows that there exists between them such a relation that if a fixed quantity of one of the constituent elements is taken, and the quantities of the elements that combine therewith are noted, there will be a remarkable repetition of the same figures (or of simple multiples thereof) for each of the elements examined.

(*a*) For instance, if we weigh the component parts of certain compounds, we find that:

1 part of hydrogen combines with 19 parts of fluorine.
1 part of hydrogen combines with 35.2 parts of chlorine.
1 part of hydrogen combines with 80 parts of bromine.
1 part of hydrogen combines with 126 parts of iodine.

23 parts of sodium combine with 19 parts of fluorine.
23 parts of sodium combine with 35.2 parts of chlorine.
23 parts of sodium combine with 80 parts of bromine.
23 parts of sodium combine with 126 parts of iodine.

7 parts of lithium combine with 19 parts of fluorine.
7 parts of lithium combine with 35.2 parts of chlorine.
7 parts of lithium combine with 80 parts of bromine.
7 parts of lithium combine with 126 parts of iodine.

39 parts of potassium combine with 19 parts of fluorine.
39 parts of potassium combine with 35.2 parts of chlorine.
39 parts of potassium combine with 80 parts of bromine.
39 parts of potassium combine with 126 parts of iodine.

16 parts of oxygen combine with 56 parts of iron.
16 parts of oxygen combine with 206 parts of lead.
16 parts of oxygen combine with 112 parts of cadmium.
16 parts of oxygen combine with 65 parts of zinc.
16 parts of oxygen combine with 24 parts of magnesium.

32 parts of sulphur combine with 56 parts of iron.
32 parts of sulphur combine with 206 parts of lead.
32 parts of sulphur combine with 112 parts of cadmium.
32 parts of sulphur combine with 65 parts of zinc.
32 parts of sulphur combine with 24 parts of magnesium.

(*b*) Careful study of the above table shows that the figures that represent the relative weights of the elements that combine with one part of hydrogen also represent the weights of the same elements that combine with 23 parts of sodium, 7 parts of lithium, and 39 parts of potassium; and that 16 parts of oxygen combine with the same relative weights of the five given elements as do 32 parts of sulphur. The list might be extended so as to include all the elements. As hydrogen enters into combination in the smallest proportion of any, its combining weight is taken as unity; the weight of the quantity of any other substance that unites with one weight of hydrogen is called the combining weight or the equivalent weight of that element.

(*c*) Some elements do not combine with hydrogen. The combining weight of each of these elements is ascertained by determining the weight of the quantity of that element that unites with the known combining weight of some other element. In the examples above given it is seen, by direct comparison with hydrogen, that the combining weight of fluorine is 19; of chlorine, 35.2; of bromine, 80; and of iodine, 126. Sodium, lithium, and potassium do not unite readily with hydrogen and so their combining weights are determined by indirect comparison with hydrogen. The combining weights of each of the four elements just mentioned unite with a uniform quantity of each of these three elements. Thus we learn that the combining weight of sodium is 23; of lithium, 7; and of potassium, 39. All elements unite with other elements in proportion to their combining weights or to some simple multiple thereof.

132. The Atomic Theory. — Up to the beginning of the nineteenth century, there were two guesses as to the ultimate constitution of matter. One of these assumed that there was no limit to the divisibility of matter. But the Greek philosophers thought that there was a limit beyond which a substance could not be divided. The ultimate particles thus assumed to exist were named atoms, a word signifying *indivisible*. When John Dalton discovered the law of definite proportions (§ 77), it occurred to him that if this hypothesis of the Greek philosophers was true, it would explain both the law of definite proportions and that of multiple proportions (§ 78). The atomic theory, as now understood, may be stated thus:

All substances are composed of minute, ultimate particles that can not be divided without destroying the identity of the substance. For any given substance, these particles are alike in size, shape, and weight. The relative weights of these ultimate particles may be ascertained from the relative weights in which the substances combine with one another. All the known facts of chemistry agree with this theory.

(*a*) If the atoms of any element are exactly alike, and differ in weight from the atoms of other elements, and if the differing atoms of a compound always unite in the same ratio to form that compound, these facts explain the law of definite proportions. Thus, if sodium and chlorine unite, one atom of the former with one atom of the latter, to form sodium chloride, and if all the sodium atoms have the same weight, and all the chlorine atoms have the same weight, then sodium chloride, wherever found, will always have exactly the same composition by weight, complying thus with the law of definite proportions. In other words, if matter consists of atoms having definite weights, and if chemical reactions always take place between definite numbers of these atoms, then chemical action always takes place between definite weights of substances. That substances do thus unite is one of the fundamental principles of chemistry.

(*b*) If two elements unite in more than one proportion, and one atom to one atom, or by one atom to two atoms, or by two atoms to three atoms, etc., that is, some simple number of atoms uniting with some simple number of other atoms, then the law of multiple proportions is thereby explained. Assuming that the weight of a nitrogen atom is 14, and that the weight of an oxygen atom is 16, and that two atoms of nitrogen unite with one atom of oxygen (N_2O), then the weights of the two elements in the nitrogen monoxide are as 28 to 16. If one atom of nitrogen unites with one atom of oxygen (NO), then the weights of the elements in the nitric oxide are as (14 to 16 or as) 28 to 32. Similarly, it is evident that on like suppositions, the gravimetric relations of the two elements in the five oxides of nitrogen are 28 parts of nitrogen to 16, 32, 48, 64, and 80 parts of oxygen. The weight of the nitrogen being constant, the weights of the oxygen in the successive oxides are represented by the ratio numbers, 1, 2, 3, 4, and 5, as shown by the table in § 78.

133. Avogadro's Law. — The corner-stone of modern chemistry, as distinguished from the chemistry that preceded it, is a proposition known as Avogadro's law, the evidence in support of which can not be satisfactorily presented in this place. It may be stated as follows: *Equal volumes of all substances in the gaseous condition, the temperature and pressure being the same, contain the same number of molecules.*

134. Molecular Weights. — The weights of equal volumes of different gases may be readily ascertained experimentally. According to the law of Avogadro, such equal volumes contain the same number of molecules. Consequently, the ratio between the weights of the molecules of different gases is the same as the ratio between the weights of equal volumes thereof. If, under the same conditions of temperature and pressure, a liter of one gas weighs eighty times as much as a liter of another gas, then the molecule of the first gas must be eighty times as heavy as the molecule of the second gas. Hydrogen, the lightest known gas, is taken as the standard. Its molecule consists of two atoms, the weight of each of which we take as unity. Accordingly, the molecular weight of hydrogen is taken as two, a convention that enables us to express molecular and atomic weights in the same terms. The density of any substance in the gaseous state indicates the weight of a molecule of that substance with respect to the weight of a molecule of hydrogen. But as the unit adopted is the weight of the hydrogen atom rather than the weight of the hydrogen molecule, it follows that the density of a gas must be multiplied by two in order to get the molecular weight of that gas. That is to say, the molecular weight of any substance is twice its vapor-density expressed in terms of the hydrogen standard for density.

(*a*) Formerly this was the only method known for the determination of molecular weights. Hence, the molecular weights of substances that could not be volatilized could not be determined directly. Certain properties of solutions have now been shown to have relations to the molecular weights of the dissolved substances analogous to those involved in Avogadro's law, and these relations may be used to determine the molecular weights of almost all substances.

135. Atomic Weights. — Since the weight of the molecule equals the sum of the weights of the atoms in the molecule, the same unit being used in both cases, it follows that if the number of atoms in a molecule is known, the weights of the component atoms may be easily ascertained. The simplest case is that of the molecule of an element. For example, the molecular weight of nitrogen is twenty-eight; of oxygen, thirty-two; of chlorine, seventy and four-tenths; of bromine, 160; and of sulphur, sixty-four. Since there is good reason for supposing that each of these molecules consists of two atoms, the atomic weight is supposed to be half of the molecular weight determined as already explained. A more general method is to combine the analysis of the compounds of an element with the determination of the molecular weights of the same compounds. This method will be best understood from an example:

(*a*) Suppose the chemist wishes to determine the atomic weight of oxygen. He begins with steam and finds, from its density, that its molecular weight is 18, and, by analysis, that $\frac{8}{9}$ of this is oxygen. He proceeds in this way with all the gaseous or volatile compounds of oxygen, and tabulates some of the results, as follows:

SUBSTANCES.		WEIGHT OF MOLECULE.	WEIGHT OF OXYGEN IN MOLECULE.	
Water	H_2O	18	16	16 × 1
Carbon monoxide . .	CO	28	16	16 × 1
Nitric oxide	NO	30	16	16 × 1
Alcohol	C_2H_6O	46	16	16 × 1
Ether	$(C_2H_5)_2O$	74	16	16 × 1
Carbon dioxide . . .	CO_2	44	32	16 × 2
Nitrogen peroxide . .	NO_2	46	32	16 × 2
Sulphur dioxide . .	SO_2	64	32	16 × 2
Acetic acid	$C_2H_4O_2$	60	32	16 × 2
Sulphur trioxide . .	SO_3	80	48	16 × 3
Methyl borate . . .	$(CH_3)_3BO_3$	104	48	16 × 3
Ethyl borate	$(C_2H_5)_3BO_3$	146	48	16 × 3
Ethyl silicate . . .	$(C_2H_5)_4SiO_4$	208	64	16 × 4
Osmium oxide . . .	OsO_4	254	64	16 × 4
etc.,				
Oxygen	O_2	32	32	16 × 2

He notices that the smallest weight of oxygen in any of these compounds is 16, and that all the others are simple multiples of this. *He can not believe that this is mere chance*, especially as he finds similar results in determining other atomic weights. The only explanation possible is that this 16 is the weight of a definite quantity of oxygen, and that it represents the least quantity of oxygen that can enter into combination (§ 4). Hence, he concludes that 16 is the atomic weight of oxygen, and that the substances analyzed contain respectively one, two, three, and four atoms of oxygen to the molecule. Of course, the symbols in the second column of the table above can not be determined until after the determination of the atomic weights of the elements involved. The table also shows that the oxygen molecule consists of two atoms. The combining weight of an element is its atomic weight.

136. Elemental Molecules. — Let us imagine a volume of hydrogen that contains 1000 hydrogen molecules. By Avogadro's law, the same volume of chlorine contains 1000 chlorine molecules. By the direct union of these, we form two such volumes of hydrochloric acid gas, which, according to Avogadro's law, must contain 2000 molecules.

$$1000\ H_2 + 1000\ Cl_2 = 2000\ HCl.$$

But each molecule of hydrochloric acid (HCl) contains one hydrogen atom and one chlorine atom. Consequently, the 2000 acid molecules contain at least 2000 hydrogen atoms and 2000 chlorine atoms. Since these 2000 hydrogen atoms of the product are identical with the 1000 hydrogen molecules of the factor (see § 140), it follows that each hydrogen molecule contains at least two atoms, or that *the hydrogen molecule is diatomic*. In the same way we see that the chlorine molecule is diatomic. The number of atoms in a molecule of most of the elements have been determined by this and other methods.

(*a*) The vapor-density and the atomic weight being known, the number of atoms in the molecule is easily determined. As the vapor of mercury is 100 times as heavy as hydrogen, the mercury molecule must, by Avogadro's law, weigh 100 times as much as the hydrogen molecule; i.e., the molecular weight of mercury is 200. As this is the same as the atomic weight of this element, we conclude that the mercury molecule contains only one atom. Similar considerations indicate that cadmium also is monatomic. On the other hand, the vapor-density of arsenic is 150; its molecular weight is therefore 300. As the atomic weight of arsenic is only 75, we conclude that an arsenic molecule contains four atoms. Similar considerations lead to the conclusion that phosphorus also is tetratomic.

137. Law of Gay-Lussac. — *The ratio in which gases combine by volume is always a simple one; the volume of the resulting gaseous product bears a simple ratio to the volumes of its constituents* (see § 78).

(*a*) The following modes of volumetric combination illustrate the truth and meaning of the law:

(1) 1 unit volume + 1 unit volume = 2 unit volumes.
Examples: HCl; HBr; HI; NO.
Condensation = 0.

(2) 2 unit volumes + 1 unit volume = 2 unit volumes.
Examples: H_2O; H_2S; N_2O; NO_2.
Condensation = $\frac{1}{3}$.

(3) 3 unit volumes + 1 unit volume = 2 unit volumes.
Examples: H_3N; SO_3.
Condensation = $\frac{1}{2}$.

In general, the gaseous product occupies 2 unit volumes.

EXERCISES.

1. Show that a molecule of bromine contains two atoms.
2. Define atom and atomic weight.
3. What is the difference between the combining weight and the atomic weight of an element?

4. What is the standard of atomic weight? What do we mean when we say that the atomic weight of oxygen is 16?

5. If the atomic weight of hydrogen is called five, what should we call the atomic weight of nitrogen?

6. Why can we not weigh different atoms, and thus directly determine atomic weights?

7. State the modern atomic theory.

8. State the law on which is based the argument that shows that chlorine is diatomic.

9. Under similar conditions, which will occupy the greater space, 100 molecules of hydrogen or 100 molecules of nitrogen?

10. What is the molecular weight of a vapor that is 23 times as heavy as hydrogen?

11. What is the molecular weight of N_2O? What is its density?

12. Define allotropism. Give an illustration of your definition.

13. How is oxygen prepared on the large scale? How may it be prepared without heat?

CHAPTER IX.

STOICHIOMETRY, ETC.

138. Reactions and Reagents. — *Any change in the composition of a molecule is called a chemical reaction. Substances acting in such a chemical change are called reagents.*

(*a*) Changes in molecular composition are of three kinds:

(1) Changes in the kind of the constituent atoms.
(2) Changes in the number of the constituent atoms.
(3) Changes in the relative positions of the constituent atoms.

(*b*) When hydrogen burns in air, the hydrogen and the oxygen react upon each other; they are the reagents used to produce a molecular change.

139. Expression of Reactions. — In any given substance of homogeneous composition, all the molecules are alike. The nature of the mass depends upon the nature of the molecule. The mass may be fittingly represented by the molecule. Any chemical change in the mass may be represented by a corresponding change in the molecule. Hence, *chemical reactions are generally expressed in molecular symbols.*

140. Factors and Products. — *The molecules that go into a reaction are called factors; the molecules that come from it are called products.*

(*a*) In the preparation of hydrogen, the factors were Zn and 2HCl; the products were $ZnCl_2$ and H_2. The total mass of the factors is always equal to the total mass of the products.

141. Chemical Equations. — *Chemical reactions are commonly and conveniently represented by equations, placing the sum of the factors equal to the sum of the products.*

(*a*) The equality results from the indestructibility of matter. The individual atoms of the factors reappear in the products; they are differently arranged, but not one is gained or lost. From this it follows that the equation also shows an equality between the total weights of the factors and of the products.

(*b*) The equation also represents the relative weights of the several substances engaged in the reaction. The equation, $H_2 + O = H_2O$, means, literally, that 2 atomic weights of hydrogen united with 16 atomic weights of oxygen yield 18 such weights of water, but the relation is equally true for larger quantities of matter. Thus, we learn from it that 2 grams of hydrogen unite with 16 grams of oxygen to form 18 grams of water, or that 12 kilograms of hydrogen unite with 96 kilograms of oxygen to form 108 kilograms of water.

(*c*) Strictly speaking, it is not proper to represent a fractional part of a molecule as entering into or resulting from a chemical reaction, as we do when we write $H_2 + O = H_2O$. To obviate the error of representing an atom of free oxygen, we should indicate twice the quantity of each substance, as follows: $2H_2 + O_2 = 2H_2O$. But, for the sake of convenience, chemists generally write the equations in the simpler form, as the gravimetric relations expressed are the same.

(*d*) When the reacting bodies are gaseous, the equation, written in complete molecules, also represents volumetric relations. Remembering Avogadro's law (§ 133), we easily see that $2H_2 + O_2 = 2H_2O$ indicates that two (molecular or other) volumes of hydrogen unite with one of oxygen to yield two volumes of dry steam; e.g., two liters of hydrogen and one liter of oxygen unite to form two liters of dry steam.

142. Gravimetric Computations. — Knowing the equation for any given reaction and the atomic weights of the several elements involved, we are able to solve all problems concerning the weight of substances appearing as factors or products. From the data now known and those given in the problem, make the following proportion:

As the number representing the total combining weights of the given substance is to the number representing the total combining weights of the required substance, so is the actual weight of the given substance to the actual weight of the required substance.

(*a*) These numbers representing combining weights are to be derived, of course, from the equation. A few examples are given. When a close approximation to exact atomic weights (see Appendix, § 1) will simplify the computation, such an approximation may be permitted in school work.

(1) How much hydrogen can be obtained from hydrochloric acid by using 20 grams of zinc?

Solution. — Write the reaction with the combining weights of the several reagents.

$$\underset{65}{Zn} + \underset{72.4}{\overset{2(1+35.2)}{2HCl}} = \underset{135.4}{\overset{65+70.4}{ZnCl_2}} + \underset{2}{H_2}$$

Form the proportion according to the above rule:

$$65 : 2 :: 20 \text{ grams} : x \text{ grams}.$$

$\therefore x = 0.61538$ grams, or 615.38 milligrams of H. — *Ans.*

(2) How much HCl will be required?

$$65 : 72.4 :: 20 :: x.$$

$\therefore x = 22.27 +$ grams of dry HCl. — *Ans.*

(3) How much $ZnCl_2$ will be produced?

$$65 : 135.4 :: 20 : x.$$

$\therefore x = 41.66 +$ grams of $ZnCl_2$. — *Ans.*

(4) How much zinc is necessary to prepare 1 Kl. of hydrogen? As 1 liter of hydrogen weighs 0.09 of a gram, 1000 liters (1 Kl.) of hydrogen weigh 90 grams.

$$65 : 2 :: x : 90.$$

$\therefore x = 2925$ grams or 2.925 Kg. of Zn. — *Ans.*

143. Gas-volumetric Computations. — It follows from the law of Avogadro that, in equations where whole molecules of gaseous substances are represented, each molecule represents one volume of gas. Hence, every equation written in the molecular symbols of aëriform substances may be read by volume. For example,

$$2H_2 + O_2 = 2H_2O$$

may be read: Two volumes of hydrogen unite with one volume of oxygen to form two volumes of dry steam.

(*a*) We give a few examples.

(1) How much steam is formed by the combustion of 1 liter of hydrogen?

Solution. — By referring to the equation just given, we see that the volumes of hydrogen and of aëriform H_2O are equal, because it shows an equal number of molecules for those substances, and we know, from Avogadro's law, that equal numbers of gaseous molecules will occupy equal volumes. Hence, the combustion of 1 liter of hydrogen will give 1 liter of dry steam.

(2) How much oxygen is needed to burn up 500 cu. cm. of hydrogen?

Solution. — The equation for the combustion of hydrogen shows that the volume of oxygen is half that of the hydrogen. Hence, it will require half of 500 cu. cm. or 250 cu. cm. of oxygen.

(3) How much hydrogen must be burned to form 4 liters of steam?

Solution. — The equation shows a relation of equality between the volumes of hydrogen and of aëriform H_2O (as in the first example). Consequently, 4 liters of steam require 4 liters of hydrogen.

(4) How much oxygen can be obtained from the electrolysis of 3 liters of steam?

Solution. — The equation shows that the volume of oxygen is half that of aëriform H_2O. Hence, 3 liters of steam will yield 1.5 liters or 1500 cu. cm. of oxygen.

144. Percentage Composition. — Since the symbol of a compound represents the number of atoms of each constituent element of the molecule, and since each atom represents a definite weight of that element, the symbol of the substance represents both its molecular weight and its composition by weight. Thus HNO_3 means that one atom of hydrogen, one atom of nitrogen, and three atoms of oxygen form a molecule of nitric acid. It also means that the molecular weight of nitric acid is sixty-three, the sum of the combining weights of the constituent atoms $(1 + 14 + 16 \times 3)$. It means, still further, that in sixty-three parts by weight of nitric acid, one part is hydrogen, fourteen parts are nitrogen, and forty-eight parts are oxygen. To find the number of parts of each of these constituents in one hundred parts of nitric acid, that is, to find the percentage composition of nitric acid, simple proportions suffice.

SOLUTION. — $63 : 1 :: 100\% : 1.59\%$, the proportion of H.
$63 : 14 :: 100\% : 22.22\%$, the proportion of N.
$63 : 48 :: 100\% : \underline{76.19\%}$, the proportion of O.
100.00%

Conversely, knowing the percentage composition (which may be found by analysis), the molecular weight of the substance, and the atomic weights of its constituent elements, the chemical formula for the substance may be calculated. For instance, the vapor-density of a certain compound is fourteen. Analysis shows that eighty-five and seven-tenths per cent of it is oxygen and that fourteen and three-tenths per cent of it is hydrogen. What is its formula?

Solution. — If its vapor-density is 14, its molecular weight is 28.

$$100\% : 85.7\% :: 28 : 24 = C_2.$$

$$100\% : 14.3\% :: 28 : \ 4 = H_4.$$

Therefore, the formula is C_2H_4.

Note. — Gaseous volumes will vary with pressure and temperature. In comparing such volumes, measured under different conditions, the proper correction must be made for this variation. It is common to refer gaseous volumes to standard conditions — a temperature of 0°, and a pressure of 760 mm. of mercury. The branch of chemistry that deals with the numerical relations of atoms is called stoichiometry or chemical arithmetic. The gravimetric, volumetric, and percentage computations just given are stoichiometrical computations.

145. Thermochemistry, etc. — Chemical changes are generally accompanied by an absorption or an evolution of heat. Such thermal changes are directly related to changes in the chemical energy (atomic attraction) of the substances involved, and conform strictly to the law of the conservation of energy (§ 8).

(*a*) When in a reaction there is an evolution of heat, as in the slacking of lime,

$$CaO + H_2O = Ca\,(OH)_2,$$

the loss of chemical energy by the factors is at least equivalent to what is called the heat of formation, and the product is less energetic than the factors. In other cases, heat is absorbed, the heat of formation is negative in value, and the product is more energetic than the factors. In the former case, the reaction and the compound are said to be exothermic; in the latter case, both are said to be endothermic. The decomposition of an exothermic compound into simpler compounds or elementary substances is attended with an absorption of heat. Similarly, the decomposition of an endothermic compound is attended with a liberation of heat.

(*b*) The branch of science that includes the various relations between chemical action and heat is called thermochemistry. The measurement of the heat thus absorbed or evolved has become an important part of chemical investigation.

(*c*) The chemical equations described in § 141 ignore the thermal changes. Sometimes these are expressed by adding some expression more or less definite for the heat of formation, as "+ heat" or "– 2700 calories."

(*d*) In a galvanic cell, part of the chemical energy of the materials employed is converted into heat and another part into another form of energy that we recognize as an electric current. Whether we consider the modern applications of such a current, or the industrial applications of steam-power which depends upon the energy of combustion, or the muscular energy and the heat of animal organisms, we are face to face with transformations of energy through chemical change.

EXERCISES.

1. What do atomic weights express? What weight of oxygen may be obtained by decomposing 9 grams of steam?

2. Give the law of multiple proportions, and illustrate it by the compounds of nitrogen and oxygen.

3. Find the percentage composition of H_2SO_4. See the third page of the cover of this book.

4. Marsh-gas is 8 times as heavy as hydrogen. Analysis shows that $\frac{3}{4}$ of its weight is carbon and the rest hydrogen. The atomic weight of carbon is 12. What is the formula for marsh-gas?

5. How much pure zinc is needed to obtain 20 grams of hydrogen?

6. (*a*) How much oxygen would be necessary to burn 500 cu. cm. of hydrogen? (*b*) If the experiment was performed in an atmosphere at a temperature of 100°, what would be the name and volume of the product? (*c*) How much oxygen would be necessary to burn 5 grams of hydrogen?

7. (*a*) What liquid is used in the preparation of HCl? (*b*) What is the greatest amount of HCl that can be prepared by using 196 grams of that liquid?

8. (*a*) What is the difference between hydrochloric acid and muriatic acid? (*b*) What is aqua regia? (*c*) Name and symbolize the five oxides of nitrogen.

9. (*a*) Explain the difference between a bivalent and an univalent metal. (*b*) What is valence?

10. When hydriodic acid gas is passed through a heated glass tube, it is decomposed, and a violet color appears. Account for the appearance of the color.

CHAPTER X.

NATURAL GROUPS.—THE PERIODIC LAW.

146. Metallic and Non-metallic Elements. — The elements may be separated into two general groups, those that form bases when combined with hydrogen and oxygen, and those that form acids when so combined. Most of the base-forming elements are solids with a more or less marked metallic luster, and are hence commonly called the metallic elements. The acid-forming elements in general have properties opposite to those of the metals. They comprise all the gaseous elements except hydrogen which does not belong distinctively to either class.

(*a*) There is no sharp line between the two classes, each merging gradually into the other. Many of the elements thus form hydroxides having both acid and basic properties, and several form two oxides each, one with basic, and the other with acid-forming tendencies.

147. Natural Families. — It was early recognized that certain of the elements possessed properties that were very similar to each other. Shortly after Dalton's hypothesis drew attention to the atomic weights, it was seen that there was some sort of relationship between the atomic weights of elements that have similar properties. For instance, it was shown that in the group of elements, chlorine, bromine, and iodine, the properties of which show remarkable analogies, the atomic weight of bromine is nearly a mean between those of chlorine and iodine.

Similar relations were seen in the case of calcium, strontium, and barium. Arranged in the order of their atomic weights, the elements fall easily into groups, the members of each group having similar chemical and physical properties. Learning the characteristics of these several groups and learning to what group any element belongs, one thereby learns the most important properties of that element. Such a classification affords a compact simplification of a multitude of facts independently ascertained, and is of great aid in systematizing the study of chemistry.

148. The Periodic Law.—In 1864, Mendeleeff, a Russian, and Lothar Meyer, a German, independently announced the law that *the properties of the elements, both chemical and physical, are periodic functions of their atomic weights.* This means that, if the elements are arranged in the order of their atomic weights, at a certain distance beyond any element, an element having similar properties will be found.

(*a*) On the following page is given a modification of Mendeleeff's table. Leaving out hydrogen which, strange to say, hardly finds a place in the system, the elements are arranged in the order of their atomic weights. Those that fall in any vertical column agree in valence and constitute a natural family or group with similar properties as above indicated. Read in horizontal lines, the elements constitute a succession of series. Passing from left to right in any series, there is a decrease in the relative quantities of hydrogen with which the elements combine, a similar increase in the relative quantities of oxygen, and a progressive change from a base-forming to an acid-forming nature. The hydroxides of the elements in Group 1 are the strongest bases; those of the elements in Group 2 are weaker bases; those of the elements in Group 3 are still weaker; while those of some of the elements in Group 4, instead of having basic properties have weak acid properties. Nearly all of the elements in Group 5 are acid-forming, while those of Group 6 and Group 7 form strong acids.

	Group 0.	Group 1.	Group 2.	Group 3.	Group 4.	Group 5.	Group 6.	Group 7.	Group 8.		Series.
H-Compounds. *Oxides.*	 *No Oxide.*	— R_2O	— RO	— R_2O_3	RH_4 RO_2	RH_3 R_2O_5	RH_2 RO_3	RH R_2O_7	— RO_4		
Series 1	—	H = 1									1
" 2	He = 4	Li = 7	Be = 9	B = 11	C = 12	N = 14	O = 16	F = 19			2
" 3	Ne = 20	Na = 23	Mg = 24	Al = 27	Si = 28	P = 31	S = 32	Cl = 35.2			3
" 4	Ar = 40	K = 39	Ca = 40	Sc = 44	Ti = 48	V = 51	Cr = 52	Mn = 55	Fe = 56 Ni = 58	Co = 58.5 Cu = 63	4
" 5	Kr = 59	(Cu) = 63	Zn = 65	Ga = 69.5	Ge = 72	As = 75	Se = 78.6	Br = 80			5
" 6	—	Rb = 85	Sr = 87	Y = 88.3	Zr = 90	Cb = 93	Mo = 95.3	— = 100	Ru = 101 Pd = 106	Rh = 102 Ag = 107	6
" 7	Xe = 128	(Ag) = 107	Cd = 112	In = 113	Sn = 118	Sb = 120	Te = 126.5?	I = 126			7
" 8	—	Cs = 132	Ba = 136	La = 137	Ce = 138	Pr = 140	Nd = 143	—	—	—	8
" 9	—	(—)	—	—	—	—	—	—			9
" 10	—	—	E = 165	Yb = 172	—	Ta = 182	W = 183	—	Os = 190 Pt = 194	Ir = 192 Au = 196	10
" 11	—	(Au) = 196	Hg = 199	Tl = 203	Pb = 206	Bi = 207	—	—			11
" 12	—	—	—	—	Th = 231	—	U = 238	—	—	—	12

Note. — Gadolinium, radium, samarium, terbium, and thulium have not yet been sufficiently studied to admit of their classification.

(*b*) Dropping Groups 0 and 8 from consideration for the moment, and passing along Series 2 from Li to F, we find that the nature of the element of next higher atomic weight, Na, forces us to return from the acid extreme to the basic extreme and to begin another series or period. In like manner, after passing along Series 3 from Na to Cl, we are forced by the nature of K, the element of next higher atomic weight, to return to Group 1, and to begin another series; etc. This periodic return being necessary in order to grade the properties of the elements according to their atomic weights, the result is known as the periodic system of the chemical elements.

(*c*) Reference to the table shows that in each group the elements are arranged in two columns, each column consisting of the alternate elements of that group. These alternate members that thus fall in any column show closer grade-relations than do the members of the group taken as a whole; their gradations are quite distinct from those of the other column in the same group. So clearly graded in respect to their properties are some of the well-known alternate elements of a group that they are studied together as a family of elements. In other cases, elements next to each other in a series may well be joined for study. It is easy to imagine that certain omissions and anomalies that pertain to the table (such as putting Na and K into different families, and putting Te before I) will disappear with fuller knowledge.

(*d*) The newly discovered elements related to argon, lacking any known valence, appear to constitute a group by themselves. They have, therefore, been so placed for convenience of study, and subject to further consideration (see § 58).

(*e*) Group 8, consisting of three series, each with four elements near each other in atomic weight, may be looked upon as lying between Group 7 and Group 1. In each there is a return from acid to basic nature and from higher to lower valence. The return from Group 8 to Group 1 is less abrupt than is the return from Group 7. For instance, some of the properties of copper, silver, and gold would place these elements in Group 8, while other properties would ally them to the members of Group 1. Zinc, cadmium, and mercury of Group 2 also have properties that relate them to Group 8. These relations arising from the divided characters of these six elements may be traced more easily if we consider Series 5 as a continuation of Series 4 (a long series of 17 members); Series 7 as a continuation of Series 6; and Series 11 as a continuation of Series 10.

(*f*) An inspection of the table shows that in Group 8 the three small groups of four elements each fall in even-numbered series. One naturally looks for similar groups in the eighth and twelfth series, but they are not yet known. Although in other respects some of the series are imperfect, the general arrangement holds good to the end. It is not easy to doubt that in some way the properties of the elements are determined by their atomic weights.

(*g*) When Mendeleeff made his table, scandium, gallium, and germanium had not been discovered. From the gap in Group 3, Series 4, it was predicted that an element would be found with an atomic weight of about 44, and with relations to calcium and titanium much like the relations of aluminum to magnesium and silicon. These predictions were soon confirmed, the newly discovered scandium fitting into the gap and answering with remarkable exactness to the description that had been given before it was discovered. Similar predictions were fulfilled in similar manner in the cases of gallium and germanium. Such verifications constitute almost indubitable evidence of the validity of an hypothesis. The gap still existing in Group 7, Series 6, calls for an undiscovered, acid-forming element with an atomic weight of about 100; one that will combine with hydrogen atom for atom, and with oxygen in certain definite relations characteristic of the chlorine family.

(*h*) The periodic law also stands as the basis of the speculative theory that the so-called elements are themselves but combinations of a small number of simple elements still unknown to us.

EXERCISES.

1. Give the physical and chemical properties of hydrogen. Explain the structure of the oxyhydrogen blowpipe.
2. What chemical process is illustrated in the preparation of hydrogen?
3. State two ways in which the analysis of water may be effected.
4. Give the composition of water by volume and by weight.
5. What is the weight of each constituent in a kilogram of water?
6. An aeronaut wants 50 kilograms of hydrogen. What substances shall he use in making it, and how much of each?
7. What is meant by atomic weight?
8. Give the law of multiple proportions.

9. What is the difference between air and water, chemically considered?

10. Give one chemical and one physical property of oxygen and of ammonia.

11. Write the reactions for the preparation of Cl and of HF, and state the leading property of each.

12. When a hot metallic wire is plunged into a certain binary acid gas, violet fumes are seen. What is the gas?

13. How is chlorine obtained? Explain the reaction. Name the most remarkable chemical properties of the substance.

14. What is the most common compound of chlorine? Find its percentage composition.

15. Give the atomic weight of each of the elements that you have studied.

16. The reaction of chlorine upon ammonia is as follows:

$$8NH_3 + 3Cl_2 = N_2 + 6NH_4Cl.$$

(*a*) What weight of chlorine is necessary to the production of 12.544 grams of nitrogen? (*b*) What volume of chlorine?

17. Is the combustion of hydrogen an exothermic or an endothermic reaction?

18. Determine the percentage composition of a substance that has the formula of C_2H_6O.

19. Complete the following equations by inserting the proper figures:

$$MnO_2 + HCl = MnCl_2 + H_2O + Cl,$$

$$Cu + 8HNO_3 = 2NO + 3Cu(NO_3)_2 + H_2O.$$

20. (*a*) Name three physical properties of oxygen. (*b*) Two chemical properties. (*c*) How can these chemical properties be shown? (*d*) Mention one use of oxygen in the arts. (*e*) Explain the terms atom and molecule as applied to H_2O.

21. (*a*) If 180 cu. cm. of ammonia are decomposed by electric sparks into its elements, what will be the volume of each of these elements? (*b*) If, then, 130 cu. cm. of oxygen are introduced and another electric spark is produced in the containing vessel, the temperature being 16°, what will be the volume of the remaining gaseous contents of the vessel?

CHAPTER XI.

THE FIRST GROUP[1] — MONADS.

(The Alkali Metals.)

SODIUM: symbol, Na; density, 0.97; atomic weight, 23; valence, 1.

149. Occurrence. — Free sodium is not found in nature because it unites so readily with oxygen and water, but its compounds are very abundant and widely diffused. Its most abundant compound is sodium chloride (common salt, NaCl), from which, on account of its abundance and cheapness, nearly all of the sodium and sodium compounds of commerce and science are derived, directly or indirectly.

(*a*) Sodium nitrate, carbonate, borate, and silicate, as well as cryolite, are found in nature.

150. Preparation. — Sodium was first prepared by the electrolysis of sodium hydroxide. Subsequently, it was extensively prepared by distilling a mixture of sodium carbonate and charcoal. A mixture of common soda-ash (Na_2CO_3), coal, and chalk were heated to whiteness in an iron cylinder.

$$Na_2CO_3 + C_2 + \text{heat} = Na_2 + 3CO.$$

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[1] From this point to the end of the book, the elements will be grouped according to the suggestions of the periodic system. Because of the anomalous separation of sodium and potassium as mentioned in § 148 (*c*), because hydrogen was considered in an earlier chapter, and because copper, silver, and gold, which are related to this group, are to be considered as members of Group 8, as suggested in § 148 (*e*), no attempt will be made to divide the members of Group 1 into families.

The escaping sodium vapor was condensed and the carbon monoxide was burned. Sodium is now prepared by heating an intimate mixture of sodium hydroxide, iron, and carbon, or by the electrolysis of caustic soda or of sodium nitrate. It must be collected and preserved out of contact with the air.

Properties of Sodium.

Experiment 139. — Wrap a piece of sodium in wire gauze and drop it into water. Collect and test the gas evolved.

Experiment 140. — Fill a test-tube with mercury and invert it over that liquid. Thrust a piece of sodium into the mouth of the tube; it will rise to the top. Introduce a little water. Explain the resulting phenomenon and write the reaction.

Experiment 141. — Throw a piece of sodium, the size of a pea, on cold water. It swims about, decomposing the water, freeing the hydrogen, uniting with the oxygen, and then dissolving in the water. It does not evolve enough heat to ignite the hydrogen.

FIG. 46.

Experiment 142. — Throw a piece of sodium upon hot water, in a large, loosely stoppered bottle. The liberated hydrogen is ignited, and gives a yellow, sodium-tinted flame.

Experiment 143. — Ignite some common alcohol in a small saucer. It burns with an almost colorless flame. Sprinkle a little common salt into the burning liquid. The flame becomes yellow.

Experiment 144. — Wrap a piece of sodium in cloth or in filter-paper and place it upon a piece of moist ice. Describe and explain what follows.

151. Properties and Uses. — Sodium is a light metal having a brilliant, silver-white luster. It quickly oxidizes in moist air and decomposes water. It is a good conductor of heat and electricity, in which respect it ranks next to gold. It is best kept under kerosene or in a liquid or atmosphere free from oxygen. It is hard and brittle at −20°; soft like wax at the ordinary temperature; semi-fluid at about 50°, and melts below the temperature of boiling water. It may be used as a reducing agent in the preparation of silicon, boron, magnesium, aluminum, and most of the metals from their oxides. Sodium and all of its compounds impart a yellow tinge to flame.

152. Sodium Oxides, Carbide, and Nitride. — Sodium oxide (Na_2O) has not yet been obtained pure. Sodium peroxide (Na_2O_2) is made by heating sodium in a stream of dry air at 300°. It is a yellowish white solid. Sodium carbide (Na_2C_2) with water yields acetylene, and sodium nitride (Na_3N) with water yields ammonia.

153. Sodium Chloride. — Sodium chloride (common salt, $NaCl$) occurs in immense beds, often hundreds of feet in thickness in this country and in Europe. At a depth of about a third of a mile, such a bed extends under eastern New York and Pennsylvania, northern Ohio, part of Michigan, and under Lake Erie into Canada. Salt is obtained by mining rock salt when the beds are near the surface, or by boring holes and forcing down hot water to form a brine, which is pumped out and evaporated, or by the evaporation of the saline waters of certain mines, springs, and lakes, or of the sea. When the concentrated brine is rapidly evaporated by boiling, a fine-grained table salt is produced; when it is evaporated slowly, a coarse salt is formed. Sodium chloride crystallizes in cubes, the edges of which are sometimes attached so as to form hopper-shaped masses. Rock salt is usually found in cubical crystals, is highly diathermanous and of great importance in physical research. The many uses of common salt are too familiar to need mention. One of the most important of these is the preservation of meats, in which it prevents putrefactive fermentation by destroying the bacteria.

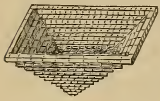


FIG. 47.

154. Sodium Sulphate. — Sodium sulphate (salt-cake, Na_2SO_4) is prepared in great quantities from salt and sulphuric acid.

(*a*) The sodium chloride and sulphuric acid are heated in large covered pans. The decomposition of NaCl, in the first stage of the process, is only partial.

$$2NaCl + H_2SO_4 = NaCl + NaHSO_4 + HCl.$$

The hydrochloric acid is absorbed in towers filled with coke, over which water is kept trickling, and thus becomes a by-product of the process. The pasty mass is then strongly heated.

$$NaCl + NaHSO_4 = Na_2SO_4 + HCl.$$

The acid is absorbed as in the former stage.

(*b*) The Na_2SO_4 dissolves easily in warm water. When such a concentrated solution cools, 10 molecules of water are taken up to form Glauber's salt (Na_2SO_4, 10 H_2O). Many salts owe their crystalline form to the presence of a definite quantity of water that may be driven off by heat — the so-called "water of crystallization." Exposed to dry air, the Glauber's salt crystals effloresce (i.e., give up their water of crystallization), and are changed to Na_2SO_4.

(*c*) Sodium-hydrogen sulphate ($NaHSO_4$) is often called sodium disulphate, or bisulphate of soda.

Sodium Carbonate.

Experiment 145. — Expose a piece of freshly cut sodium weighing about half a gram on a watch-glass, and note during several days the changes that follow. The metal quickly tarnishes, becomes coated with the white hydroxide, and is moistened by the water it absorbs from the air.

$$2Na_2 + O_2 = 2Na_2O,$$

$$Na_2O + H_2O = 2NaOH.$$

As above indicated, both the oxide and the hydroxide are deliquescent. The absorption of water will continue until the whole mass becomes liquid. The liquid then absorbs carbon dioxide from the air, and the resulting carbonate unites with the water present to form soda crystals.

$$2NaOH + CO_2 = Na_2CO_3 + H_2O,$$

$$Na_2CO_3 + 10H_2O = Na_2CO_3, 10H_2O.$$

These crystals in turn effloresce and fall to a white powder of partly dehydrated soda.

155. Sodium Carbonate. — Sodium carbonate (soda, Na_2CO_3) is made in immense quantities from common salt by the Leblanc process, so called from the name of its inventor.

(*a*) The first step is the preparation of the salt-cake, as described in the last paragraph. The Na_2SO_4 is then heated in a reverberatory furnace with an equal weight of calcium carbonate (chalk or limestone, $CaCO_3$), and about half its weight of coal. The resulting product, called black-ash, is essentially a mixture of sodium carbonate and calcium sulphide.

$$Na_2SO_4 + 4C = Na_2S + 4CO.$$

$$Na_2S + CaCO_3 = Na_2CO_3 + CaS.$$

Although the changes may be considered as taking place in succession, as above indicated, in the actual process the two reactions take place simultaneously. The calcium sulphide thus produced is not readily soluble in water, as is the Na_2CO_3. When the black-ash is lixiviated with water, and the solution is evaporated to dryness and calcined, the result is soda-ash, the common name of the commercial article. The sulphur of the CaS is recovered and made into sulphuric acid. This process was invented in France at the time of the French revolution, when the supply that had formerly come from the ashes of sea-plants was cut off.

(*b*) Although large quantities of the soda are still made in this way, the process is now carried on largely on account of what was formerly a by-product and a nuisance — the hydrochloric acid. This acid is utilized in the manufacture of chlorine for bleaching-powder. When processes for making chlorine directly from chlorides are perfected, the Leblanc process will give way for the cheaper Solvay, or ammonia-soda, process.

156. The Ammonia Process. — The Solvay process depends upon the fact that when a solution of sodium chloride is mixed with a solution of ammonium-hydrogen carbonate, the less soluble sodium-hydrogen carbonate is formed and separates from the solution of ammonium chloride.

$$NaCl + NH_4HCO_3 = NaHCO_3 + NH_4Cl.$$

In practice, a saturated salt-brine is treated in tanks with gaseous ammonia until the solution is saturated. After cooling, the liquid is pumped to the top of a steel tower about six feet in diameter and about fifty feet high. In the tower are perforated iron plates at intervals of about three feet, and so arranged that the descending liquid is brought into intimate contact with the ascending gases. Carbon dioxide is pumped in at the bottom of the tower, and under pressure sufficient to force it up through the descending solution of salt and ammonia. As the liquid and the gas come into contact, sodium-hydrogen carbonate is formed, ready for separation at the bottom of the tower.

$$NaCl + NH_3 + CO_2 + H_2O = NaHCO_3 + NH_4Cl.$$

The ammonium-chloride solution thus formed is treated with slacked lime (calcium hydroxide).

$$2NH_4Cl + Ca(OH)_2 = 2NH_3 + CaCl_2 + H_2O.$$

The gaseous ammonia thus recovered is again used for the saturation of brine. The calcium chloride is a waste product of the process. The carbon dioxide used is supplied by the burning of limestone ($CaCO_3$) in kilns.

$$CaCO_3 + \text{heat} = CO_2 + CaO.$$

The quicklime (CaO) so made is slacked to the hydroxide and used for the recovery of the ammonia, as above indicated. Thus, the substances consumed are salt, limestone, and the coal used to evolve the necessary heat; the exit-products are sodium-hydrogen carbonate and calcium chloride, the latter being of no present value. By gently heating the sodium-hydrogen carbonate, it is converted into sodium carbonate and carbon dioxide.

$$2NaHCO_3 + \text{heat} = Na_2CO_3 + CO_2 + H_2O.$$

The gas thus produced is returned to the carbonating tower.

(*a*) No soda has ever been made in this country by the Leblanc process, but very large Solvay soda plants are located at Syracuse, New York; Detroit, Michigan; and Barberton, Ohio.

(*b*) By dissolving soda-ash in hot water and allowing the solution to cool and stand for several days, large transparent crystals of "washing-soda" (soda-crystals, sal-soda, $Na_2CO_3, 10\,H_2O$) are formed. These crystals part with their water of crystallization by efflorescence or heating. The dry residue is Na_2CO_3 purified by the process of crystallization, one of the most valuable known means of purification.

157. Sodium-hydrogen Carbonate. — Sodium-hydrogen carbonate (soda, baking-soda, sodium bicarbonate, $NaHCO_3$) is easily prepared by passing a stream of carbon dioxide through a solution of sodium carbonate or by exposing soda-crystals to an atmosphere of carbon dioxide.

$$Na_2CO_3 + H_2O + CO_2 = 2NaHCO_3$$

or $$Na_2CO_3, 10\,H_2O + CO_2 = 2NaHCO_3 + 9\,H_2O.$$

Sodium bicarbonate is used in medicine, in cooking, in the manufacture of baking-powders and of carbon dioxide, and for many purposes where a mild alkali is needed.

NOTE. — In common speech, the word soda is applied both to sodium carbonate and to sodium-hydrogen carbonate. It is even used as a synonym for sodium hydroxide.

158. Baking-powders. — These are mixtures of sodium bicarbonate with some acid or acid salt, capable of setting the carbon dioxide free from the former when the mixture is wet. To prevent the reaction from taking place prematurely, some inert substance like flour or starch is added to the mixture to keep it as dry as possible. The acids and the acid salts most generally used are tartaric acid, potassium acid tartrate or cream of tartar (see § 299), calcium acid phosphate (see § 353, *c*), and alum (see § 217). With tartaric acid or with cream of tartar, a neutral tartrate of sodium or of sodium and potassium is formed, and is left in the baked bread or biscuit. When calcium acid phosphate is used, the residue is calcium phosphate and sodium phosphate. When alum is used, the residual products of the reaction are potassium and sodium sulphates and aluminum hydroxide. This aluminum hydroxide has an astringent action when it is dissolved, for which reason alum powders are objected to by many persons. One of the products in each of the above reactions is carbon dioxide, the evolution of which causes the bread to become light. Hence, the baking-powder is valuable in proportion to the amount of this gas given off under the conditions of baking, provided the residual products are harmless.

159. Sodium Hydroxide. — Sodium hydroxide (caustic soda, sodium hydrate, $NaOH$) is formed when sodium is thrown upon water, but in practice it is made from sodium carbonate by treating its solution with lime, or by the electrolysis of common salt. It is a white, opaque, brittle solid of fibrous texture. It deliquesces in the air, absorbing moisture and carbon dioxide, and changing thus to the non-deliquescent carbonate the coating of which protects the hydroxide from further loss. It is a strong base, a powerful cautery, and is largely used in the laboratory and in various industrial processes. An impure variety is known as "concentrated lye."

(*a*) Crude Na_2CO_3 is dissolved in boiling water. Cream of lime is added until the hot solution is free from CO_2.

$$Na_2CO_3 + Ca(OH)_2 = 2NaOH + CaCO_3.$$

The insoluble $CaCO_3$ is removed from the solution of $NaOH$ by precipitation and filtration. The $NaOH$ is then evaporated until an oily liquid is obtained. This liquid solidifies on cooling. The purified product is usually cast in the form of sticks.

(*b*) Caustic soda is made in large quantities as an incidental product of the manufacture of Na_2CO_3, being cheaply prepared from the liquor from which the black-ash is deposited.

Experiment 146. — Make a strong solution of caustic soda and put it into a retort or a flask with some granulated zinc. Heat the flask over a sand-bath or wire gauze until the liquid boils. A gas will be evolved. Collect it over water and find out what it is.

EXERCISES.

1. Write the formula for decahydrated sodium sulphate.
2. Write the formula for anhydrous sodium carbonate.
3. What is the formula for sodium chloride?
4. Write the graphic formula for the disulphate of soda.

5. The sodium obtained in practice being one-third the theoretical yield, what weight of the metal can be prepared from 159 kilograms of sodium carbonate?

6. What is the percentage composition of $NaNO_3$?

7. What weight of $KClO_3$ is needed to furnish enough oxygen to burn the hydrogen evolved by the action of 200 grams of sodium upon water?

8. (*a*) Find the weight of 1 liter of each of the following: N, CO_2, O, CH_4. (*b*) Find the volume of 1 gram of each.

9. Write the name and full graphic formula for

$$(HO)-(SO_2)-S-(SO_2)-(HO).$$

10. Why is sulphuric acid said to be dibasic?

11. Name some monobasic acid. Name some tribasic acid.

12. What is the difference between a normal salt and an acid salt?

13. How many tons of soda-ash will result from the calcination of fifty tons of sodium-hydrogen carbonate?

14. How much sodium hydroxide can be made from 1000 grams of sodium carbonate? How much calcium hydroxide will be required? How much calcium carbonate will be formed?

POTASSIUM: symbol, K; density, 0.875; atomic weight, 39; valence, 1.

160. Source. — Potassium compounds are found widely distributed in nature, forming an essential constituent of many rocks and of all fruitful soils. These compounds are taken from the soil by the rootlets of plants, none of which can live without them. It is essential to animal life also. Free potassium is not found in nature.

161. Preparation. — Potassium is generally prepared by heating intensely a mixture of its carbonate with charcoal.

$$K_2CO_3 + C_2 = K_2 + 3CO.$$

It is also prepared by the electrolysis of its hydroxide.

Properties of Potassium.

Experiment 147. — Drop a piece of potassium, half the size of a pea, upon water. It decomposes the water, the hydrogen burns with a flame beautifully violet tinted, with the vapor of potassium. If the water is in an open dish, stand at a distance of a meter or more, as the combustion will terminate with a slight explosion. Test the water at the end of the experiment with reddened litmus-paper.

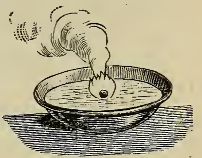


Fig. 48.

Experiment 148. — Stretch a piece of blotting-paper upon a wooden tray, wet the paper with a red solution of litmus and throw upon it a small piece of sodium or of potassium. The track of the metal as it runs over the moistened paper will be written in blue lines, showing the formation of an alkaline product.

Experiment 149. — Hold a small piece of potassium under water by means of a wire gauze or filter-paper. Collect the gas evolved as shown in the figure. What is this gas?

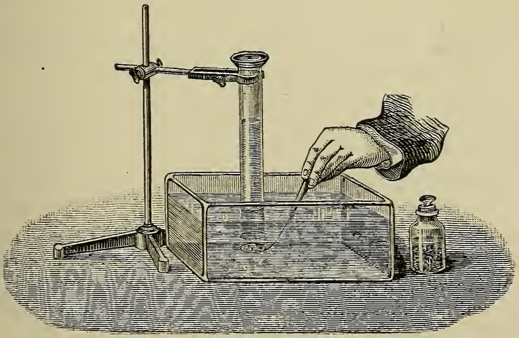


Fig. 49.

Experiment 150. —In Fig. 50, *a* represents a bottle for the generation of carbon dioxide; *c*, a drying-tube containing calcium chloride; *e*, a tube of Bohemian (hard) glass with a delivery-tube, *t*, dipping into the bottle, *i*. When a lighted match thrust into *i* is quickly extinguished, we may know that the apparatus is filled with carbon dioxide. Then, dry a piece of potassium the size of a pea by pressing it between folds of filter- or blotting-paper, remove *t*, thrust the potassium into *e*, and replace *t*. When the potassium is heated by the lamp-flame it will burn, taking oxygen from the carbon dioxide and depositing black carbon upon the walls of *e*.

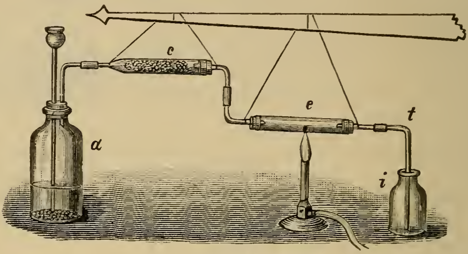


FIG. 50.

$$2K_2 + 3\ CO_2 = 2K_2CO_3 + C.$$

The particles of black carbon may be made more evident by placing *e* in a bottle of clear water, to dissolve the K_2CO_3.

Experiment 151. — Repeat Experiment 150, using a current of hydrochloric acid instead of carbon dioxide. Collect over water the gas delivered through *t*. What is this gas? Write the reaction.

Experiment 152. — Repeat Experiment 151, using ammonia instead of HCl. Write the reaction.

Experiment 153. — Bore a half-inch hole two inches deep in a block of ice. Enlarge the *bottom* of the cavity to the size of a hickory nut. Into this cavity, drop a piece of potassium, the size of a pea, and notice the beautiful volcanic action. Make the experiment in a warm and darkened room.

162. Properties. — Potassium is a light metal having a brilliant bluish white luster. In electropositive characteristics, it ranks third among the metals, and in lightness, second. It is brittle at zero; soft like wax at 15°, and easily welded when the surfaces are clean; it melts at about 63°. Its physical and chemical properties closely resemble those of sodium, but it is less used on account of its greater cost. Like sodium, it is best kept under petroleum. Its salts communicate a violet tint to flame.

(*a*) Potassium forms two oxides, K_2O and K_2O_2.

163. Potassium Chloride. — Potassium chloride (KCl) is found in sea-water and other salt waters, and is largely prepared from the mother-liquor from which the sodium chloride has crystallized, and from the Stassfurt deposit of carnallite ($KCl, MgCl_2, 6\ H_2O$). It resembles sodium chloride in appearance and taste but is more easily soluble in water. It dissolves in about three times its weight of water at the ordinary temperature, producing great cold. Like sodium chloride, it crystallizes in cubes. Potassium chloride is largely used in the manufacture of potassium hydroxide, and as a source of potassium in fertilizers.

(*a*) The other potassium halogen salts, potassium bromide, potassium iodide, and potassium fluoride also crystallize in cubes, have a saline taste, and easily dissolve in water. Potassium bromide and potassium iodide are used in medicine and in photography.

164. Potassium Cyanide. — Potassium cyanide (KCN or KCy) is a white, fusible, deliquescent and intensely poisonous solid. It is used in photography and as a laboratory reagent. It is a powerful reducing agent. As its solution dissolves silver and gold cyanides, it is largely used in electroplating, and in the extraction of gold and silver from their ores.

Caution. — Potassium cyanide is poisonous not only when taken internally, but also when brought into contact with an abrasion of the skin, a cut, or a scratch. Its best antidote is the inhalation of chlorine, which may be quickly prepared from bleaching-powder, and the inhalation of ammonia as a stimulant. Cold douches and artificial respiration may also be helpful, but the action of the poison is usually too quick for the successful application of the remedy.

165. Potassium Carbonate. — Potassium carbonate (K_2CO_3) is generally prepared in this country by leaching wood-ashes to form potash-lye and evaporating the lye in large pots or kettles, whence the name of the crude article, potash. The potash, when refined, is called pearl-ash. A pure carbonate, prepared by igniting the bicarbonate, is called salt of tartar. Potassium carbonate is a deliquescent salt with a strong alkaline taste and reaction.

(*a*) Potassium carbonate was formerly of more importance than now, as the Leblanc and the Solvay processes have rendered sodium carbonate so much cheaper that it has largely replaced the former in commerce and the arts. As K_2CO_3 is hygroscopic and Na_2CO_3 is not, the latter is much more convenient for storing and handling.

(*b*) As Na_2CO_3 is used in making hard soap, so K_2CO_3 is used in making soft soap.

(*c*) The rapid extinction of American forests has greatly checked the manufacture of American potash. Similar causes have operated in Europe. Hence, other sources have been sought and large quantities are now made from the refuse material of the beet-root sugar manufacture and also from K_2SO_4 by a process similar to the Leblanc process for preparing Na_2CO_3.

166. Potassium-hydrogen Carbonate. — Potassium-hydrogen carbonate (saleratus, potassium bicarbonate, $KHCO_3$) is prepared by passing a current of carbon dioxide through a strong solution of potassium carbonate.

$$K_2CO_3 + H_2O + CO_2 = 2KHCO_3.$$

The pure, crystalline potassium bicarbonate is used in medicine. The somewhat impure quality known as saleratus was formerly used extensively in cooking, but its place has been almost completely taken by the better and cheaper sodium bicarbonate, which is sometimes called soda saleratus.

167. Potassium Hydroxide. — Potassium hydroxide (caustic potash, potassium hydrate, KOH) may be prepared from potassium carbonate as sodium hydroxide is from sodium carbonate. Its physical and chemical properties closely resemble those of sodium hydroxide. It combines with fats and oils to form soft soap, and is one of the strongest bases known.

(*a*) As KOH absorbs water and carbon dioxide from the air, it is gradually changed to K_2CO_3. As this salt is deliquescent, the change goes on until all of the KOH is changed to a syrup of K_2CO_3. Consequently, it should be kept in closely stoppered bottles. It is usually cast in the form of sticks.

(*b*) Caustic potash is easily but not cheaply prepared by the action of potassium upon water.

(*c*) A solution of caustic potash quickly destroys both animal and vegetable substances. It is best clarified by subsidence and decantation, though it may be filtered through glass, sand, asbestos, or guncotton.

Experiment 154. — Repeat Experiment 146, using KOH instead of $NaOH$.

168. Potassium Nitrate. — Potassium nitrate (niter, saltpeter, KNO_3) is found as an efflorescence on the soil in various tropical regions, especially in Bengal. It does not extend into the soil to a depth greater than that to which the air can easily penetrate. It is extracted by solution in water and evaporation. It is also found in many caverns, and is seldom wanting in a fruitful soil. It is chiefly used in the preparation of nitric acid and the manufacture of gunpowder. It is a white, inodorous solid, permanent in the air and very soluble in hot water.

(*a*) When animal or vegetable matter decays in the presence of air and in contact with an alkaline or earthy base, the NH_3 produced is gradually oxidized to HNO_3 and "fixed" by the alkali. Thus the well-waters of most towns contain nitrates, showing that they have been contaminated by sewers, cesspools, or other causes. The artificial production of potassium nitrate is regularly carried on in Sweden, Switzerland, and other parts of continental Europe.

LITHIUM: symbol, Li; density, 0.59; atomic weight, 7; valence, 1.

169. Lithium. — This element is the lightest known solid. It is a rare, silver-white metal with a grayish tinge. It is ductile and malleable, harder than sodium or potassium and softer than lead. It melts at about 180°. In appearance and chemical properties, it is similar to sodium and potassium, but it is less violent in its reactions. For example, it decomposes water, but not with combustion of the hydrogen or ignition of the metal. It was first prepared in the metallic state in 1855.

RUBIDIUM: symbol, Rb; density, 1.52; atomic weight, 85; valence, 1.

170. Rubidium. — This is a rare, lustrous, silver-white metal with a tinge of yellow. It resembles potassium so closely that it can be distinguished from it only by spectroscopic analysis, the most delicate of determinative processes. It was discovered by this means in 1861. It melts at a temperature of 38.5°, and at $-10°$ is as soft as wax. It oxidizes rapidly in the air with the evolution of much heat that results in ignition. It does not keep well under petroleum, and is best preserved in hydrogen. Excepting cæsium, it is the most strongly electropositive of the metals. Like the other alkali metals, it does not occur free in nature.

Cæsium : symbol, Cs ; density, 1.88 ; atomic weight, 132 ; valence, 1.

171. Cæsium. — This is a ductile, silver-white metal, very soft at ordinary temperatures. It closely resembles potassium and rubidium, with which it usually occurs. It melts at a temperature of 27°. It burns rapidly when heated in air, and takes fire when thrown on water. It may be kept under petroleum. It is the most decidedly electropositive of the metals. It was discovered by the spectroscope in 1860, the first element so discovered ; its detection still requires the spectroscope.

172. Ammonium. — As stated in § 62 (*b*), ammonium is a name given to the compound radical, NH_4. It acts, as do the other members of this group, as an alkaline monad metal, but it has not been isolated.

(*a*) The assuming of this hypothetical metal makes the analogies between the composition of the salts of the "volatile alkali" and the composition of those of the fixed alkalies as evident as are the analogies between their properties ; e.g.,

Ammonium hydroxide.	*Potassium hydroxide.*	*Sodium hydroxide.*
$\left.\begin{matrix}NH_4\\H\end{matrix}\right\}O$	$\left.\begin{matrix}K\\H\end{matrix}\right\}O$	$\left.\begin{matrix}Na\\H\end{matrix}\right\}O.$

173. Ammonium Chloride. — Ammonium chloride (salammoniac, NH_4Cl) is found native in certain volcanic regions, and is artificially prepared in large quantities from the ammoniacal liquors of gas-works. It occurs in commerce as tough, fibrous masses. It is used in medicine, in soldering to dissolve the metallic oxides, in dyeing, and in the laboratory as a convenient source of ammonia and for other purposes.

(*a*) The ammoniacal liquor of gas-works is heated with lime and the gaseous ammonia thus evolved is passed through dilute hydrochloric acid until it is saturated. The solution is evaporated and the NH_4Cl purified by recrystallization from hot water or by sublimation.

Experiment 155. — Dissolve 6 grams of ammonium nitrate in 10 cu. cm. of ice-cold water. Stir the mixture with a thermometer and notice the resulting temperature.

174. Ammonium Nitrate. — Ammonium nitrate (NH_4NO_3) is prepared by neutralizing dilute nitric acid with dilute ammonia-water or a solution of ammonium carbonate and evaporating the solution. It decomposes by heat into water and nitrogen monoxide. It has a saline taste, and dissolves easily in half its weight of water with the absorption of heat.

NOTE. — Ammonium salts are very numerous, most of them being prepared directly or indirectly from the ammoniacal liquors of gasworks. They are generally soluble in water.

EXERCISES.

1. The practical yield being half the theoretical, how much potassium may be prepared from 138,080 grams of potassium carbonate?

2. What is the percentage composition of $KClO_3$? Of KNO_3?

3. What is the object of having the room warm for Experiment 153?

4. Give at least one reason in favor of each of the following formulas for sal-ammoniac: NH_3HCl and NH_4Cl.

5. Complete the following equations:

(*a*) $HNO_3 + NH_3 =$
(*b*) $H_2SO_4 + 2\,KOH =$
(*c*) $2HNO_3 + PbO =$

6. What is the molecular weight of caustic potash?

7. I explode a mixture of 4 liters of hydrogen and 5 liters of chlorine. (*a*) What volume of HCl is produced? (*b*) Which of the original gases and how much of it remains uncombined?

8. What volume of N_2O may be formed by heating 30 grams of NH_4NO_3?

9. Assuming that water will absorb half its weight of ammonia, calculate the amount of NH_4Cl necessary to the production of 3 kilograms of NH_4HO.

10. The name and formula for potassium cyanide suggest a compound radical. Consult the index of this book and hunt up references that look "promising" until you find the name of that compound radical. Then write the graphic formula for potassium cyanide and determine the valence of each of the three elements and of the compound radical.

11. Name two chemical properties of hydrogen that are the reverse of two of oxygen.

12. (*a*) How is nitric acid prepared on a large scale? (*b*) How can you show that an acid is an acid? (*c*) What are alkalis? (*d*) What is "laughing-gas"?

13. (*a*) What are bases? (*b*) What class of elements forms acids? (*c*) What class of elements forms bases? (*d*) What is a salt?

14. (*a*) What is the combining weight of a chemical compound? (*b*) $HNO_3 + KHO = KNO_3 + H_2O$. What is the relative amount of the substances used?

CHAPTER XII.

THE SECOND GROUP — DYADS.

I. THE CALCIUM FAMILY.

BERYLLIUM: symbol, Be; density, 1.85; atomic weight, 9; valence, 2.

175. Beryllium. — This rare element is also known as glucinum (Gl). It is a silver-white, malleable, and strongly electropositive metal. It generally occurs as a silicate with aluminum, and in its general properties, stands between the other alkaline earth metals and aluminum. Its oxide is found in the mineral beryl from which it was first discovered. It is prepared by heating its chloride ($BeCl_2$) with sodium in a closed iron crucible, or by heating its oxide (BeO) with magnesium.

CALCIUM: symbol, Ca.; density, 1.6 to 1.8; atomic weight, 40; valence, 2.

176. Calcium. — Calcium compounds occur largely diffused in nature, especially the carbonate in the forms of calcite, chalk, marble, limestone, coral, etc. They are found in all animal and vegetable bodies. The metal was first obtained by Davy, in 1808, by the electrolysis of its chloride. It has recently been prepared by the electrolysis of fused calcium iodide (CaI_2), and also by heating a mixture of calcium iodide and sodium in a closed crucible.

$$CaI_2 + Na_2 = Ca + 2NaI.$$

Calcium is a yellowish-white, soft, ductile, and malleable metal. It is scarcely oxidizable in dry air, is easily oxidizable in moist air, burns vividly with a very bright yellow light when heated to redness in the air, and decomposes water with evolution of hydrogen.

177. Calcium Oxides, etc. — Calcium monoxide (lime, quicklime, CaO) is prepared by heating calcium carbonate. In some parts of the country, it is "burned" from limestone ($CaCO_3$) in a kiln of rude masonry often built in the side of a hill, the process requiring several days, and a temperature of 400° or more.

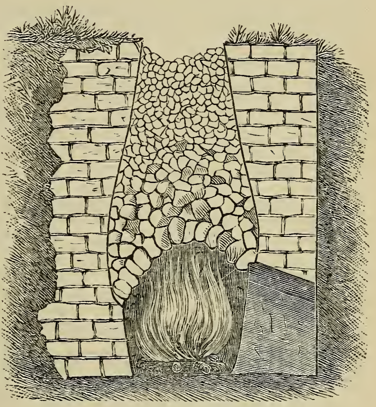


Fig. 51.

(*a*) In such a kiln, a limestone arch is built above the fire and the remaining limestone placed upon this arch from above. When the lime has been burned, the kiln is allowed to cool, the CaO is removed, and a new charge is introduced. This requires the cooling of the furnace for each lot burned. In most places, the process is continuous, the limestone and coal or coke being fed in at the top of a shaft furnace from the bottom of which the CaO is removed while still hot. These kilns are similar in shape to the blast-furnaces used in making pig-iron. They are about 50 ft. high, 6 to 8 ft. in diameter, made of heavy iron plate on the outside, and lined with fire-brick. In many places, the CO_2 expelled from the limestone is absorbed and used, as in the manufacture of soda and of sugar.

(*b*) Calcium dioxide (CaO_2) has been prepared by precipitation from lime-water with H_2O_2.

(*c*) Calcium hydride (CaH_2), calcium carbide (CaC_2), and calcium nitride (Ca_3N_2) decompose water on contact.

$$CaH_2 + 2H_2O = Ca(OH)_2 + 2H_2.$$

$$Ca_3N_2 + 6H_2O = 3Ca(OH)_2 + 2NH_3.$$

Calcium carbide is made on the large scale by heating a mixture of lime and charcoal to the intense temperature made available by the electric furnace. It is a comparatively cheap commercial article. Its reaction with water yields acetylene gas (see § 264).

178. Properties, Uses, etc. — Lime is a white, amorphous substance about three times as heavy as water. It is infusible in the oxyhydrogen flame, and when so heated emits an intense light known as the lime or calcium light (see Experiment 46). It fuses and volatilizes at the temperature of the electric arc. It is largely used in making mortars and cements, in the manufacture of sugar, in the Solvay process for making soda, and in the Clark method of softening hard water (§ 184, *a*), in the preparation of sodium hydroxide, in many industries where a cheap alkali is needed for neutralizing acids, and, in the laboratory, for drying gases and liquids, and for other purposes.

(*a*) When CaO is exposed to the air, it absorbs water and carbon dioxide and falls to a powder known as air-slacked lime — a mixture of calcium hydroxide (CaO_2H_2) and calcium carbonate ($CaCO_3$).

179. Calcium Chloride. — Calcium chloride ($CaCl_2$) is easily prepared by the action of hydrochloric acid upon marble, and the evaporation of the solution. It has a strong attraction for water, is deliquescent, and is used for drying gases.

(*a*) Calcium chloride may be crystallized from a saturated solution. These crystals ($CaCl_2$, 6 H_2O), when mixed with snow, produce a temperature of $-48°$.

Caustic Lime.

Experiment 156. — Add a few drops of water to a small quantity of slacked CaO, and rub it to a paste between the fingers. It has a slightly caustic effect, dissolving the surface of the cuticle.

Experiment 157. — Put 30 grams of recently burned CaO upon a saucer, hold the saucer in the palm of the hand, and pour 20 cu. cm. of water upon it. Notice the increase of bulk and the rise of temperature. Thrust a friction match into the crumbling mass. It will be heated to the point of ignition. Sprinkle a little gunpowder upon the slacking lime; perhaps it will take fire.

180. Calcium Hydroxide. — When fresh, well-burned lime is treated with one-third its weight of water, the direct synthesis yields calcium hydroxide [calcium hydrate, caustic lime, slacked lime, $Ca(OH)_2$] with the evolution of great heat. Calcium hydroxide is a white, alkaline, caustic powder. It dissolves more easily in cold than in hot water, yielding an alkaline, feebly caustic liquid called lime-water. Lime-water readily absorbs carbon dioxide. Lime-water containing solid particles of calcium hydroxide in suspension is called milk of lime, or cream of lime, according to the consistency of the mixture.

(*a*) The power of absorbing carbon dioxide and hydrogen sulphide leads to the use of $Ca(OH)_2$ in the purifiers of gas-works. Its caustic action leads to its use (as milk of lime) in removing the hair from hides for tanning. Large quantities are used in the preparation of mortar, and for absorbing chlorine in the manufacture of bleaching-powder.

(*b*) Slacked lime mixed with water and sand makes a mortar that hardens or sets in the air but not in water. This mortar slowly absorbs carbon dioxide from the air and becomes a mixture of calcium hydroxide, calcium carbonate, and sand. The burning of a limestone that contains more than about 15 per cent of siliceous clay (aluminum silicate) yields "hydraulic" lime. Such lime is used in making hydraulic mortar or cement, which sets or hardens even under water (see § 327, *i*). The theory of the hydraulicity of cement is not clearly understood.

Calcium Carbonate.

Experiment 158. — Place a little lime-water in a test-tube and pass through it a stream of CO_2. Notice the precipitation of $CaCO_3$ that renders the liquid turbid. Notice also that as the passage of CO_2 into the liquid continues, the latter becomes clear again, the precipitate being dissolved. Boil the clear liquid to expel some of the absorbed dioxide, and the precipitate again appears. Test the liquid at each step of the experiment with litmus-paper to determine whether it gives an acid or an alkaline reaction.

181. Calcium Carbonate. — Calcium carbonate ($CaCO_3$) occurs in many forms, both crystallized and amorphous. The shells of oysters, clams, and other mollusks are almost wholly calcium carbonate. It forms the greater part of egg-shells and of bones. As marble and limestone, it is found in immense masses. It is barely soluble in water. Water charged with carbon dioxide dissolves it more easily, forming calcium bicarbonate.

$$CaCO_3 + H_2CO_3 = CaH_2(CO_3)_2.$$

When such waters are exposed to the air, they lose part of their carbon dioxide and, consequently, precipitate the calcium carbonate previously held in solution. Hence, the formation of stalactites, stalagmites, tufa, travertine, etc. As carbon dioxide is present in many natural waters, caves are often formed by them in limestone rocks. All the forms of calcium carbonate are easily acted upon by even dilute acids, the action being attended by effervescence due to the escape of the expelled carbon dioxide.

(*a*) Limestone is used in immense quantities as a building-stone, as a flux in smelting many ores, in the manufacture of quicklime and Portland cement (§ 327, *i*), and in the preparation of carbon dioxide.

182. Calcium Sulphate. — Calcium sulphate ($CaSO_4$) is found in nature as the mineral anhydrite. The hydrated sulphate ($CaSO_4, 2H_2O$) is the mineral gypsum, which, when in the crystalline form, is called selenite. By heating gypsum to about 120° it parts with its water of crystallization forming plaster of Paris. When this plaster is mixed to a paste with water, it again unites with the water and hardens or "sets" with increase of volume. Hence, its use as a cement and for making casts of various objects. Calcium sulphate is sparingly soluble in water.

183. Calcium Phosphate. — There are several calcium phosphates, the most important of which is bone-phosphate, $Ca_3(PO_4)_2$. It is the chief inorganic constituent of the bones of animals. It is important as a source of phosphorus, and, when ground to a powder and treated with acid, is valuable as a fertilizer.

Hard Water.

Experiment 159. — Dissolve about half a gram of calcium chloride in about 200 cu. cm. of water, and add a slight excess of ammonium carbonate. Calcium carbonate will be precipitated. Allow it to settle, decant the solution, and wash the precipitate once or twice by decantation. Add about 200 cu. cm. of cold water to the washed precipitate and pass in a slow current of carbon dioxide, shaking often, until the precipitate dissolves. To a third of this solution, add lime-water a little at a time until no more precipitate is formed on standing for several minutes. Boil another third of the solution until about a quarter of it has been evaporated. In each case, test the precipitate formed for calcium carbonate. To the remaining third of the solution, add a solution of soap and notice that a lather can not be produced until all the calcium salt is removed.

184. Hard Water. — Natural waters that contain calcium or magnesium salts in solution are called hard, because vegetables do not soften so readily when boiled in them as they do when boiled in pure water. Such waters are ill-fitted for many industrial purposes, especially for use in steam-boilers or for washing. These salts are generally bicarbonates, sulphates, or chlorides. Boiling such a water results in the decomposition of the bicarbonates, the formation of carbon dioxide and the less soluble carbonates.

$$CaH_2(CO_3)_2 = CaCO_3 + CO_2 + H_2O.$$

This reaction also takes place very slowly when the water is exposed to the air. For these reasons, such hardness caused by bicarbonates is called "temporary hardness," while that due to sulphates and chlorides is called "permanent hardness."

Calcium sulphate is less soluble in water at high than at low temperatures. The bicarbonates and the calcium sulphate are precipitated from solution when heated in steam-boilers, the precipitate usually forming a hard and tenacious coating on the boiler-flues. As these compounds are poor conductors of heat, a boiler so coated is wasteful of fuel. The scale often becomes so thick that the fuel necessary for the generation of steam is doubled. Various substances are used to prevent such precipitated salts from adhering to the boiler, but, when possible, it is better to remove the cause of the hardness before the water is put into the boiler.

(*a*) Clark's method of softening water that is hard by reason of the presence of bicarbonates consists in adding lime-water. The calcium hydroxide combines with half the carbon dioxide of the bicarbonates, thus forming carbonates that are precipitated.

$$CaH_2(CO_3)_2 + Ca(OH)_2 = 2CaCO_3 + 2H_2O.$$

Of course, just the right quantity of lime-water must be used. If too little of the lime-water is added, the water will remain hard; if too much is added, the softened water will be made hard by the excess. The quantity of lime-water used is determined by analysis of the hard water to be treated.

In like manner, calcium and magnesium sulphates may be removed by adding a solution of sodium carbonate which precipitates the carbonates of calcium and magnesium respectively.

$$CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4.$$

After adding the precipitating reagents, the water is allowed to stand until the carbonates have settled. As the sodium sulphate is not precipitated, it forms no scale.

(*b*) Hard waters react with soap to form insoluble calcium or magnesium soaps that rise to the surface as a curdy scum. In such waters, soap must be added until these insoluble salts are precipitated before a lather can be formed or any washing value obtained from the soap used. Hence, for washing purposes, hard waters are not economical.

185. Strontium and Barium. — These rare metals resemble calcium in appearance and properties. The mineral strontianite is strontium carbonate; the mineral celestine is strontium sulphate. The mineral witherite is barium carbonate; heavy spar is barium sulphate.

(*a*) The relations of these metals to calcium sufficiently appear in the formulas of some of their compounds:

CaO	CaO_2	$CaCO_3$	$CaSO_4$
SrO	SrO_2	$SrCO_3$	$SrSO_4$
BaO	BaO_2	$BaCO_3$	$BaSO_4$

186. Erbium. — This is a metallic element found along with yttrium, terbium, etc., in gadolinite and other rare minerals. Erbium metal has not yet been prepared.

187. Radium, etc. — To the calcium family belongs the element radium, typical of a class of substances known as radioactive. This term is applied to substances that possess the power of spontaneously and continuously emitting rays that are capable of passing through substances opaque to ordinary light, of darkening a photographic plate, and of rapidly discharging an electroscope. The discovery of this phenomenon was made in 1896 by Henri Becquerel while investigating certain uranium compounds. These rays are, therefore, sometimes known as Becquerel rays. Although not visible in themselves, they cause many substances to become visibly luminous. An X-ray screen in a darkened room is made faintly luminous by the very close presence of a small quantity of a pure salt of radium. Thorium and uranium appear to be feebly radioactive, but the three recently discovered elements — radium, polonium, and actinium — possess the power in a remarkable degree. Radium has a high atomic weight and some properties in common with those of barium. It has been produced only in minute quantities. Its chief source has been uraninite or pitchblende (see § 373). Some of its salts, especially radium bromide and radium chloride, which in appearance much resemble common salt, have been obtained in minute quantities. The pure metal is very unstable; so easily oxidizable that its preparation and preservation have, so far, been practically impossible. Polonium and actinium have so far been found only in quantities insufficient for their isolation in a pure state. Theoretically considered, these three are very interesting elements, and may serve to advance our knowledge of the constitution of matter, and of the structure of the atoms themselves.

(*a*) The radium radiations appear to be of three distinct kinds, designated respectively as α (alpha), β (beta), and γ (gamma) rays. The α-rays have a slight power of penetrating opaque substances and can be deflected by a magnet. The β-rays have a considerable power of penetrating opaque substances, produce phosphorescence in many substances, and can be deflected by a magnet. In many respects, they are similar to the cathode rays produced by an electric discharge in a vacuum tube. The γ-rays have a remarkably high penetrating power, and are not deflected by a magnet; they are thus similar to Roentgen or X-rays.

(*b*) The explanation of the phenomena of radium can not be considered as satisfactorily established. The disintegration theory has been more vigorously advanced than any other. According to this theory, the α-rays consist of streams of positively electrified bodies, approximately the size of hydrogen atoms, and moving with a velocity of about 20,000 miles a second. Because of this enormous velocity, these particles have an energy so great that their impacts on a zinc-sulphide screen produce a faint light, and are microscopically visible as separate starlike flashes. Each colliding particle, however, is so minute, that there is no perceptible loss of weight in the radioactive substance itself. Most of the particles projected from the interior portion of such a substance are intercepted before they leave the radiating mass; for this reason pure radium is always a few degrees warmer than its surroundings, the impacts of the arrested particles generating heat. In like manner, the β-rays are supposed to consist of streams of negatively charged particles of almost inconceivable minuteness, approximating a thousandth part of the mass of a hydrogen atom, and moving with a velocity of about that of light. The γ-rays are not electrically charged, and therefore can not be deflected by a magnet.

EXERCISES.

1. Write the reaction for the burning of lime.
2. Write the reaction for the preparation of $CaCl_2$.
3. Write the reaction for preparing calcium hydroxide.
4. Why is the formula for calcium hypochlorite $CaCl_2O_2$ instead of CaClO, the formula for hypochlorous acid being HClO?
5. When a current of carbon dioxide is passed through an aqueous solution of BaO_2, hydroxyl and $BaCO_3$ are formed. Write the reaction.

6. How much potassium nitrate and sulphuric acid shall I need to prepare enough nitric acid to neutralize 5 kilograms of chalk?

7. What is the property that chiefly distinguishes chlorine and the elements most like it from potassium and the elements most like it?

8. Write the graphic formula for a compound radical that acts as an alkaline, monad metal.

9. What are the characteristic properties of chlorine?

10. Write the graphic formulas for common salt, caustic potash, and manganese dioxide.

11. Is the reaction involved in the slacking of quicklime endothermic or exothermic?

12. Compare and contrast chlorine and iodine, respecting their physical and chemical properties.

13. What is the difference between potassium nitrate and Chile saltpeter?

14. What is the lightest known metal?

15. What is the weight of a cubic decimeter of quicklime?

16. Is calcium chloride a solid or a liquid? Give a reason for your answer based upon some statement in this section of this chapter.

17. Explain the formation of a stalactite.

18. What kind of hard water may be softened by the addition of caustic lime? Explain the process.

19. Sometimes the inner surfaces of boiler-flues have to be scraped clean. Explain the cause of such a necessity.

20. Why is it more easy to cleanse greasy hands with rain-water than with hard water?

II. THE ZINC FAMILY.

MAGNESIUM: symbol, Mg; density, 1.75; atomic weight, 24; valence, 2.

188. Magnesium. — Magnesium compounds are widely and abundantly distributed but the metal is not found free in nature. The metal is prepared in considerable quantities by fusing together magnesium chloride ($MgCl_2$) and sodium or potassium, by electrolysis of the chloride or sulphate, and in other ways. It has a silver-white appearance, is malleable and ductile, preserves its luster in dry air, and tarnishes in moist air. It is readily acted upon by most acids with the evolution of hydrogen and, as it is perfectly free from arsenic, is often used, instead of zinc, in Marsh's test for arsenic. It is found in commerce, usually in the form of ribbon. This ribbon, when ignited, burns with a brilliant light of high actinic power.

Magnesia.

Experiment 160. — Coil 15 cm. of magnesium ribbon around a lead pencil. Change the pencil for a knitting-needle or an iron wire, hold the wire horizontal, and ignite one end of the ribbon. The coil of magnesium will burn to an imperfect coil of magnesium oxide.

189. Magnesium Oxide. — Magnesium oxide (magnesia, MgO) is formed when the metal is burned in air. It is generally prepared by the ignition of magnesium carbonate. It is used for making crucibles and furnace-linings, as it does not melt below the temperature of the oxyhydrogen flame. It is also used in medicine.

190. Magnesium Salts. — Magnesium chloride ($MgCl_2$) is found in sea-water, in many saline springs, and as a constituent of carnallite. It is largely used in dressing cotton goods. Magnesium sulphate ($MgSO_4$) is found in nature as kieserite. The hydrated salt ($MgSO_4$, 7 H_2O) is called Epsom salt, and is found in many mineral waters. It is used in medicine and in dressing cotton goods. Magnesium carbonate ($MgCO_3$) occurs as native magnesite. A mixture of the carbonate and the hydroxide [$Mg(OH)_2$], prepared by adding sodium carbonate (Na_2CO_3) to a solution of magnesium chloride or of Epsom salt, is called magnesia alba.

ZINC : symbol, Zn ; density, 7.14 ; atomic weight, 65 ; valence, 2.

191. Sources of Zinc. — Metallic zinc is not found in nature. The carbonate (smithsonite, zinc spar, $ZnCO_3$), the silicate (calamine, Zn_2SiO_4), the sulphide (sphalerite, blende, ZnS), and the oxide (red zinc ore, zincite, ZnO) are found as minerals and used as ores of zinc.

192. Preparation. — The zinc ore is first roasted and thereby converted to an oxide. This oxide is then heated in clay retorts with half its weight of coal. The carbon of the coal takes the oxygen from the zinc oxide, reducing the latter to a metal which distills and is condensed in receivers outside the furnace. The zinc, when melted and cast into cakes, is called spelter.

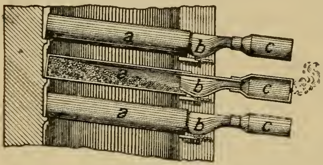


FIG. 52.

(*a*) Zinc and mercury are the only common metals that are vaporized easily enough to be distilled and purified in this way. The clay retorts from which the zinc is distilled are arranged in rows in a furnace where they are heated white-hot by coal or gaseous fuel.

Experiment 161. — Dissolve 10 grams of lead acetate (sugar of lead) in 250 cu. cm. of water and add a few drops of acetic acid. In this solution, suspend a strip of zinc. The zinc and the lead will change places, leaving a solution of zinc acetate and a metallic "lead tree." The tree will be more beautiful if the ends of the zinc are slit into branches before immersion. The weights of the dissolved zinc and the precipitated lead will be in the ratio of their atomic weights.


FIG. 53.

193. Properties. — Zinc is a bluish white, crystalline metal. It is ductile and malleable at about 130° or 140°, under which circumstances it may be drawn into wire, or rolled into sheets or plates. At the ordinary temperature and at temperatures above 200°, it is so brittle that it may be easily powdered in a mortar. The commercial article is seldom pure, generally containing lead, iron, and carbon, while traces of arsenic and antimony are often found. Metallic zinc in the form of fine dust and mixed with zinc oxide is obtained in considerable quantities in the manufacture of the metal. This mixture, technically known as zinc-dust, is a valuable reducing agent. Zinc is readily acted upon by a boiling solution of sodium and potassium hydroxides and by most acids, with the evolution of hydrogen. It melts at about 418°, and distills at about 1000°. Pure zinc is not easily soluble in dilute sulphuric acid while impure zinc is thus soluble. Zinc is not much affected by air, either dry or moist. It readily precipitates most metals from solutions of their salts.

(*a*) Brass is an alloy of zinc and copper. German silver is an alloy of zinc, copper, and nickel.

(*b*) Galvanized iron is simply iron coated with zinc. The term is a misnomer, as galvanic action is not involved in the process.

194. Zinc Compounds. — The mineral zincite, an impure zinc oxide, is found as an ore in New Jersey. Its color is due to the presence of red oxide of manganese. Pure zinc oxide (ZnO) is known in commerce as zinc white, and is prepared on a large scale for use as a paint. Zinc chloride ($ZnCl_2$) is formed by dissolving zinc in hydrochloric acid. It is used for preserving timber, as a caustic in surgery, in cleansing the surfaces of metals for soldering and, very largely, for the fraudulent purpose of weighting cotton goods. It is soluble in alcohol and very deliquescent. Zinc sulphate (white vitriol, $ZnSO_4, 7\,H_2O$) is used in medicine, in dyeing, and in galvanic batteries.

CADMIUM: symbol, Cd; density, 8.6; atomic weight, 112; valence, 2.

195. Cadmium. — This rare metal occurs in nature associated with zinc ores. As it is more volatile than zinc, its vapor comes over with the first portion of the zinc distilled. It forms compounds very similar to the corresponding zinc compounds. It has a tin-white color, is susceptible of a high polish, and gives a crackling sound when bent, as tin does. As its vapor-density is about 56, we conclude that its molecule contains but a single atom (§ 136, *a*).

MERCURY: symbol, Hg; density, 13.6; atomic weight, 199; valence, 1, 2.

196. Source. — Mercury, or quicksilver, is found native in small quantities, but chiefly as a sulphide (HgS) called cinnabar. The best known deposits of cinnabar are at Idria in Austria, Almaden in Spain, and New Almaden in California. Mercury is also brought from the Ural, China, and Japan.

197. Preparation. — Sometimes the ore is roasted with a regulated supply of air.

$$HgS + O_2 = Hg + SO_2.$$

The sulphide is generally mixed with quicklime or iron-scale or turnings, and distilled. The sulphur unites with the lime or the iron, and the mercury vapor is condensed by being brought into contact with water.

$$4HgS + 4CaO = 3CaS + CaSO_4 + 4Hg.$$

198. Properties. — Mercury is a silver-white metal, the only metal that is liquid at the ordinary temperature. It vaporizes slowly at ordinary temperatures, and boils at a temperature of about 357°. It freezes at a temperature of about − 39°, becoming a ductile, malleable, white solid that can be cut with a knife. At a very low temperature it becomes hard and brittle. It is a good conductor of electricity. The liquid metal is hardly affected by exposure to the air but, when heated for a long time in the air, it oxidizes. It is soluble in strong, boiling sulphuric acid, but its best solvent is nitric acid. As its vapor-density is about 100, we conclude that its molecule contains but a single atom (§ 136, *a*).

199. Uses. — Mercury is largely used in the construction of thermometers, barometers, and other physical and chemical apparatus, for the collection of gases that are soluble in water, for the preparation of mirrors, for the extraction of gold and silver from their ores, and for the preparation of various mercurial compounds.

Amalgams.

Experiment 162. — Prepare an amalgam by adding bits of sodium to mercury slightly warmed in an evaporating-dish.

200. Amalgams. — Compounds or mixtures of the metals with mercury are called amalgams. They are generally formed by the direct union of the two metals. Many of these amalgams, or mercury alloys, are largely used in the arts. Tin amalgam is used in "silvering" mirrors; silver and tin amalgam gradually hardens and is used for filling teeth; zinc and tin amalgam is used for coating the rubbers of electric machines.

201. Mercury Oxides. — Mercury forms two oxides, mercurous oxide (suboxide of mercury, gray oxide of mercury, Hg_2O) and mercuric oxide (red oxide of mercury, red precipitate, HgO). The latter is a powerful poison. It is prepared by heating mercury for a long time in air or, on the large scale, by heating an intimate mixture of mercury and mercuric nitrate. It decomposes, at a red heat, into its elementary constituents (see Experiment 29).

202. Mercury Sulphide. — This compound (HgS) is largely found native as cinnabar. When prepared artificially, it is called vermilion. It is of a brilliant red color, and is used as an oil and water-color paint, in lithographers' and printers' inks, and in coloring sealing-wax.

Mercury Salts.

Experiment 163. — Place a drop of a solution of mercurous nitrate or of corrosive sublimate upon a clean copper coin. Rub the drop over the coin and mercury will be deposited upon the copper.

203. Mercury Salts. — Mercury forms two series of salts, corresponding to the two oxides, the mercurous salts and the mercuric salts. The members of the two series are widely different in their properties. The mercuric compounds are very much more poisonous than are the mercurous.

(*a*) Mercury may be detected in almost any of its salts by placing a piece of clean copper in a solution of the salt.

204. Mercurous Salts. — The most important mercurous salt is mercurous chloride (calomel, $HgCl$). It is tasteless, odorless, and insoluble in water, and is largely used in medicine. It is commonly prepared by sublimation from an intimate mixture of mercury and mercuric chloride.

(*a*) Mercurous nitrate ($HgNO_3$) is formed by the action of cold, dilute nitric acid on mercury. Mercurous sulphate (Hg_2SO_4) is formed by heating concentrated sulphuric acid with an excess of mercury or by precipitating $HgNO_3$ with sulphuric acid.

(*b*) Mercurous bromide ($HgBr$) may be precipitated by adding hydrogen bromide or potassium bromide to a solution of $HgNO_3$. Similarly, mercurous iodide (HgI) may be precipitated by adding potassium iodide to a solution of $HgNO_3$. It is also formed when iodine is rubbed with the right proportion of mercury, a small quantity of alcohol being added. It is a green powder and gradually decomposes into HgI_2 and Hg.

205. Mercuric Salts. — Mercuric chloride (corrosive sublimate, $HgCl_2$) is a powerful poison. It coagulates albumen, forming an insoluble compound, in consequence of which the white of eggs furnishes the best antidote in case of poisoning by this salt. It unites with many other organic substances to form insoluble, stable compounds. It is somewhat soluble in cold water and easily soluble in hot water. It is prepared by subliming a mixture of mercuric sulphate and sodium chloride. It is one of the most efficient germicides known and is therefore used as an antiseptic and for preserving animal and vegetable tissues from decay.

(*a*) Botanical and zoological specimens are preserved from decay and from the attacks of insects by brushing over them a solution of $HgCl_2$ in alcohol.

(*b*) Mercuric nitrate [$Hg(NO_3)_2$] is prepared by boiling mercury in nitric acid until a portion of the liquid no longer gives a precipitate with common salt. Mercuric sulphate ($HgSO_4$) is prepared by heating mercury with at least one and a half times its weight of sulphuric acid.

(*c*) Mercury combines directly with bromine forming mercuric bromide ($HgBr_2$), and evolving heat. When mercury is rubbed in a mortar with iodine and a small quantity of alcohol, it forms mercuric iodide (HgI_2), and evolves heat. Mercuric iodide may be precipitated by adding potassium iodide to a solution of $HgCl_2$. It is a scarlet powder (see Experiment 10).

EXERCISES.

1. In the preparation of magnesium from magnesium chloride and sodium, what is the other product of the reaction? How may it be separated from the metal?

2. How much ZnO can be obtained by oxidizing 100 grams of zinc?

3. If 150 cu. cm. of oxygen and 400 cu. cm. of hydrogen are mixed and exploded, what volume of steam is produced? Which gas and how much of it remains in excess?

4. By a series of electric sparks, I decompose 100 cu. cm. of NH_3. I then add 90 cu. cm. of oxygen, and explode the mixture. Give the name and volume of each of the remaining gases.

5. Name an element that is thought to be monatomic, and give a reason for such belief.

6. A certain salt absorbs water from the air and then dissolves in the water. What word describes the salt in this respect?

7. Complete and read aloud the following equations:

$$Na + H_2O = NaHO$$
$$CaO + H_2O =$$

8. An old process of preparing HgCl was to sublime a mixture that gave this reaction: $HgSO_4 + Hg + 2NaCl = Na_2SO_4 + 2HgCl$. Write this equation in full molecular symbols.

9. Is cinnabar a mercurous or a mercuric compound?

10. How many pounds of mercury may be obtained from a ton of pure cinnabar?

CHAPTER XIII.

THE THIRD GROUP — TRIADS.

I. THE BORON FAMILY.

BORON: symbol, B; density, 2.45 (amorphous) to 2.68 (crystalline); atomic weight, 11; valence, 3.

206. Boron. — This element is not found free in nature. It is prepared by heating its oxide with sodium or with aluminum, by electrolysis, and in other ways. In the crystalline form, it is nearly as hard, lustrous, and highly refractive as the diamond. It may also be prepared as an amorphous, soft brown powder, or in scales with a graphite-like luster. It has one oxide (boron trioxide, boric or boracic anhydride, B_2O_3). Its most important compound is borax (sodium pyroborate, $Na_2B_4O_7$), large quantities of which are found in California.

(*a*) It forms BCl_3, BF_3, BH_3, and BBr_3. In the heat of an electric furnace, it unites with carbon to form boron carbide. This carbide is similar to carborundum (silicon carbide), but even harder.

Boric Acid.

Experiment 164. — Dissolve 6 grams of powdered borax in 15 or 20 cu. cm. of boiling water. Add 3 or 4 cu. cm. of hydrochloric acid or 2 cu. cm. of sulphuric acid; stir and allow to cool. Crystals of boric acid will be formed.

Experiment 165. — Heat some boric acid crystals in a clean iron spoon. The heated crystals first melt, and then become viscous as the water is driven off. Touch this mass with a glass rod and draw out the adhering mass into long threads. This viscous substance is B_2O_3.

207. Boric Acids. — Boric acid (H_3BO_3) is a white, crystalline, lustrous solid that may be freed from any borate by the action of almost any other acid, in consequence of which it is considered a very feeble acid. It may be formed by the union of the oxide with water. Upon fusion, it gives up this water, forming a glassy mass of boric anhydride. Large quantities of boric acid are used as a preservative for milk and canned meats and vegetables.

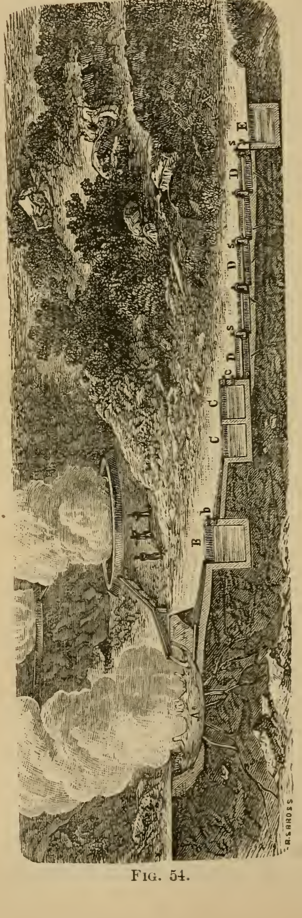


Fig. 54.

(*a*) In addition to the boric (or orthoboric) acid above mentioned, two other acids may be formed by the union of boron oxide with water, as follows:

$$B_2O_3 + 3H_2O = 2H_3BO_3,$$

boric or orthoboric acid.

$$B_2O_3 + H_2O = 2HBO_2,$$

metaboric acid.

$$2B_2O_3 + H_2O = H_2B_4O_7,$$

tetraboric or pyroboric acid.

(*b*) Native boric acid is found free in the volcanic regions of Tuscany whence nearly all that is brought into commerce is obtained. Volcanic jets of steam, charged with H_3BO_3, issue into natural or artificial ponds or lagoons, the water of which condenses the steam and becomes charged with the acid. Upon evaporation, these waters yield pearly crystals of H_3BO_3.

Test for Boric Acid.

Experiment 166. — Dissolve a few crystals of H_3BO_3 in alcohol. Upon igniting the alcohol and stirring the solution, the flame will be of a beautiful green color; or add a little alcohol and sulphuric acid to a solution of borax. Heat the materials and ignite the vapor; the flame will be tipped with green.

Experiment 167. — To a very dilute solution of borax add a few drops of hydrochloric acid and, with the solution, moisten a strip of turmeric-paper, i.e., filter-paper colored with a solution of turmeric. Upon drying the paper, its color changes to a bright pink.

208. Tests. — The color that boric acid imparts to an alcohol-flame, and the color that it yields with turmeric-paper afford the most convenient tests for its presence. The turmeric test enables the detection of boric acid in the ash of food products that have been adulterated with it.

Borax.

Experiment 168. — Make a small loop at the end of a platinum wire, the other end of which has been fused into a piece of glass tubing for a handle. Heat the loop red-hot, touch it to some powdered borax, and heat the borax that adheres to the loop, thus forming a clear, glassy bead. Into this bead fuse a minute particle of some cobalt compound, closely observing it, until a transparent blue glass is formed. If too much of the cobalt compound is added, the glass will be opaque. After observing the color of the bead when cold and when heated in different parts of the blowpipe-flame, dip the hot bead quickly into water, and clean the wire. Repeat the experiment with a compound of copper, with one of chromium, and with manganese dioxide.

209. Borax. — Borax (sodium pyroborate, $Na_2B_4O_7$, $10H_2O$), is found in certain lakes of India, China, Persia, Ceylon, Peru, and Bolivia. Large quantities are obtained from Borax Lake, California, and from Pyramid Lake, Nevada, by evaporating the water and purifying the separated borax by crystallization. When heated, it intumesces and loses the water of crystallization, finally fusing to a clear glass. Fused borax dissolves many metallic oxides, forming colored glass-like substances. Hence it is extensively used in the glazing of porcelain, in porcelain paints, in some kinds of glass and enamels, and for freeing metal surfaces from oxides preparatory to soldering.

210. Rare Elements of the Boron Family. — The other elements of this family, scandium, yttrium, lanthanum, and ytterbium, are rare metals, so rare that they need little more than mention here. Their properties are sufficiently indicated by their grouping (see tables in Chapter X., and Appendix, § 1). As already stated, the existence and properties of scandium were predicted by the aid of the periodic law.

EXERCISES.

1. What is the molecular weight of boron trioxide?

2. What per cent of boron is there in orthoboric acid?

3. Write the formula for calcium (Ca'') pyroborate; for boric anhydride.

4. What is the basicity of H_3BO_3?

5. (*a*) Write the symbols for the most common oxygen and hydrogen compounds with elements of the chlorine group. (*b*) Give the valence of each element. (*c*) State the gradation of physical and chemical properties among these elements. (*d*) Give easy tests for chlorine and iodine.

6. Write the equation for the reaction involved in Experiment 165.

7. By strongly heating manganese dioxide it is reduced to a lower oxide, thus:

$$3MnO_2 = Mn_3O_4 + O_2.$$

What weight and what volume of oxygen can be thus prepared from 50 grams of MnO_2?

8. State the method of preparing nitric acid and the amount of each substance needed for 10 pounds of the acid.

9. How does a chloride differ from a chlorate? Illustrate by potassium compounds.

10. What is the weight of the chlorine in 5 pounds of common salt? What per cent of oxygen is there in potassium chlorate?

11. State the economic properties of chlorine, and show on what they depend.

12. Name two of the most useful compounds of nitric acid, with some use of each.

13. The formula for acetylene is C_2H_2. Acetylene and benzene have the same percentage composition, but the former has a vapor-density of 13, and the latter a vapor-density of 39. From these data determine the formula for benzene.

II. THE ALUMINUM FAMILY.

ALUMINUM: symbol, Al; density, 2.6; atomic weight, 27; valence, 3.

211. Source. — Aluminum ranks third among the elements and first among the metals in quantity and extent of distribution. It is not found native; its oxide is found in the minerals emery and corundum, among the purer varieties of which are the ruby and the sapphire; its fluoride, in cryolite; its silicates, in the feldspars and micas, the disintegration of which, by weathering, gives rise to the several kinds of clay. It is also found in the topaz, emerald, and garnet. It constitutes about one-twelfth of the earth's crust, and is contained in all fertile soils, but is not taken up by any plants except a few cryptogams.

212. Preparation. — Aluminum was first obtained by Wöhler, in 1827, by heating aluminum chloride with sodium. It was first prepared on a commercial scale by St. Claire-Deville, in 1856, by reducing sodium-aluminum chloride by sodium.

$$AlCl_3, NaCl + 3Na = 4NaCl + Al.$$

The price of the metal made by this method never fell much below that of silver. At present, it is prepared by electrolyzing a solution of aluminum oxide in a bath of molten cryolite. The principal works are at Niagara Falls, and at Shaffhausen in Switzerland. This method of production has so reduced the price of the metal that aluminum competes with copper and other metals for many uses. A great many methods have been patented.

213. Properties. — Aluminum is a remarkably light and sonorous metal. It is of a bluish-white color and susceptible of a bright polish. It is tenacious, and very malleable and ductile. It is about as hard as silver and melts at about 655°. It is best worked at a temperature of from 100° to 150°. It does not readily oxidize in air. At ordinary temperatures, it is soluble in nitric and sulphuric acids. Its best solvents are hydrochloric acid and boiling solutions of the alkali hydroxides.

214. Uses. — The lightness, luster, strength, unalterability in air and in hydrogen sulphide. ease of working, sonorous and non-poisonous qualities of aluminum adapt it for many uses. It is used in large quantities for electrical conductors, for light castings and sheet-metal, for boats, canteens, cooking utensils, and for making delicate balances, light weights, opera glasses, and physical, surgical, and other instruments calling especially for lightness and moderate strength. Aluminum bronze (ninety per cent copper plus ten per cent aluminum) is very hard and malleable, yields fine castings, has the tenacity of steel and the color of gold, and takes a high polish.

215. Aluminum Oxide. — Aluminum oxide (alumina, Al_2O_3) occurs native in corundum, ruby, sapphire, etc. Its crystals are second in hardness only to the diamond. Small artificial rubies and sapphires, having all the properties of the natural crystals, have been made. An impure granular variety is called emery.

Aluminum Hydroxide.

Experiment 169. — To a solution of common alum in water, add ammonia-water or ammonium sulphide until a gelatinous mass is formed. This mass is aluminum hydroxide.

216. Aluminum Hydroxide. — Aluminum hydroxide [$Al(OH)_3$] is largely used as a mordant in dyeing textile fabrics. In crystallized form, it occurs in nature as hydrargillite. It is soluble in acids and in alkalis. In one case it acts like a base; in the other, like an acid. See § 148 (*a*). The salts thus formed with the alkalis are called aluminates, the alkali metal replacing the hydrogen of the hydroxyl, thus $Al(OK)_3$ or $Al(ONa)_3$.

217. Alums. — Common alum is a double sulphate of aluminum and potassium [$AlK(SO_4)_2, 12H_2O$]. Ammonium alum or sodium alum differs in composition by having ammonium or sodium in place of the potassium.

218. Other Aluminum Compounds. — Cryolite is a double fluoride of aluminum and sodium. A deposit eighty feet thick and three hundred feet long is known on the west coast of Greenland. But the most important of the aluminum compounds are the silicates, some of which have been mentioned. One of the most important constituents of the great rock masses of the earth is feldspar, a double silicate of aluminum and potassium ($AlKSi_3O_8$). Exposed to the weather, feldspar undergoes a natural decomposition. The soluble potassium salts thus formed are washed out and find their way into the soil. The insoluble aluminum silicate is carried down the sides of the hills and mountains upon which it was formed into the valleys and streams. The purest form of this natural product is called kaolin; the impure varieties constitute ordinary clay. The color of the clay is largely determined by the presence of iron hydroxides.

(*a*) When kaolin is mixed with feldspar, or some other flux, and melted, it forms a translucent substance called porcelain. Ordinary clay is largely used in the production of earthenware, which, like the porcelain products, may be glazed or unglazed. The most common variety of unglazed earthenware is bricks, the color of which is largely due to the presence of iron oxides.

219. Rare Elements of the Aluminum Family. — Gallium, indium, and thallium are rare metals that were discovered by the spectroscope in the latter half of the nineteenth century. The existence of gallium had been predicted by the aid of the periodic law. Thallium forms two oxides, the monoxide (Tl_2O) and the trioxide, or sesquioxide (Tl_2O_3). There are two corresponding series of salts, the thallious and the thallic.

Note. — The atomic weights assigned to the unclassified elements, gadolinium, samarium, terbium, and thulium, indicate that some of them have properties not widely different from those that characterize this group. In fact, some authorities count samarium and terbium (as well as erbium) as triads.

EXERCISES.

1. Which of the metals mentioned in this chapter is of the greatest industrial importance?
2. (*a*) How many cu. cm. of oxygen may be obtained by the electrolysis of 10 grams of water? (*b*) How many of hydrogen?
3. How many pounds of aluminum might be made by the complete electrolysis of a ton of pure aluminum oxide?
4. Write the formula for the oxide of gallium.
5. The symbol for water was formerly written HO and (for some years subsequently) H_2O_2. What inconsistency do you see in these formulas other than any based on atomic weights?
6. Write the formula for thallious chloride and thallic oxide.
7. Spinel is a mineral of varying color and the hardness of topaz. It may be regarded as magnesium aluminate [$Mg(AlO_2)_2$]. Write the formula for an hypothetical acid of which spinel may be regarded as a magnesium salt.
8. Write the formula for ammonium alum.
9. Write a graphic symbol for $Ca\overset{\mathrm{v}}{N}_2O_4$.
10. Correct the following equations:

$$Zn + HCl_2 = 2ZnCl + H_2.$$

$$2K(NO)_3 + H_2(SO)_4 = K_2SO_4 + 2HNO_3.$$

CHAPTER XIV.

THE FOURTH GROUP—TETRADS.

I. CARBON.

Symbol, C; atomic weight, 12; valence, 4.

220. Occurrence. — Two allotropic modifications of carbon, the diamond and graphite, are found free in nature. Combined with hydrogen, carbon occurs in coal, petroleum, bitumen, etc. Combined with oxygen, it forms a constituent of the atmosphere upon which all vegetable life is directly dependent. United with oxygen and calcium, it is found as limestone, chalk, and marble. All animal and vegetable bodies contain carbon; in fact, carbon is the chemical center of organic nature. When any of these "organic" bodies is sufficiently heated out of contact with oxygen there remains amorphous carbon or charcoal, a third allotropic variety.

(*a*) The chemical identity of these several allotropic forms is shown by the fact that, when highly heated with oxygen, they all form the same compound, CO_2, 12 parts of any variety of carbon uniting with 32 parts of oxygen to form 44 parts of the oxide.

221. The Diamond. — Diamond is a crystalline solid, brilliant, transparent, and generally colorless. Diamonds are most frequently found in the form of rounded pebbles which are cut into desirable forms by pressing the surface of the stone against a revolving metal wheel covered with a mixture of diamond-dust and oil. It is the hardest known substance. It is a very poor conductor of heat and electricity and, when polished, has a magnificent luster and high refractive power upon light. These properties, together with its permanence and rarity, make it the most precious of gems. Its density is 3.5.

(*a*) The diamond undergoes no change at the ordinary temperature, but, when heated between the carbon electrodes of a strong electric current, it softens, swells up, and is changed to a black mass resembling coke. When heated in oxygen to 800°, it burns to carbon dioxide. "The Regent" diamond is valued at more than half a million dollars. Small artificial diamonds have been produced.

222. Graphite. — Graphite or plumbago is familiarly known as the black lead of the common "lead pencil." It is found abundantly in nature in the crystalline and amorphous forms, the crystals being wholly unlike those of the diamond. It is opaque, nearly black, and has a semi-metallic luster. It is very friable and has an unctuous feel. It is unalterable in the air at ordinary temperatures. Its density varies from 2 to 2.5. It is used in making pencils, lubricating machinery, in making crucibles especially for the manufacture of steel, as a stove-polish, and in electrotyping. Artificial graphite has been prepared by heating charcoal or some other amorphous variety of carbon in an arc furnace, or by dissolving it in molten iron from which the graphite separates on cooling.

(*a*) For many years, graphite was supposed to contain lead; whence the names plumbago and black lead.

223. Mineral Coal. — Mineral coal consists of the luxuriant vegetation of past geological ages. In the intervening period, inconceivably long, the woody fiber, a compound of carbon, hydrogen, and oxygen, was, by pressure and in some cases by heat, changed to the various kinds of coal. The principal chemical change was in the gradual loss of hydrogen and oxygen; the degree in which this loss took place determines the character of the coal produced. At the earlier stage of the process, the product was lignite or brown coal, usually found in the later geological strata. A further loss of hydrogen and oxygen resulted in the various kinds of bituminous coal. When the carbonaceous material was also subjected to heat, the loss of hydrogen and oxygen was greatest, and the resultant product was either anthracite or graphite. Thus there is a gradation of coals from anthracite down to lignite or to peat in which the woody fibre is but little changed.

(*a*) Mingled with the carbonaceous material of the coal, there is always more or less earthy material, limestone, and pyrite. When coal is burned, these remain as ashes. In the combustion, the sulphur of the pyrite is converted into sulphuric acid, which, with the soot, chiefly caused by careless firing, often does great injury to trees, fabrics, etc., in large cities and manufacturing districts.

224. Wood Charcoal. — This familiar substance is generally prepared by the distillation or incomplete combustion of wood. In the distillation, the wood is decomposed in such a way that a part of the carbon and nearly all the hydrogen and oxygen are evolved as water, acetic acid, methyl alcohol, methane, and smaller quantities of many other compounds containing carbon, hydrogen, and oxygen. The greater part of the carbon remains as charcoal.

(*a*) A common method of burning charcoal is to pile up sticks of wood in a large heap around a central flue, covering it with turf and earth, leaving holes at the bottom for the admission of air and a hole at the top of the central flue. The fire is kindled at the bottom of the central flue, and the rate of combustion controlled by regulating the supply of air. The process often requires several weeks. At the proper time, all of the openings are closed and the fire thus suffocated. The method depends upon the fact that the volatile constituents of the wood are more easily combustible than is the carbon and therefore unite with the limited supply of oxygen.

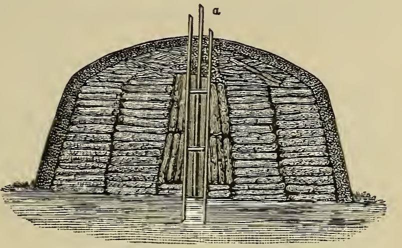


FIG. 55.

(*b*) When it is desired to save the volatile products of the distillation, two kinds of retorts are used. One kind is made of fire-brick. In this case, the heat necessary for the distillation is furnished by the combustion of a part of the wood in the kiln or retort. By this process much of the alcohol is lost, and alcohol is the most valuable of the by-products of the distillation. Such loss is prevented by the use of closed retorts made of metal and heated by external firing. As no air is admitted to the wood that is to be charred, this process yields the highest proportion of the valuable volatile by-products, but the plant and its operation are more costly than they are in the other case.

(*c*) The charcoal retains the form of the wood from which it was made, the shape of the knots and even the concentric rings being plainly visible. Its volume is about 65 or 70 per cent and its weight about 25 per cent of the wood from which it was formed.

225. Bone-black. — Bone-black, which is the most important variety of "animal charcoal," is prepared by charring powdered bones in iron retorts. The calcium phosphate of the bone remains and forms about ninety per cent of the black porous mass. The charcoal is consequently left in a very finely divided condition, spread over the particles of the phosphate or distributed among them. For this reason, it has greater absorptive and decolorizing power than vegetable charcoal.

Chemical Reduction.

Experiment 170. — Mix 2.5 grams of black copper oxide (CuO) with 0.25 grams of powdered charcoal. With some of the mixture, partly fill a small ignition-tube and heat it strongly. Metallic copper will remain in the tube while the carbon will unite with the oxygen of the CuO and escapes as a gas. The carbon has reduced the copper oxide, and the copper oxide has oxidized the carbon.

226. Charcoal as a Reducing Agent. — Owing to the energetic union of carbon and oxygen at high temperatures, charcoal is largely used as a reducing agent. Anthracite and coke are also used for the same purpose. The preparation of metals from their ores (metallurgy) depends in a very large degree upon this property of carbon.

Charcoal as an Absorbent.

Experiment 171. — Break a piece of charcoal into two. Attach a sinker to one of the fragments and immerse it in water. Notice the bubbles rise as the water enters the pores of the charcoal and forces out the air previously absorbed. The experiment may be improved by placing the beaker containing the water and the carbon under the receiver of an air-pump and exhausting the air.

Experiment 172. — Place the other fragment of the charcoal on the fire, and when it has been heated to full redness for some time, plunge it quickly into water. Notice that it needs no sinker to keep it submerged and that very few bubbles escape from it through the liquid.

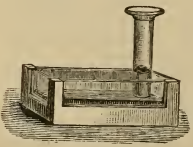


FIG. 56.

Experiment 173. — Fill a long glass tube with dry ammonia at the mercury bath. Heat a piece of charcoal to redness to remove the air from its pores, and plunge it into mercury. When the charcoal is cool, thrust it into the mouth of the cylinder. The gas will be absorbed by the charcoal and mercury will rise in the tube. Explain.

Experiment 174. — Repeat the last experiment, using dry hydrochloric acid instead of ammonia.

227. Charcoal as an Absorbent. — The porous nature of charcoal gives it a remarkable power of absorbing gases. Beech-wood charcoal has been known to absorb 170 times its own volume of dry ammonia. Other gases are absorbed in large but variable proportions. This power depends upon the fact that all gases condense in greater or less degree upon the surface of solid bodies with which they come into contact. The more easily the gas is liquefied the more largely is it absorbed by charcoal.

Charcoal as a Purifier.

Experiment 175. — Into a bottle of hydrogen sulphide (see Experiment 260) put some powdered charcoal. Shake the bottle for a moment. The offensive odor of the hydrogen sulphide will disappear.

Experiment 176. — Into the neck of a funnel, thrust a bit of cotton-wool and cover it to the depth of 2 or 3 cm. with powdered charcoal. Through this solution, pass a quantity of water charged with hydrogen sulphide. The filtered liquid will be free from offensive odor.

Experiment 177. — Place a small crucible filled with freshly ignited and nearly cold powdered charcoal into a jar kept supplied with hydrogen sulphide. When the charcoal is saturated with the gas, quickly transfer it to a jar of oxygen. The charcoal will burst into vivid combustion.

228. Charcoal as a Purifier. — By condensing offensive and injurious gases and bringing them into intimate contact with condensed oxygen, charcoal acts as an energetic purifier. The fetid products of animal and vegetable decay are not only gathered in but actually burned up. This property is retained by the charcoal for a long time and, when lost, may be restored by ignition. This oxidizing power of charcoal forms the foundation of much of the utility of charcoal filters for water.

Fig. 57.

Charcoal Filters.

Experiment 178. — Place a dilute solution of the blue compound of iodine and starch (see Experiment 102), of indigo dissolved in Nordhausen acid, of cochineal, and of potassium permanganate in each of four flasks. To each, add recently ignited bone-black. Cork the flasks, shake their contents vigorously, and pour each liquid upon a separate filter. The several filtrates will be colorless. If the first part of any filtrate is colored, pour it back upon the filter for refiltration.

229. Charcoal as a Decolorizer. — As illustrated in the above experiment, charcoal, and especially animal charcoal, is able to remove the color as well as the odor from many solutions. This power seems to depend more upon the adhesion between the carbon and the particles of coloring matter than upon oxidation. Brown sugar is purified by filtering its colored solution through layers of bone-black. Bone-black is also largely used in decolorizing vaseline and other petroleum products. If ale or beer is treated thus, it loses both its color and its bitter taste. This property of charcoal is utilized in the preparation or purification of many chemical or pharmaceutical compounds.

Lampblack.

Experiment 179. — Set fire to a lump of rosin and hold a cold plate over the flame. Soot will be deposited upon the plate.

Experiment 180. — Press a spoon or a plate down upon a candle-flame so as nearly to extinguish the flame. Soot will be deposited upon the spoon or the plate.

Experiment 181. — Partly fill a lamp with spirit of turpentine, light the wick, and cover the lamp with a bell-glass or a wide-mouthed jar. Thrust a pencil or a crayon under one edge of the bell-glass so as to raise it from the table and to admit a small supply of air to the flame. Soot will collect upon the sides of the bell-glass.

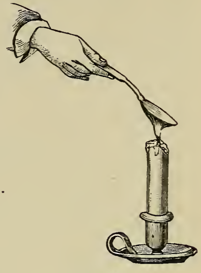


FIG. 58.

230. Lampblack. — When a hydrocarbon, like rosin, turpentine, wax, petroleum, etc., is burned, the hydrogen is first oxidized. If the supply of oxygen is insufficient for the complete combustion, the carbon set free by the decomposition of the compound will be left in a finely divided amorphous state, as soot or lampblack. The same effect will appear if the temperature of the flame is reduced below that at which carbon burns, as was the case in Experiment 179. Lampblack is manufactured on the large scale by burning tar, rosin, turpentine, petroleum, or natural gas in a supply of air insufficient for complete combustion, and leading the smoky products into large chambers where they are deposited. It is largely used as a pigment, and in the manufacture of india and printer's inks, and of electric-light carbons.

NOTE. — Coke and gas-carbon are two other varieties of amorphous carbon. See § 268 (*b*).

231. Other Properties of Carbon. — Carbon, in all of its forms, is practically infusible and non-volatile at ordinary high temperatures, but it is volatile at the high temperature of the electric furnace. It is insoluble in ordinary solvents, but dissolves in many metals melted at high temperatures. Although it has great chemical activity at high temperatures, it seems to be unalterable at the ordinary temperature of the air. The lower ends of stakes and fence posts are often charred before embedding them in the earth to render them more durable. Charred piles driven in the river Thames by the ancient Britons in their resistance to the invasion of their country by Julius Cæsar, about 54 B.C., are still well preserved. Perfectly legible manuscripts, written in ink made of lampblack, have been exhumed with Egyptian mummies.

NOTE. — Binary compounds of carbon were formerly called carburets.

EXERCISES.

1. Is charcoal lighter or heavier than air? How may it be dissolved?
2. What becomes of a piece of wood burned in the open air?
3. State the useful properties of charcoal.
4. State the characteristics of three allotropic modifications of carbon.
5. How would you prepare a solution of hydrochloric acid?
6. Give a proof of the fact that diamond is carbon.
7. In what way does the disinfecting power of charcoal differ from that of chlorine?
8. Is carbon a bleaching agent? Why?
9. Symbolize compounds of C^{iv} with L', M'', Q''', R^{iv}, and X^{v}, these last letters symbolizing hypothetical elements.
10. Can a hydrogen-flame deposit soot? Why?
11. Write the systematic chemical name and the molecular formula for alum.

II. CARBON OXIDES, ETC.

232. Carbon Oxides. — There are two oxides of carbon, having the molecular symbols CO and CO_2. The first may be considered the product of incomplete combustion of carbon; the second, that of complete combustion. Both of them are gaseous.

Preparation of Carbon Monoxide.

Experiment 182. — Pulverize 5 grams of potassium ferrocyanide and place it in a Florence flask of about 250 cu. cm. capacity. Add 25 cu. cm. of strong sulphuric acid and heat gently, removing the lamp as soon as the gas begins to come off rapidly. The gas may be passed through a solution of potassium hydroxide (KOH) and collected over water.

Experiment 183. — Place a small quantity of oxalic acid ($H_2C_2O_4$) in a small Florence flask, add enough strong sulphuric acid to cover it, place upon a sand-bath, and heat gently. The sulphuric acid removes the elements of water from the $H_2C_2O_4$, and leaves a mixture of CO and CO_2.

$$H_2C_2O_4 + \text{heat} = CO_2 + CO + H_2O.$$

The dioxide may be removed by passing the mixed gases through a solution of KOH, as in the last experiment, or by collecting over water rendered alkaline by such a solution.

233. Carbon Monoxide. — Carbon monoxide (carbon protoxide, carbonic oxide, carbonous oxide, carbonyl, CO) yields, when burned, the characteristic blue flame often seen playing over a freshly-fed coke or anthracite fire. It may be prepared by passing steam over highly heated carbon, as will be explained in the description of the manufacture of water-gas.

234. Properties. — Carbon monoxide is a colorless, odorless, poisonous gas. It is a little lighter than air, having a density of 14. It is scarcely soluble in water, but is wholly absorbed by an acid or an ammoniacal solution of cuprous chloride ($CuCl$). It is liquefiable only with extreme difficulty. Like hydrogen, it does not support combustion, but is combustible. It burns with a pale-blue flame and yields carbon dioxide (CO_2) as the sole product of its combustion. It is an active poison and doubly dangerous on account of its lack of odor. One per cent of it in the air is fatal to life, which it destroys, not merely by excluding oxygen (suffocation), as hydrogen, nitrogen, etc., do, but by direct action as a true poison. It acts as a poison by uniting chemically with the red corpuscles of the blood, thus destroying their oxygen-carrying capacity. For this reason, the best antidote is the free inhalation of pure oxygen. As this gas is formed in charcoal and anthracite fires, and as it passes easily through faulty joints and even through cast iron plates heated to redness, it is the frequent cause of oppression, headache, and danger in stove- or furnace-heated and ill-ventilated rooms. Carbon monoxide is rightly chargeable with many of the ill effects usually attributed to the less dangerous dioxide.

(*a*) Carbon monoxide is readily oxidized to the dioxide, and the dioxide is easily reduced to the monoxide. Thus, when air enters at the bottom of an anthracite fire, the oxygen unites with the carbon to form carbon dioxide. As this gas rises through the glowing coals above, it is reduced.

$$CO_2 + C = 2CO.$$

When this heated monoxide comes into contact with the air above the coals, it burns with its characteristic blue flame.

$$CO + O = CO_2.$$

If the oxygen necessary for this second combustion is not present, the dangerous monoxide will escape.

(*b*) Under the influence of sunlight, two volumes of carbon monoxide unite directly with two volumes of chlorine, forming two volumes of carbonyl chloride or phosgene gas ($COCl_2$). It will be noticed that here, CO acts as a dyad compound radical.

Chemical Reduction.

Experiment 184. — Pass a stream of carbon monoxide over some copper oxide (CuO) heated in a hard-glass bulb-tube, and thence into clear lime-water. Write the reaction.

235. Uses. — Carbon monoxide is an important agent in many metallurgical operations, on account of its power of reducing metallic oxides. It furnishes the principal fuel value of "producer-gas," and is one of the important constituents of coal-gas and of water-gas.

Preparation of Carbon Dioxide.

Experiment 185. — Repeat Experiment 40. The white precipitate that causes the turbidity is calcium carbonate.

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O.$$

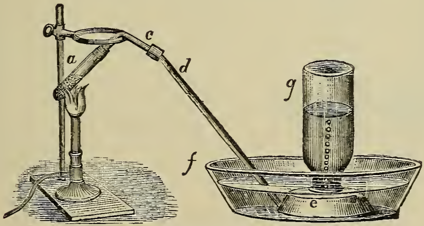


FIG. 59.

Experiment 186. — Mix 11 grams of red oxide of mercury and 0.3 grams of powdered charcoal. Heat the mixture and collect over water the gas that is given off. Test the gas with lime-water. The oxygen that united with the carbon came from the mercury oxide.

$$2HgO + C = CO_2 + 2Hg.$$

Examine the ignition-tube carefully for traces of metallic mercury. In similar manner, many solid, liquid, and gaseous bodies that are rich in oxygen give it up readily to unite with carbon and form carbon dioxide. In other words, such bodies are "reduced" by the carbon.

Experiment 187. — Into a bottle, arranged as described in § 21, put a handful of small lumps of marble ($CaCO_3$). Cover the lumps with water, and add small quantities of hydrochloric acid from time to time as may be needed to secure a continued evolution of gas. Collect several bottles of the gas over water. As carbon dioxide is heavier than air, it may be collected by downward displacement, as we collected chlorine.

$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2.$$

NOTE. — Hydrochloric acid is better than sulphuric acid in preparing CO_2 from $CaCO_3$ because $CaCl_2$ is more easily soluble than is $CaSO_4$. Old mortar, powdered oyster-shells, coral, or limestone will answer instead of marble, but marble is preferable as there is less frothing.

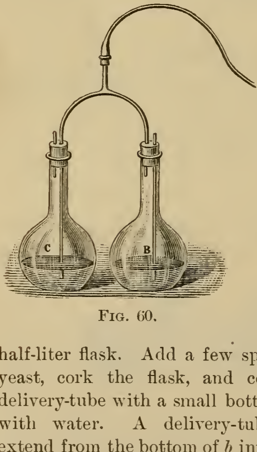


FIG. 60.

Experiment 188. — Arrange, as shown in Fig. 60, two flasks containing lime-water. Apply the lips to the tube and inhale and exhale air through the apparatus. In a few moments, the lime-water in *C*, through which the air passes *from* the lungs, will become milky, while that in *B*, through which the air passes *to* the lungs, remains clear.

Experiment 189. — Dissolve 50 cu. cm. of molasses in about 400 cu. cm. of water and place the liquid in a half-liter flask. Add a few spoonfuls of yeast, cork the flask, and connect its delivery-tube with a small bottle, *b*, *filled* with water. A delivery-tube should extend from the bottom of *b* into a cup, *c*. Keep the apparatus at a temperature of 21° or 22°, and fermentation will soon begin. As the liquid in *F* ferments, bubbles of gas will rise through it and

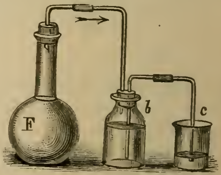


FIG. 61.

pass over into *b*, forcing a corresponding quantity of water into *c*. When *b* is nearly full of this gas, remove its stopper and test its contents with a flame and with lime-water. The gas is CO_2. Let the liquid in *F* remain in a warm place for two or three days. Cork the bottle and save the liquid for future use. The sugar ($C_6H_{12}O_6$) of the molasses was decomposed into alcohol, (C_2H_6O) and CO_2. The alcohol remains dissolved in the liquid in *F*.

236. Carbon Dioxide. — Carbon dioxide (carbonic anhydride, CO_2, often improperly called carbonic acid or carbonic acid gas) is formed when carbon or any carbon compound is burned under conditions that afford an abundant supply of oxygen. It is produced in large quantities in burning limestone to quicklime.

$$CaCO_3 + \text{heat} = CaO + CO_2.$$

It may be easily obtained by the decomposition of carbonates, such as marble, chalk, or limestone. It is a product of animal respiration, of fermentation, and of the decay and putrefaction of all animal and vegetable matter. It is a constituent of the atmosphere, and of carbonates that are found in extensive layers of the earth's crust, and is found in most natural waters. It issues from the earth in some volcanic regions, and is a principal constituent of all furnace gases. It is frequently met with in mines, the dreaded choke-damp.

Physical Properties of Carbon Dioxide.

Experiment 190. — Suspend a light glass or paper jar from one end of a scale-beam and counterpoise it in any convenient way. Pour CO_2 into the jar and it will descend (see Fig. 62).

Experiment 191. — Partly fill a wide-mouthed jar with CO_2. Throw an ordinary soap-bubble into the jar. It will float on the surface of the heavy gas.

Experiment 192. — Fill a long-necked Florence flask with CO_2. Pour in a little water, close the mouth with cork or finger, shake the bottle, and then open the mouth under water. Part of the gas will have been dissolved in the water, and more water will enter the flask to fill the partial vacuum. Close the flask, shake it again, and once more open its mouth under water. More water will enter. In this way, all of the gas may be dissolved in water. After agitating CO_2 and water in a test-tube closed by the thumb or palm of the hand, the tube and contents may be held hanging from the hand, supported by atmospheric pressure.

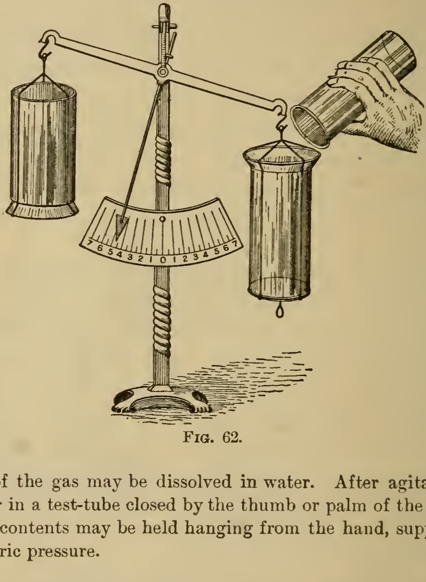


FIG. 62.

237. Physical Properties. — Carbon dioxide is a colorless gas, so heavy that it may easily be poured from one vessel to another. Its density is 22, it being one and a half times as heavy as air. It, therefore, diffuses but slowly, and often accumulates in wells, mines, and caverns (see article, "Grotto del Cane," in any cyclopædia). Under a pressure of fifty atmospheres at the ordinary temperature, it condenses to a liquid. This liquid has a density of 0.83, and its boiling-point is − 78°. Its rapid expansion, when released from pressure, produces a temperature low enough to freeze part of itself to a white, snowlike mass that melts at − 65°. This solid carbon dioxide, when mixed with ether, produces a degree of cold that quickly freezes mercury, and in a vacuum, yields a temperature of − 110°. Liquid carbon dioxide contained in strong steel cylinders is a common article of commerce. The gas is soluble in water, volume for volume, at ordinary temperatures and pressures; more largely at lower temperatures or higher pressures. It imparts a sparkling appearance and pleasant taste to water and contributes to the refreshing qualities of aërated beverages of all kinds.

Chemical Properties of Carbon Dioxide.

Experiment 193. — From a large vessel filled with CO_2, dip a tumblerful of the gas and pour it upon the flame of a taper burning at the bottom of another tumbler. The flame will be extinguished.

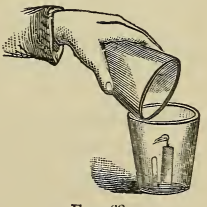


Fig. 63.

Experiment 194. — Fasten a tuft of cotton-wool to the end of a wire or a glass rod, dip it into alcohol, ignite it, and quickly thrust the large flame into a bottle of CO_2. The flame will be instantly extinguished.

Experiment 195. — Fasten a piece of magnesium ribbon, 15 or 20 cm. (6 or 8 in.) long to a wire, ignite the ribbon, and quickly plunge it into a jar of CO_2. It will continue to burn, leaving white flakes of magnesium oxide (MgO) mixed with small particles of black carbon. Rinse the jar with a little distilled water, pour the water into an evaporating-dish, add a few drops of hydrochloric acid and heat. The MgO will dissolve, leaving the black particles floating in the clear liquid.

Experiment 196. — Pass a stream of CO_2 through lime-water. Notice that the formation of calcium carbonate ($CaCO_3$) soon renders the water turbid, but that, the current being continued, the turbidity soon disappears. When the water has thus lost its milky appearance, boil it. The excess of CO_2 will escape in bubbles; the liquid will become turbid again and deposit a precipitate of $CaCO_3$. This illustrates the way in which lime may be carried in solution in spring waters and deposited as travertine when these waters are exposed to the air or heated in boilers.

238. Chemical Properties. — Carbon dioxide, being the product of complete combustion, is incombustible. It is a non-supporter of ordinary combustion. Its solution in water may be considered as containing true carbonic acid (H_2CO_3). The salts of this unstable acid are called carbonates. The gas may be completely absorbed by a solution of potassium hydroxide with which it unites to form potassium carbonate.

$$2KOH + CO_2 = K_2CO_3 + H_2O.$$

$$2KOH + H_2CO_3 = K_2CO_3 + 2H_2O.$$

Note. — As carbonic acid is dibasic, there are two types of carbonates (§§ 92, 94). Thus we have normal sodium carbonate (Na_2CO_3), and acid sodium carbonate (sodium bicarbonate, $NaHCO_3$).

239. Uses, etc. — Carbon dioxide has been successfully used for extinguishing fires in coal mines. The efficiency of many of the common, portable "fire extinguishers" depends partly upon this same property of carbon dioxide. Water charged with large quantities of the gas is sold under the meaningless name of "soda water." While the dioxide is not poisonous when taken into the stomach, it is injurious when breathed into the lungs, although the bad effects of living in ill-ventilated rooms are due less to carbon dioxide than to other waste products and living organisms given off in breathing. When largely diluted with air, carbon dioxide has a narcotic effect and its presence to the extent of nine or ten per cent of the atmosphere is sufficient to cause suffocation and death. While thus destructive of animal life it is essential to vegetable existence.

Water containing carbon dioxide in solution is capable of dissolving calcium carbonate and other substances that are insoluble in pure water. In this way, many rocks are disintegrated, stalagmites and stalactites formed, or the soil fitted for the needs of plants. The gas is also used in "corroding" lead for use as a paint ("white lead"), and in the preparation of sodium and other carbonates.

240. Tests. — The precipitation of calcium carbonate when carbon dioxide is passed through lime-water or shaken with it, is the most common test for the gas. The presence of carbonates is indicated by the escape of carbon dioxide with effervescence when they are treated with hydrochloric, nitric, sulphuric, or any other strong acid.

241. Cyanogen. — This compound of carbon and nitrogen (CN) is an univalent radical ($-C \equiv N$). It was the first compound radical isolated, and has played a prominent part in the development of synthetical "organic" chemistry. Under ordinary circumstances, carbon and nitrogen do not unite, but at very high temperatures and in the presence of certain metals they form compounds known as cyanides of those metals. Cyanogen is generally prepared by heating the cyanide of gold, silver, or mercury, and collecting over mercury.

$$Hg(CN)_2 = Hg + (CN)_2.$$

It is a colorless, poisonous, inflammable gas, easily soluble in water or in alcohol. It acts like a monad element, forming compounds corresponding to the chlorides, e.g.:

Free chlorine	Cl_2	Free cyanogen	$(CN)_2$
Potassium chloride . . .	KCl	Potassium cyanide . . .	KCN
Hydrochloric acid	HCl	Hydrocyanic acid . . .	HCN

242. Hydrocyanic Acid. — Hydrocyanic acid is a volatile, inflammable, intensely poisonous liquid; "the onset of symptoms is reckoned by seconds rather than by minutes." Its aqueous solution is well known as prussic acid; it is used in medicine. It occurs in nature in bitter almonds and in the leaves of the cherry, laurel, etc. It may be prepared by passing a current of hydrogen sulphide over heated mercury cyanide, or by treating a cyanide with sulphuric or with hydrochloric acid. (Dangerous; do not try it.)

$$Hg(CN)_2 + H_2S = 2HCN + HgS.$$

$$2KCN + H_2SO_4 = 2HCN + K_2SO_4.$$

$$KCN + HCl = HCN + KCl.$$

243. Other Cyanides. — Potassium cyanide has already been considered (§ 164). Potassium ferrocyanide and potassium ferricyanide will be considered further in a later chapter. At present, it will be enough to say that this ferrocyanide is industrially produced from potassium carbonate, iron-filings, and animal refuse, and that it is the common starting-point for the production of the other cyanides by laboratory methods.

244. Tests. — With solutions of silver nitrate, the cyanides produce precipitates insoluble in nitric acid. The odor of the acid is also characteristic.

EXERCISES.

1. Explain and illustrate what you understand by valence.

2. Write graphic formulas and the names of H_2CO_3, Na_2CO_3, and $NaHCO_3$.

3. Write an equation showing what becomes of the CO_2 removed from the CO in Experiment 183.

4. Give the densities of CO_2, NH_3, HCl, and H_2, with the principle by which they are easily determined.

5. When free cyanogen is mixed with an excess of oxygen and an electric spark passed through the mixture, an explosion occurs. On cooling, the residual gases, one of which is nitrogen, have the same volume as the original mixed gases. Write the reaction.

6. What is the weight of a liter of cyanogen gas?

7. How would you prove the solubility of HCl, NH_3, and CO_2?

8. (*a*) What weight of carbon dioxide would be produced by burning 5 grams of carbon? (*b*) What volume?

9. (*a*) What weight of CO_2 may be obtained from 100 grams of $CaCO_3$ by the action of HCl? (*b*) What volume?

10. What is the weight of 10 liters of CO_2?

11. (*a*) If 20 cu. cm. of CO and 10 cu. cm. of oxygen are mixed in an eudiometer and an electric spark is passed, what will be the name and volume of the product? (*b*) Write the reaction. (*c*) If this product is agitated with a solution of potassium hydroxide, what will be the effect upon the gaseous volume?

12. How is nitric acid prepared? Write the reaction.

13. Give the laboratory mode of liberating carbon dioxide with the reaction, and the percentage composition of the source of the gas.

14. How many liters of CO_2 can be obtained from 200 grams of $CaCO_3$?

15. Describe a method of preparing oxygen, and express, by symbols, the changes that take place.

16. Modify Experiment 170 by providing the ignition-tube with a bent delivery-tube, and determine the nature of the gas evolved. Write the reaction for the chemical changes involved in the reduction.

17. How much oxygen is needed to burn 500 grams of charcoal? How many liters of CO_2 will be produced?

18. What volume of air will be required for the combustion of 100 tons of coal, assuming that the coal is pure carbon and burns to carbon dioxide?

19. Calculate the weight of air required to burn a ton of coal having the percentage composition: C, 88.42; H, 5.61; O, etc., 5.97.

20. Write the reaction for the combustion of spirit of turpentine in Experiment 181. Assume that the turpentine has the composition indicated by the formula $C_{10}H_{16}$.

III. THE RELATION OF CARBON TO VEGETABLE AND ANIMAL LIFE.

245. Constituents of Organized Matter. — Every compound formed by the action of a living organism, i.e., every animal and vegetable substance, contains carbon as an essential constituent. In addition to the carbon, many of them contain only hydrogen, oxygen, and nitrogen; some of them only hydrogen and oxygen. A few contain also phosphorus or sulphur, or both. Most of them also contain small proportions of mineral substances that form the ash when the organic matter is burned or otherwise fully oxidized. The bones of animals consist largely of such mineral constituents, containing large proportions of the phosphates and carbonates of calcium and other metals.

246. Variety of Carbon Compounds. — The number of the carbon compounds formed in living animal and vegetable bodies is greater than the number of the compounds of all the other elements taken together. Until recently, none of the substances formed by living organisms could be produced by any other means. This fact was considered so important that the carbon compounds were placed in a class by themselves and studied under the style and title of "organic chemistry." It was assumed that they were essentially the products of a so-called "vital force."

Since it has become possible artificially to produce many of them, the old distinction between the organic and the inorganic branches of chemistry has been abandoned. When the term "organic chemistry" is now used, it is with a changed meaning — the chemistry of the compounds of carbon.

(*a*) The laboratory production of a typical compound of this class, i.e., the synthetic preparation of an "organic" compound from "dead matter," was first accomplished in 1828 by Friedrich Wöhler, a German chemist.

247. The Food of Plants. — About three parts in ten thousand parts of the atmosphere, by volume, is carbon dioxide. This may seem an insignificant proportion until we realize that each cubic mile of the atmosphere near the earth contains more than seven hundred tons of carbon. All the carbon essential to plant life comes from this atmospheric supply. Plants breathe in the air through the pores of their leaves. Under the influence of sunlight, the carbon dioxide thus inhaled is broken up, the carbon being appropriated as a constituent of living tissue, while the freed oxygen is returned to the air. As only about twenty per cent of green wood is carbon, the supply of carbon in the atmosphere within a mile of the surface of the earth is adequate for a considerable growth of forest. After life ceases, all of this carbon is returned to the atmosphere as carbon dioxide — the ultimate product of all combustion and decay of carbon compounds.

(*a*) It is probable that in former ages the atmosphere contained a larger proportion of carbon dioxide than it does at present, that vegetation was more luxuriant then than now, and that carbon was stored away as coal, petroleum, and gas.

248. The Food of Animals. — The food of animals comes, directly or indirectly, from plants. In the animal body much of the food taken is burned, the oxidation furnishing the heat necessary for animal warmth. The carbon dioxide produced by this combustion is returned through the lungs to the air.

249. Solar Energy. — Carbon is the great agent for transferring the energy of the sun to the living animal. The energy of sunlight expended in breaking up the carbon oxide that is absorbed by the leaf is stored up as potential energy in the vegetable tissue, and again set free as heat in the animal body. The sun's energy that is transformed into the chemical energy of carbon compounds that become parts of vegetable tissue is the physical source and foundation of all life. The plant breathes in carbon dioxide; the animal breathes out carbon dioxide. Each carbon particle involved may go through the same cycle of changes again and again, carrying with it on each round the energy necessary for the maintenance of vegetable and animal life.

EXERCISES.

1. Assuming that a square meter of leaf will decompose a liter of carbon dioxide per hour, what weight of carbon will be assimilated in an hour by 1,000 trees, each of which has 100,000 leaves, each leaf measuring 25 sq. cm.?

2. Is $Hg(CN)_2$ a mercurous or a mercuric compound? What is its name?

3. Describe the usual method of preparing chlorine, and write the reaction. Find the percentage of chlorine in the substance that furnishes it.

4. Zinc nitrate and potassium carbonate react as follows:

$$Zn(NO_3)_2 + K_2CO_3 = ZnCO_3 + 2\,KNO_3.$$

How much $Zn(NO_3)_2$ is required to give 103.17 grams of $ZnCO_3$?

5. How much $ZnCO_3$ may be obtained from 156 grams of $Zn(NO_3)_2$?

6. How much K_2CO_3 is needed to decompose 75 grams of $Zn(NO_3)_2$?

7. What quantity of potassium nitrate will result?

8. How much K_2CO_3 must be used to obtain 54 grams of $ZnCO_3$?

9. How much potassium nitrate will be produced?

10. Why is the term "organic chemistry" less frequently used than formerly?

11. Trace the muscular energy of a carnivorous animal to solar energy as its source.

12. When oxygen is prepared by heating manganese dioxide, Mn_3O_4 is formed. Write the reaction.

13. Complete the following equation with the formula for a single molecule:

$$BaO_2 + 2HCl = BaCl_2 +$$

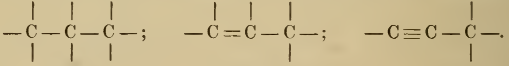
IV. HYDROCARBONS IN HOMOLOGOUS SERIES.

250. The Hydrocarbons. — The compounds of hydrogen and carbon are called hydrocarbons. They and their derivatives are so numerous that an attempt to name them would lead beyond the proper limits of an elementary text-book. Fortunately, the relations between them are so simple that their study is not difficult. They exist in great quantities in nature as the sole constituents of petroleum and natural gas, and as the principal constituents of the various asphalts and similar substances. They are also formed when most carbon compounds are highly heated without access of air, as in the manufacture of coal-gas. They have been classified, each individual member of a series differing but little in composition and properties from its neighbors in that series.

251. Hydrocarbon Skeletons. — The great diversity of the hydrocarbon compounds arises from the fact that carbon atoms have the peculiar property of combining with themselves to form a variety of molecular skeletons to which other elements may be attached, forming compounds so numerous that their names and brief descriptions would fill many volumes. The single atom of carbon is capable of fixing four atoms of hydrogen, and is, therefore, quadrivalent. It forms but one compound with hydrogen, CH_4.

(*a*) Two atoms of carbon may be united together with a single bond, forming $-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-$, leaving six bonds unsaturated. If they are united with two bonds, $\overset{|}{\underset{|}{C}}=\overset{|}{\underset{|}{C}}$, four bonds are left open. When they are united by three bonds, $-C\equiv C-$, only two bonds are left open. We have, therefore, the three different compounds, ethane (C_2H_6), ethelyne (C_2H_4), and acetylene (C_2H_2), each molecule containing two atoms of carbon that unite with hydrogen as above.

(*b*) Three atoms of carbon give the following possible skeletons:



$$-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-; \quad -\overset{|}{C}=\overset{|}{C}-\overset{|}{\underset{|}{C}}-; \quad -C\equiv C-\overset{|}{\underset{|}{C}}-.$$

C_3H_8	C_3H_6	C_3H_4
C_nH_{2n+2}	$C_nH_{\ n}$	C_nH_{2n-2}

(*c*) In a similar way, the higher members give rise to several series, each differing from the next by H_2. There are, in this way, the following: C_nH_{2n+2}; $C_nH_{\ n}$; C_nH_{2n-2}; C_nH_{2n-4}; C_nH_{2n-6}; and so on with no exception up to C_nH_{2n-36}.

252. Isomers. — The power of carbon atoms to unite thus with each other almost without limit is not possessed by any other element. It is the cause of the vast number of the carbon compounds. The fact that carbon atoms combine with each other in different ways results also in the formation of many compounds of the same composition, but with different physical properties. *These compounds that have the same percentage composition and that differ in the arrangement of the atoms in the molecule, and hence have different physical properties, are called isomers.*

(*a*) Isomers that differ in molecular weight are called polymers, of which acetylene (C_2H_2) and benzene (C_6H_6) are examples. Isomers that have the same molecular weight are called metamers, of which ammonium cyanate (NH_4CNO) and urea [$(NH_2)_2CO$] are examples. In like manner, aldehyde and ethylene oxide have the same molecular weight, and their elements are combined in the same proportion (C_2H_4O), but they differ widely in their chemical properties.

253. Molecular Structure. — These isomeric forms increase in number very rapidly as the complexity of the molecule increases. There are three known isomers having the formula of C_5H_{12}; five, having the formula C_6H_{14}. There are nine possible forms of C_7H_{16}, four of which are known. It has been calculated that for the hydrocarbon $C_{13}H_{28}$, there are 799 possible isomers. In such ways, an almost endless variety of carbon compounds arises.

(*a*) The recognized variations in molecular structure that underlie isomerism have made it important for chemists to resolve the empirical formulas into atomic groups that shall at least suggest some of the known facts in any given case. By way of illustration, we may take one of these isomeric compounds, acetic acid ($C_2H_4O_2$). Experiment shows that acetic acid is monobasic; i.e., that only one of its four hydrogen atoms can be replaced by a metal to form a salt. This suggests that one of the four hydrogen atoms is held in the molecule in a way different from the way or ways in which the other three are held. This fact is expressed by writing the formula for acetic acid, $H(C_2H_3O_2)$.

It is also possible to substitute one atom of chlorine for one of hydrogen, and one of oxygen in the acetic acid molecule, yielding C_2H_3OCl. No greater part of the hydrogen and oxygen can be thus replaced, and the properties of the derived substance indicate that the hydrogen atom now displaced in company with the oxygen atom is the same one that in the previous experiment was replaced by the metal. These facts are expressed by writing the formula for acetic acid $HO(C_2H_3O)$.

The synthetic preparation of acetic acid shows that the group CH_3 passes without change from one of the factors into the product, $HO(C_2H_3O)$. This fact leads to the separation of the group C_2H_3O into two groups, CH_3 and CO.

The original molecule, $C_2H_4O_2$, has now been resolved into the three atomic groups, HO, and CO, and CH_3. This final result is expressed by the structural or constitutional formula for acetic acid, $CH_3 - CO - OH$, or $CH_3 \cdot CO \cdot OH$.

(*b*) In some such way as that just described, the molecular structure of many complex substances has been determined. Such theoretic conceptions have led the way to some of the most brilliant achievements of synthetic chemistry.

254. The Leading Hydrocarbon Series. — The most important of these are the following:

The marsh-gas series, having the composition C_nH_{2n+2}.
The ethylene series, having the composition C_nH_{2n}.
The acetylene series, having the composition C_nH_{2n-2}.
The benzene series, having the composition C_nH_{2n-6}.

(*a*) Examples of the above are included in the following list:

C_nH_{2n+2}; methane or marsh-gas (CH_4), ethane (C_2H_6), etc.
C_nH_{2n}; methene[1] or methylene (CH_2), ethene or ethylene (C_2H_4), etc.
C_nH_{2n-2}; ethine or acetylene (C_2H_2), allylene (C_3H_4), etc.
C_nH_{2n-4}; very few are known.
C_nH_{2n-6}; benzene (C_6H_6), toluene (C_7H_8), etc.

(*b*) A series of carbon compounds, each differing from the next in the series by CH_2, is called an homologous series.

255. Petroleum. — This liquid mineral which, since 1860, has been abundant in the markets of the world and

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[1] CH_2 exists only in combination.

has come into use in many ways, is chiefly a mixture of the marsh-gas and the ethylene series of hydrocarbons. Some of these constituents are gaseous under ordinary conditions and pass off when the pressure under which they were confined in the earth is removed. A mixture of petroleum vapors with air is explosive and the thicker constituents of the native oil clog lamps and wicks. The petroleum therefore needs refining to fit it for domestic use.

256. Refining Petroleum. — The crude petroleum is pumped from wells into storage tanks where water, dirt, and other impurities separate and settle to the bottom. The clear oil is then distilled from large iron retorts and thus separated into several products as the density of the distillate changes (see Fig. 64). As the first four members of the marsh-gas series are gaseous under ordinary conditions, they are not now taken into consideration although, in greater or less quantities, they are probably held in solution. Among these distillates are the following:

(*a*) **Naphtha Group.** — This includes the lighter oils from pentane to nonane inclusive (see § 257). Their boiling-points range from 0° to about 150°. The most important of these is gasolene, which forms a considerable proportion of most petroleums. It is extensively used in the extraction of oils, for cleansing purposes, for prime motors or engines, and as a fuel in stoves peculiarly constructed for this purpose. Its great volatility, or low boiling-point, renders hazardous its use, especially by those who are lacking in intelligent care.

(*b*) **Illuminating-oils.** — These are sold as kerosene, paraffin oil, etc. The safety of illuminating-oils is determined by the flashing-point, or the temperature at which they give off an inflammable vapor. In most states, inspectors are appointed to see that only such as bear the legal test, as to flashing-point, are sold for illuminating purposes.

(*c*) **Lubricating-oils and Vaseline.** — These are the heavier oils occurring in petroleum.

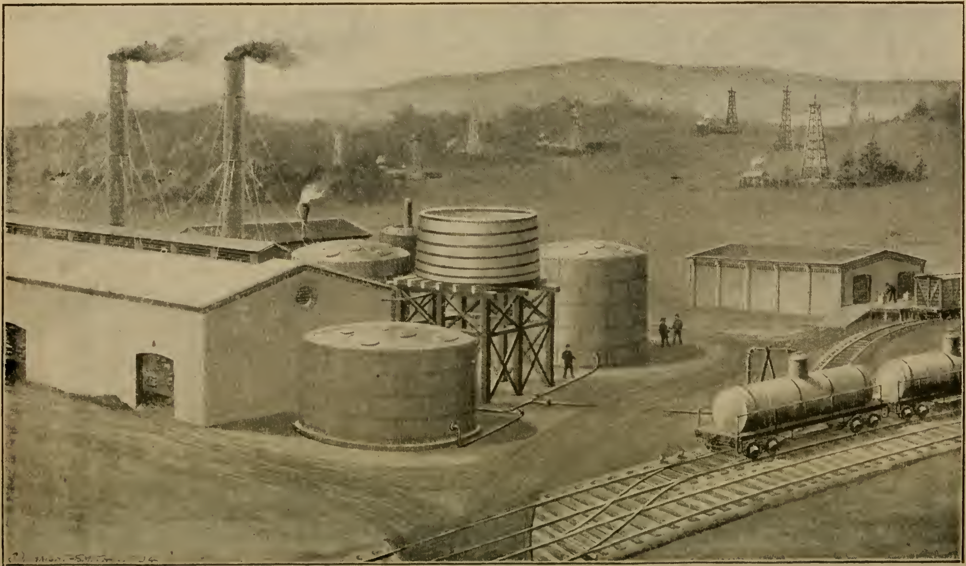


Fig. 64.

(*d*) **Solid Paraffins.** — These amount to about 2 per cent of the petroleum, and are used for candle-making, coating for the ends of matches to cause them to kindle readily, etc.

The proportion of these various constituents existing in crude petroleum is widely different in the supplies obtained from different localities. After the volatile constituents are thus removed by fractional distillation, there remains a solid, black residue that is nearly pure carbon. This coke is used in the manufacture of carbons for arc electric lighting, for electric batteries, and for electrolytic cells. Each of the fractions is freed from the colored and ill-smelling compounds and otherwise purified by washing with sulphuric acid, then with alkali, and then with water. The heavy, dark-colored products are sometimes made light-colored by filtering them through bone-black or through fullers' earth and bleaching in sunlight.

257. The Paraffins. — The marsh-gas series (C_nH_{2n+2}) are called paraffins because of their chemical inertness (*parum*, little; and *affinis*, affinity).

(*a*) The first ten members of the series are:

Methane (CH_4),	gas at 0°,	Hexane (C_6H_{14}),	boils at 78°,
Ethane (C_2H_6),	gas at 0°,	Heptane (C_7H_{16}),	boils at 98°,
Propane (C_3H_8),	gas at 0°,	Octane (C_8H_{18}),	boils at 125°,
Butane (C_4H_{10}),	boils at 1°,	Nonane (C_9H_{20}),	boils at 148°,
Pentane (C_5H_{12}),	boils at 38°,	Decane ($C_{10}H_{22}$),	boils at 168°.

These and many more of the series have been isolated from petroleum.

(*b*) Each of the members of this series differs from its immediate neighbors by CH_2. The marsh-gas series is, therefore, an homologous series.

(*c*) The members of this series may be considered hydrides of a corresponding series of univalent compound radicals, thus:

Methyl (CH_3),
Ethyl (C_2H_5),
Propyl (C_3H_7),
Butyl (C_4H_9),
Pentyl (C_5H_{11}),
Hexyl (C_6H_{13}),
Heptyl (C_7H_{15}),
Octyl (C_8H_{17}),
Nonyl (C_9H_{19}),
Decyl ($C_{10}H_{21}$).

The use of the Greek numerals in the nomenclature of radicals and of paraffins, and the corresponding number of carbon atoms in each may serve as a mnemonic aid.

258. The Chemical Relations of the Paraffins. — The paraffins are saturated compounds, having no unsatisfied bonds (§ 101). They, therefore, can form no compounds by uniting directly with other chemical substances. Compounds can be formed only by the removal of one or more atoms of hydrogen to make room for other elements that may enter into combination by substitution in exact measure for the hydrogen removed. CH_4 or C_2H_6, as they stand, can not combine with other substances; they have no unsatisfied bonds with which to hold them. But, if deprived of one or more atoms of hydrogen, they become $(-CH_3)'$; $(=CH_2)''$ or $(-C_2H_5)'$; $(=C_2H_4)''$, and acquire the power to enter into combination according to the chemical value of the hydrogen thus lost. The known compounds CH_3Cl, CH_2Cl_2, C_2H_5Cl, and $C_2H_4Cl_2$, illustrate the combining power now under consideration.

259. Metallic Character of Hydrocarbon Radicals. — It will be apparent from the examples given above, that the compound radicals formed by removing one or more atoms of hydrogen from any of the saturated hydrocarbons, behave very much as the metals do under the same chemical conditions. Like the metals, they form oxides, hydroxides, chlorides, nitrates, sulphates, etc.

Sodium chloride, $NaCl$;	*Sodium nitrate,* $NaNO_3$;	*Sodium sulphate,* Na_2SO_4;	*Sodium hydroxide,* $NaOH$;
Methyl chloride, CH_3Cl;	*Methyl nitrate,* CH_3NO_3;	*Methyl sulphate,* $(CH_3)_2SO_4$;	*Methyl hydroxide,* CH_3OH;
Ethyl chloride, C_2H_5Cl;	*Ethyl nitrate,* $C_2H_5NO_3$;	*Ethyl sulphate,* $(C_2H_5)_2SO_4$;	*Ethyl hydroxide,* C_2H_5OH.

Preparation of Methane.

Experiment 197.—Into a gas-pipe retort (see Appendix, § 21) 15 or 20 cm. long, put an intimate mixture of 3 grams of sodium acetate ($NaC_2H_3O_2$), 3 grams of sodium hydroxide (caustic soda, $NaOH$), and 6 grams of quicklime. Place the retort in a stove, heat it to redness, and collect over water the gas that is evolved.

$$NaC_2H_3O_2 + NaOH = CH_4 + Na_2CO_3.$$

The lime is added to keep the mixture from fusing, and to prevent the escape of carbon dioxide.

260. Marsh-gas.—The first member of the paraffin series is marsh-gas (methyl hydride, hydrogen monocarbide, methane, CH_4). It occurs free in nature as a constituent of petroleum and as a product of the decay of vegetable matter confined under water. In warm summer weather, bubbles often rise to the surface of stagnant pools. If the vegetable matter at the bottom of the pond is stirred, gas-bubbles will rise rapidly. The gas may be collected by filling a bottle with water, tying a funnel to its mouth, and inverting it over the ascending bubbles. Of this gas, about seventy-five per cent is marsh-gas; the rest is chiefly carbon dioxide and nitrogen. The

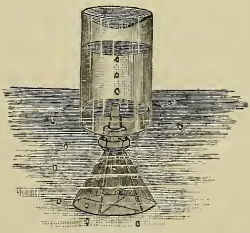


Fig. 65.

carbon dioxide may be removed by agitating the mixed gases with lime-water. Marsh-gas also escapes from seams in some coal-mines and forms the dreaded "fire-damp" of the miner. Mixed with air in the right proportion and ignited by a spark or a lamp, it explodes with great violence. It also escapes in large quantities from gas-wells, constituting about ninety-five per cent of most natural gas. It is formed when wood or coal is heated without access of air, and is therefore one of the principal constituents of coal-gas.

(*a*) Methane may be made from its elements by the following reactions:

$$C + S_2 + \text{heat} = CS_2.$$

$$Fe + S + \text{heat} = FeS.$$

$$H + Cl + \text{heat} = HCl.$$

$$FeS + 2\,HCl = FeCl_2 + H_2S.$$

$$CS_2 + 2\,H_2S + 8\,Cu + \text{heat} = 4\,Cu_2S + CH_4.$$

Beginning with CH_4, many of the most complex hydrocarbon molecules may be built up.

Properties of Marsh-gas.

Experiment 198. — The levity and inflammability of CH_4 may be shown as in the case of hydrogen, by introducing a lighted taper into an inverted jar of it. The gas will burn at the mouth of the jar, and the candle-flame, as it passes up into it, will be extinguished.

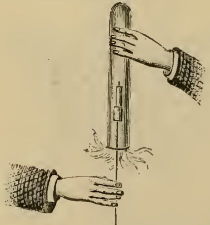


FIG. 66.

Experiment 199. — Fill a tall bottle of at least one liter capacity with warm water, invert it over the water-pan, and pass CH_4 into it, until a little more than one-third of the water is displaced; cover the bottle with a towel, to exclude the light, and then fill the rest of the bottle with chlorine. Cork the bottle tightly, and shake it vigorously, to mix the gases together, keeping the bottle covered with the towel. Then open the bottle and apply a flame to the mixture. Hydrochloric acid will be produced, and the sides and mouth of the bottle will become coated with solid carbon in the form of lampblack. Test for hydrochloric acid with moistened blue litmus-paper and with a rod wet with ammonia-water.

261. Properties. — Marsh-gas is a colorless, odorless, tasteless gas, slightly soluble in water. It is one of the lightest known substances. It is combustible, burning with a feebly luminous flame. Its heating power is very great. It forms an explosive mixture with air or with oxygen and has been the cause of many fatal explosions in ill-ventilated coal-mines. When decomposed by electric sparks, it yields twice its volume of hydrogen. Under great pressure and cold, it may be condensed to a colorless liquid having a density of 0.415. Under ordinary atmospheric pressure, liquid methane boils at −164°.

262. Other Members of the Marsh-gas Series. — Ethane and propane are colorless gases with properties very similar to those of methane. Butane is a liquid at about 0°. The immediately following members of the series are liquids, but those of highest carbon contents are white solids at ordinary temperatures. These latter constitute the paraffin derived from petroleum.

263. The Olefines. — The members of the ethylene series (C_nH_{2n}) are called olefines. Methylene (CH_2) has not been isolated. The next two members of the series, ethylene (olefiant gas, C_2H_4), and propylene (C_3H_6), are colorless gases, similar in their physical properties to those just described. They and the higher members of the series have been isolated from petroleum. They burn with a luminous flame, and differ from the compounds of the marsh-gas series in that they are very active chemically, uniting directly with many substances as bivalent compound radicals.

(*a*) Notice the relation between the nomenclature of these compounds and that of the univalent compound radicals mentioned in § 257 (*c*).

Preparation of Acetylene.

Experiment 200. — Put several lumps of calcium carbide into a gas-bottle (Fig. 6), and pour in alcohol enough to seal the lower end of the funnel-tube. Add water in very small quantities, and so as to regulate the flow of gas from the delivery-tube. Collect the gas over water.

264. Acetylene. — Acetylene (C_2H_2), the first member of the C_nH_{2n-2} series, is a colorless gas found in coal-gas. It may be made from its elements by passing electric sparks between carbon terminals in an atmosphere of hydrogen. It is more easily made by treating calcium carbide with water.

$$CaC_2 + 2H_2O = C_2H_2 + Ca(OH)_2.$$

The gas may be condensed to a liquid that boils at $-83°$. It has a peculiar odor, and is explosive when under pressure. Because of the facility with which it is prepared and of its intensely luminous power when properly burned, it is largely used as an illuminant, both on the small scale, as in bicycle lanterns, and on the large scale, for house and street lighting.

265. Benzene. — Benzene (C_6H_6), the first member of the C_nH_{2n-6} series, is a liquid obtained from coal-tar by distillation. It is a good solvent of oils and of rubber. Like toluene, the next member of the series, it is largely used as a starting substance in the manufacture of coal-tar dyes (see § 309).

(*a*) Benzene is a hydrocarbon of constant composition, while benzine is a mixture of hydrocarbons derived from the distillation of petroleum.

EXERCISES.

1. Many bicycle lamps burn a gas that is produced as needed by water dropping upon a certain solid. Give the names of the solid used and of the gas produced. Write the reaction for the production of the gas.

2. Explain the fact that two atoms of carbon may unite with two atoms, or with four atoms, or with six atoms of hydrogen.

3. Symbolize and name ten successive members of an homologous series of compounds, and explain what is meant by such a series.

4. Symbolize and name the compound radicals of the sixth, seventh, and eighth members of the series just named, and state the valence of the radicals.

5. Write the graphic formula for ethyl hydride.

6. What volume of hydrogen may be obtained by decomposing three liters of hydrogen monocarbide by electric sparks?

7. What descriptive term is applied to a series of chemical compounds having CH_2 as its increment of composition?

8. Butylene is the fourth member of the olefine series. What is its formula?

9. What is meant by the statement that acetylene is endothermic?

10. Put a small quantity of sodium sulphite into the gas-bottle, add hydrochloric acid in small quantities, collect the evolved gas by dry downward displacement, and test it with a burning taper and (very carefully) for odor. Write the equation for the reaction that evolved the gas.

11. Allylene is the second member of the acetylene series. What is its formula?

12. Toluene is the second member of the benzene series. Write its formula.

13. Xylene is the third member of the benzene series. What is its formula?

14. When ordinary alcohol (C_2H_6O) is heated with sulphuric acid, the acid abstracts the elements of water from the alcohol, leaving a hydrocarbon gas of the C_nH_{2n} series. Give the name and formula for this gas.

15. What weight of carbon dioxide is formed by the burning of a liter of marsh-gas?

V. ILLUMINATING-GASES.

266. Luminosity of Flames. — Flame is a phenomenon of burning gas; in general, what we call flame is a gas combining with oxygen. It is a matter of common observation that flames differ in their power to emit light, i.e., in their luminosity. For instance, the hydrogen flame gives practically no light, while the acetylene flame is intensely luminous. A solid substance in a non-luminous flame, like a spiral of platinum wire in a hydrogen flame, or a bit of lime in an oxyhydrogen flame, or a Welsbach mantle in a natural-gas flame, becomes luminous. Similarly, particles of unburned carbon in ordinary gas-flames make them luminous, as in the case of the acetylene flame or the flame of a "rich" coal-gas. In each instance, *the light is due to the incandescence of a solid.*

(*a*) The illuminating power of a gas is generally expressed in terms of candles. For instance, the statement that a certain product is of eighteen candle-power means that a jet of the gas in question burning at the rate of five cubic feet an hour gives eighteen times as much light as a standard candle, i.e., a spermaceti candle that burns at the rate of 120 grains an hour.

267. Illuminating-gases. — The four kinds of illuminating-gas in most common use are coal-gas, water-gas, natural gas, and acetylene.

Experiment 201. — In a gas-flame heat some fine wood-shavings contained in a dry test-tube fitted with a cork and a short glass delivery-tube drawn out to a jet. Notice the appearance of moisture. Ignite the gas evolved as it issues from the apparatus. When gas is no longer given off, notice the residual charcoal and the tarry liquid formed by this dry or destructive distillation of the wood.

Experiment 202. — Into a gas-pipe retort, put some fragments of bituminous (soft) coal. To the delivery-tube, attach a piece of glass tubing drawn out to a jet. Place the retort in a hot fire, and, as the illuminating-gas is delivered, ignite it at the jet.

Experiment 203. — Heat some pieces of bituminous coal in the gas-pipe or other retort and pass the gas as it is evolved through the apparatus shown in Fig. 67. The volatile liquid products will condense in the receiver, *m*, or "hydraulic main." Thence, the gas passes through the first arm of the U-tube and changes the color of a moistened strip of red litmus-paper to blue, thus showing the presence of ammonia. In the second arm, it is tested for hydrogen sulphide. In the bend of the second tube, is placed lime-water, which becomes milky, thus showing the presence of carbon dioxide. The gas is then collected over water. By lowering the capped receiver into the water or by pouring more water into the water-bath and opening the stopcock, the gas may be forced out and burned as it issues.

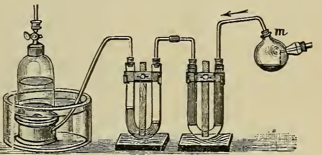


Fig. 67.

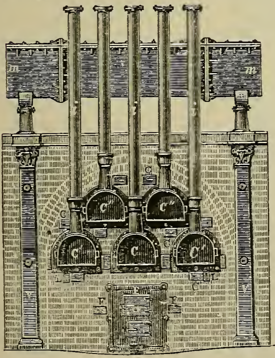


Fig. 68.

268. Coal-gas. — Illuminating-gases are sometimes prepared by distilling substances consisting in whole or in part of hydrogen and carbon. For this purpose, wood, resin, or petroleum is sometimes used, but, more commonly, a mixture of cannel and caking bituminous coals furnishes the desired products. A sectional view of the apparatus used is shown in Fig. 68. The coal is placed in ⌓-shaped retorts, six or seven feet long made of fire clay. The charge is about 200 pounds of coal to each retort. The retorts, *C*, are arranged in groups or "benches" of from three to seven. All the retorts of a bench are heated to a temperature of about 1200° by a single coke fire. After charging the retorts, their mouths are quickly closed by heavy iron plates.

(*a*) The products of the distillation, when cooled to the ordinary temperature, are solid, liquid, and gaseous.

(*b*) The solid products are coke and gas-carbon. The coke is coal from which the volatile constituents have been removed by intense heat. It bears about the same relation to coal that charcoal does to wood. It is largely used as a fuel for domestic, metallurgical, and other purposes. The gas-carbon is an incrustation that gradually forms on the inside of the retorts. It is used for making plates for galvanic batteries and "carbons" for arc electric lamps.

(*c*) The liquid portion of the distillate is chiefly an aqueous solution of ammonium compounds, and a viscous coal-tar that is complex in its composition. The coal-tar is a prolific source of carbon compounds. Among the hydrocarbons obtained from coal-tar are benzene (C_6H_6), toluene (C_7H_8), xylene (C_8H_{10}), naphthalene ($C_{10}H_8$), and anthracene ($C_{14}H_{10}$).

(*d*) The chief constituents of coal-gas are hydrogen and marsh-gas, the two making about 80 per cent of the whole volume. There is also about 6 per cent of carbon monoxide. The remainder of the coal-gas consists of small quantities of a large number of gases, including ethelyne, acetylene, nitrogen, oxygen, carbon dioxide, sulphurous oxide, hydrogen sulphide, carbon disulphide, ammonia, and water.

(*e*) When the volatile products leave the retort, they pass up through the ascension pipes, *i*, down the dip pipes, and bubble through the seal of tar and water already collected in the long, horizontal iron tube, *mm*, called the hydraulic main. From this point forward, cooling ensues, accompanied by the condensation of vapors and the falling of the tar particles mechanically carried along in the hot rush of the gas from the retorts.

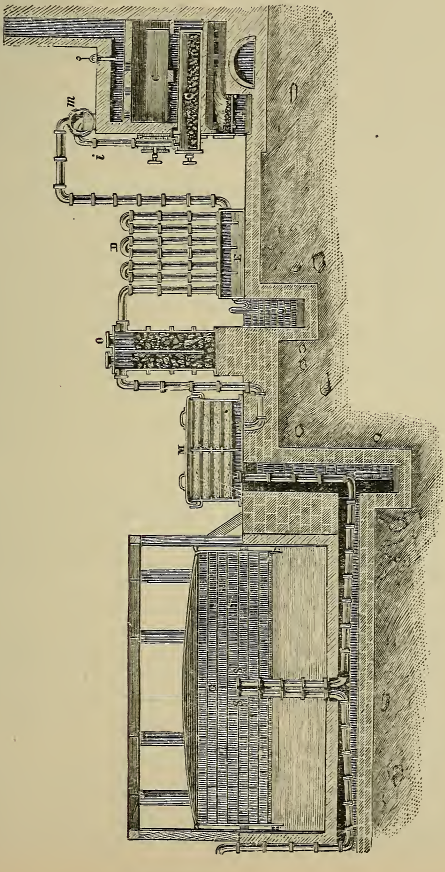


FIG. 69.

(*f*) From the hydraulic main, where it leaves much of its tar and water, the gas passes through the vertical cooling pipes, *D*, called the condensers. Here it is cooled to 20° or 25° and largely freed from its tar, oils, and ammonium compounds. In large gas-works, there are many sets of these condensers, each set measuring several hundred linear feet. Every particle of gas has to pass the whole length of one of these sets of condensers.

(*g*) In large works, an "exhauster" is placed between the hydraulic main and the condensers. By this means, the gas is pumped from the retorts and forced through the condensers, thus reducing the pressure in the retorts.

(*h*) Chief among the impurities still remaining, are ammonium compounds, carbon dioxide, and hydrogen sulphide. The ammonium compounds are easily soluble in water. Therefore, the gas is next washed in the tower or "scrubber," *O*. Here the gas, in a finely divided state, rises through a shower of minute particles of water and, thus, has its easily soluble impurities washed out by the spray. To prevent the ascent of the gas in large bubbles, of which only the surfaces would come into contact with the water, the scrubber is filled with coke, brush, or lattice work for breaking up both gas and water into minute particles. This scrubbing also cools the gas still more and removes some of the dioxide and sulphide. The tower is generally three or four feet in diameter and thirty or forty feet high. More than one are used in some works.

(*i*) The gas next passes through the purifiers, *M*, the object of which is to remove the remaining carbon dioxide and hydrogen sulphide. The purifier consists of boxes containing trays with perforated bottoms. These trays contain the material that removes the impurities as the gas filters through, namely, a mixture of copperas (iron sulphate, $FeSO_4$) or of iron oxide, sawdust, and slacked lime. At manufacturing establishments where iron and steel articles are polished, the grindstone dust is intimately mixed with minute particles of the metal. This inexpensive mixture is sometimes used in the purifiers.

(*j*) From the purifiers, the gas is conducted to the gas-holders, *G*. These gas-holders are sometimes 60 feet high and more than 100 feet in diameter.

(*k*) The gas, as delivered to the consumer, consists chiefly of the three diluents mentioned above, the marsh-gas constituting about a third of the gas sold. These feebly luminous gases, hydrogen, carbon monoxide, and marsh-gas serve as carriers of the 6 or 7 per cent of more highly luminous constituents, while the combustion of the former furnishes much of the heat needed for the decomposition of the latter and the raising of its carbon particles to the temperature of incandescence.

(*l*) Other conditions being the same and within certain limits, the higher the temperature, the greater the quantity of gas produced; the lower the temperature, the richer the quality. Similarly, the longer the time of the charge, the greater the quantity; the shorter the time, the richer the quality. A skillful mixture of grades of coal and regulation of temperature and time of charge enables the gas-engineer to vary the products of the chemical processes in the retort and to furnish an article that is satisfactory to the consumer or profitable to the manufacturer, or to compromise between these conflicting interests. Coal-gas is generally made more luminous by mixing with it a small proportion of the gases made by heating petroleum to a very high temperature.

269. Water-gas. — Water-gas is prepared by bringing superheated steam into contact with incandescent coal or coke. The steam is decomposed, and hydrogen and carbon monoxide are produced.

$$C + H_2O = CO + H_2.$$

These products are combustible, yield a non-luminous flame and intense heat, and may, without further preparation, be used for heating purposes. Of course, the supply of atmospheric oxygen in the generators must be cut off to prevent the combustion of the mixed product. Generally, hydrogen sulphide and other gases are also formed from impurities in the coal. By enriching water-gas with a gas made by highly heating petroleum or other cheap hydrocarbons, the gas-flame is rendered luminous. Water-gas, thus enriched, is now used as an illuminating-gas, but, owing to the large proportion of carbon monoxide, it is held to be more dangerous in use than coal-gas.

(*a*) The apparatus most commonly used for making water-gas is that patented by Lowe. In many of the small cities and in some of

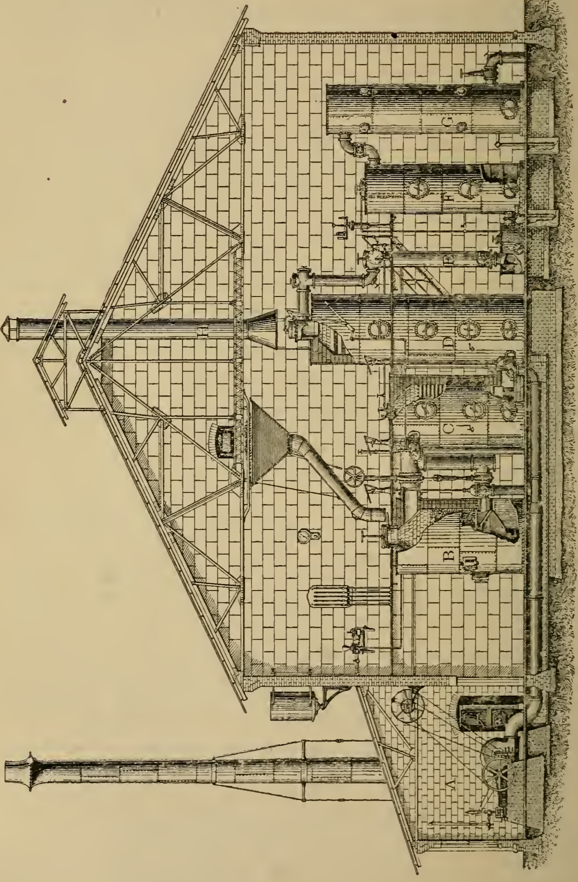


FIG. 70.

the larger ones, the process is used for making illuminating-gas. The apparatus for this method of making illuminating-gas consists of a boiler for generating the steam, a blower, *A*, for forcing air through the coke fire, a generator, *B*, where the coke is burned and gasified by the steam, the two chambers, *C* and *D*, where the petroleum added for making the gas luminous is heated so hot that it is converted into a permanent gas, and the chambers, *E*, *F*, and *G*, where the gas is purified.

(*b*) The process consists in blowing air and steam alternately through the thick bed of coke in *B*. The reaction between the coke and the steam whereby the water-gas is produced absorbs heat, so that during the steam-blow the generator gets colder and colder. If the steam-blow was continued too long, the coke would become so cold that the reaction would cease. The steam is, therefore, blown through *B* only four or five minutes at a time, and is then replaced by a blast of air from the blower, *A*, for about the same length of time. This air-blast burns coke to carbon monoxide, the reaction producing heat enough to make the remaining coke bright red. The hot monoxide, with all the nitrogen of the air that was blown in, passes up through the bed of coke and over into the chamber, *C*, at the top of which it meets enough fresh air to burn about half of the CO to CO_2. The heat generated by this reaction makes bright red-hot the loose brickwork with which *C* and *D* are filled. The carbon dioxide made in *C*, with the nitrogen from the air and the unburned portion of the carbon monoxide from *B*, pass down through the checkered brickwork in *C* and thence to the bottom of *D*. Here they meet a second draft of air just sufficient to burn the remaining CO to CO_2. The heat from this combustion makes the brick in this chamber also bright red-hot. The exhausted nitrogen and the products of combustion pass up and out through the flue, *H*. After this heating process has been continued for four or five minutes, or until the attendant decides that the apparatus is hot enough, the air from the blower is cut off, the valve at the top of *D* connecting that chamber with the flue, *H*, is closed, the valve between *D* and the trap, *E*, is opened, and steam is blown in either at the top or bottom of the generator, *B*. Passing through the bed of hot coke, the steam is converted into hydrogen and carbon monoxide. These gases pass over into the chamber, *C*, at the top of which they meet a spray of petroleum. In passing down through the heated brickwork of *C* and up through that of *D*, the petroleum that is carried along by the hydrogen and the carbon monoxide is changed by the intense heat into a permanent gas of high luminous and heating value. From *D*, the gaseous products pass down into the tar trap, *E*, and through the purifying apparatus, *F* and *G*. The water-gas is then ready for distribution.

270. Natural Gas. — At many places, especially in petroleum-producing regions, subterranean accumulations of combustible gases have been found. Just as the natural gas from volcanic vents is characterized by a great preponderance of carbon dioxide, so the natural gas in question is characterized by a great preponderance of the first four members of the marsh-gas series. Borings into the earth's crust often penetrate to these accumulations and allow the pent-up gases to escape from the pressure to which they had been subjected. This pressure is sometimes high enough to make possible the easy transportation of the gas through pipe-lines to great distances. Natural gas has come into prominence in the United States and Canada within the last few years as an illuminant and fuel. It consists almost wholly of methane and, volume for volume, has the highest heating value of any of the commercial gases.

EXERCISES.

1. Read the following symbols, thus: N_2 represents one molecule of nitrogen consisting of two atoms: O, O_2, O_3, H_2O, $2H_2O$, H_2, CO_2, CO, Cl_2, NH_3.

2. Write down the weights represented by each of the following expressions: $2HgO$, $10H_2O$, $12CH_4$.

3. Name the compounds symbolized as follows: CaO, MgO, KCl, $NaBr$, HI, KCN.

4. If two volumes of C_2H_4 and four of Cl are mixed, a black smoke and hydrochloric acid are formed. Write the reaction.

5. How much NH_3 will just neutralize 10 grams of HCl?

6. How many liters of oxygen are necessary to combine (complete combustion) with 12 grams of carbon?

7. How many liters of chlorine are necessary to decompose 12 liters of hydriodic acid?

8. (*a*) Distinguish between the properties of CO and those of CO_2. (*b*) How does each destroy life? (*c*) Give a test for each.

9. Steam and chlorine are passed through a porcelain tube heated to redness. What takes place?

10. (*a*) What is meant by the basicity of an acid? (*b*) By the acidity of a base? (*c*) How is the name of a salt derived from that of an acid?

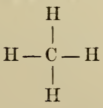
11. Write the reaction for the decomposition of steam in the manufacture of water-gas.

VI. SOME DERIVATIVES OF THE HYDROCARBONS.

271. Chloroform and Iodoform. — Many carbon compounds may be considered and classified as derivatives of the hydrocarbons, formed by the substitution of other elements or of compound radicals for one or more of the hydrogen atoms of the hydrocarbon. The simplest of these cases are those in which some of the hydrogen atoms are replaced by halogens. When chlorine acts on methyl hydride, the hydrogen of the latter is gradually replaced, the successive products being CH_3Cl, CH_2Cl_2, $CHCl_3$, and CCl_4. Commercially, the most important of these halogen substitution-products are chloroform ($CHCl_3$) and iodoform (CHI_3). Both of these compounds are used in medicine and surgery.

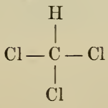
(*a*) Chloroform may be considered as methane in each molecule of which three atoms of hydrogen have been replaced by three atoms of chlorine. It is a heavy, colorless liquid of pleasant odor. When continuously inhaled, it produces anæsthesis.

Marsh-gas.



$$\begin{array}{c} H \\ | \\ H-C-H \\ | \\ H \end{array}$$

Chloroform.



$$\begin{array}{c} H \\ | \\ Cl-C-Cl \\ | \\ Cl \end{array}$$

(*b*) Similarly, iodoform may be considered as methane in each molecule of which three atoms of hydrogen have been replaced by three atoms of iodine. It is a yellow solid, having a characteristic, disagreeable odor.

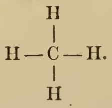
272. The Alcohols. — *When an atom of the hydrogen in the hydrocarbon molecule is replaced by the radical hydroxyl* (OH), *a class of compounds called alcohols is produced.* The term "alcohol" is generally applied to the characteristic product of the fermentation of sugar, but in chemistry it is applied to a large class of bodies.

(*a*) The molecular formula of an alcohol may be built up as above indicated by substituting the radical, OH, for an atom of hydrogen in the formula of a hydrocarbon molecule, or by substituting a hydrocarbon radical for an atom of hydrogen in the formula of water. In either case, it will appear that an alcohol is a hydroxide of an univalent hydrocarbon radical. This will appear more clearly in some of the illustrations given below.

273. Methyl Alcohol. — The simplest and one of the most important of the alcohols is called methyl alcohol (CH_4O or CH_3OH). It is also called wood-spirit, because it is made by the distillation of wood.

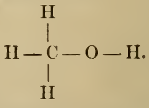
(*a*) By substituting the radical hydroxyl (OH) for hydrogen in marsh-gas, we have,

Methane.



$$\begin{array}{ccccc} & & H & & \\ & & | & & \\ H & - & C & - & H. \\ & & | & & \\ & & H & & \end{array}$$

Methyl alcohol.



$$\begin{array}{ccccccc} & & H & & & & \\ & & | & & & & \\ H & - & C & - & O & - & H. \\ & & | & & & & \\ & & H & & & & \end{array}$$

By substituting the radical methyl (CH_3) for hydrogen in water, we have,

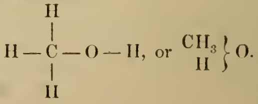
Water.

$$H-O-H,$$

or

$$\left.\begin{array}{l} H \\ H \end{array}\right\} O.$$

Methyl alcohol.



$$\begin{array}{ccccccc} & & H & & & & \\ & & | & & & & \\ H & - & C & - & O & - & H, \\ & & | & & & & \\ & & H & & & & \end{array} \text{ or } \left.\begin{array}{l} CH_3 \\ H \end{array}\right\} O.$$

274. Properties. — Methyl alcohol is a mobile, colorless liquid. When pure, its odor is pleasant, but usually the odor is penetrating and disagreeable. Its taste is burning and nauseous. It unites with water and alcohol in all proportions, burns with a feebly luminous flame, boils at about 55°, and has a density of 0.8. It is a solvent of many resinous matters.

275. Uses. — On account of its solvent powers, methyl alcohol is used in the preparation of varnishes. It is used instead of common alcohol for heating purposes. It is now largely used in the manufacture of aniline colors. In Great Britain, common alcohol containing about ten per cent of methyl alcohol is sold free of duty. This mixture is called methylated spirits, and is unfit for use as a beverage.

Common Alcohol.

Experiment 204. — Pour half of the fermented liquid of Experiment 189 into a flask, *F*, placed on the ring of a retort-stand. Connect *F* with an empty flask or bottle, *b*, having a capacity of about 100 cu. cm., and placed in a water-bath. Connect *b* with a flask or bottle, *c*, immersed in cold water. Boil the liquid in *F*; the vapors of alcohol and of water pass into *b*, the temperature of which is *a little below* the boiling-point of water because its water-bath is kept barely boiling. Here, most of the steam is condensed while the alcohol vapor passes on to *c*, and is there condensed. The

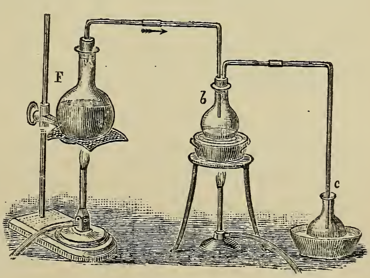


FIG. 71.

distillate condensed in *c* is dilute alcohol. If it is not strong enough to burn when a flame is brought into contact with it, it may be distilled again, or a second bottle and water-bath, *b′*, may be interposed between *b* and *c*. The experiment should not be continued after a quarter of the liquid in *F* has been vaporized. Instead of condensing the alcohol in the flask, *c*, the Liebig condenser, shown in Fig. 72, may be used. Some water will remain in the alcohol even after redistillation. This may be removed by quicklime.

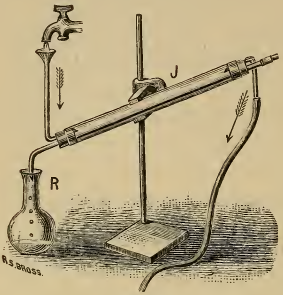
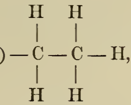


FIG. 72.

276. Ethyl Alcohol. — Common alcohol or spirits of wine (C_2H_6O or C_2H_5OH) is formed by the fermentation of any liquid that contains sugar. When the juices of plants and fruits that contain sugar, e.g., the juice of the grape or the apple, stand for some time in a warm place, they begin to ferment. The fermentation may be caused by the action of yeast. The fermented liquid lacks the sweet taste of the sugar because the sugar ($C_6H_{12}O_6$) has been decomposed into carbon dioxide and alcohol.

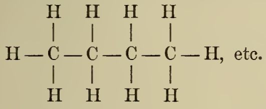
$$C_6H_{12}O_6 = 2C_2H_6O + 2CO_2.$$

(*a*) We have here a good illustration of the facility with which carbon atoms unite themselves one to another and thus constitute the framework of various hydrocarbon molecules. For example, we have the methane molecule, $\begin{array}{c} \mathrm{H} \\ | \\ \mathrm{H—C—H} \\ | \\ \mathrm{H} \end{array}$. By replacing one atom of this hydrogen with the univalent radical methyl (CH_3), we have $\begin{array}{c} \mathrm{H}\ \ \mathrm{H} \\ |\ \ \ \ | \\ \mathrm{H—C—C—H} \\ |\ \ \ \ | \\ \mathrm{H}\ \ \mathrm{H} \end{array}$

or ethane (ethyl hydride). By substituting the univalent radical, HO, for one atom of the hydrogen in ethane, we have 

$$\begin{array}{ccccccc} & & \mathrm{H} & & \mathrm{H} & & \\ & & | & & | & & \\ \mathrm{(HO)} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{H}, \text{ or} \\ & & | & & | & & \\ & & \mathrm{H} & & \mathrm{H} & & \end{array}$$

ordinary alcohol (ethyl hydroxide). By successive substitutions of $(CH_3)'$ for H, we may pass from CH_4 to C_2H_6, C_3H_8, C_4H_{10}, or



$$\begin{array}{ccccccccccc} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \\ & & | & & | & & | & & | & & \\ \mathrm{H} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{H}, \text{ etc.} \\ & & | & & | & & | & & | & & \\ & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \end{array}$$

277. Distilled and Fermented Liquors. — By the action of a substance called diastase, formed in barley and other grains during germination, starch is converted into sugar. Great quantities of starch are thus converted into sugar for the manufacture of alcohol. In Europe, the cheapest source of the starch used for this purpose is the potato; in the United States, the starch of Indian corn is more commonly used. The maize is ground, heated with steam until disintegrated, cooled, mixed with germinated barley (i.e., malt), and allowed to stand until the starch is converted into sugar. Yeast is then added and the liquid allowed to ferment until the sugar is converted into alcohol. The resulting liquid is then distilled, the distillate being whisky. A second or third distillation produces nearly pure alcohol. Beer is made in a somewhat similar manner from malt, hops, and water without distillation. Wine is made by the fermentation of fruit juices. The distillation of wine yields brandy.

(*a*) A great deal of alcohol is made by the fermentation of the refuse molasses of sugar manufacture. Beer generally contains from 4 to 6 per cent of alcohol; wine, from 10 to 20 per cent; and brandy and whisky, about 50 per cent.

278. Fermentation. — The change of sugar into alcohol is caused by minute organized bodies that grow in the solution of sugar and feed upon it. When properly fed and kept at a temperature of about 20°, these organisms increase with great rapidity. They are a species of plants and the chief products of their growth are carbon dioxide and alcohol. The germs or seeds of the yeast-plant are generally present in the air so that when a liquid suitable to their growth is exposed to the air under favorable conditions of temperature, the growth of the germs is sure to begin. This is why fruit juices that contain sugar may be changed to alcohol without the addition of yeast. *This process whereby chemical changes are effected by the growth of minute organisms is called fermentation.*

(*a*) There are many kinds of fermentation, each caused by the growth of a special organism or ferment. That caused by the yeast-plant is called the alcoholic fermentation. The souring of milk is caused by another organism called the lactic ferment; such changes are called lactic fermentation. Another organism feeds upon the alcohol produced by the yeast-plant and converts it into acetic acid, so that, under suitable conditions of temperature and exposure, sugar solutions ultimately become sour and are converted into vinegar as will soon be explained more fully. Still other organisms cause the decay of nitrogenous organic substances — the putrefactive fermentation.

(*b*) In general, these ferments tend to break up complex into simpler chemical compounds, to convert the carbon compounds of organized nature back to the final oxidation products, water and carbon dioxide.

(*c*) When the growth of the ferments is prevented, decay ceases; substances may thus be preserved indefinitely. Most of the ferments are killed by long boiling; a few kinds require a higher temperature. In canning fruits and vegetables, the ferments are destroyed by heat, and the access of other germs from the air is prevented by sealing the hot liquid in cans. If air is admitted after the contents of the can are cool, the ferments enter with the air, growth begins, and the fruit is spoiled. A similar result is secured in embalming processes, the ferments being destroyed by poisons, such as arsenic and corrosive sublimate.

279. Properties of Alcohol. — Alcohol is a colorless, volatile, inflammable liquid. It is about four-fifths as heavy as water; its boiling-point is 78°; it remains liquid at very low temperatures, but freezes at about −130°. It absorbs moisture from the atmosphere, and is capable of mixing with water in all proportions. Alcohol that contains no water is called absolute alcohol. The strength of alcohol is generally spoken of by its percentage of "proof-spirits." Proof-spirit is of such a strength that it will just burn; it contains forty-nine per cent of absolute alcohol and fifty-one per cent of water.

280. The Physiological Action of Alcohol. — Concentrated alcohol is an active poison; diluted alcohol taken in large quantities has caused death. As alcohol is partly oxidized in the animal system, it furnishes some heat, but its physiological action is so much more important than its heating value that the temperature of the body is usually lowered by its use. The prolonged use of alcoholic beverages is accompanied by general degenerative changes that usually result in enfeebled vital organs, especially the heart and liver. Alcohol should undoubtedly be classed as a poisonous drug and not as a food. The evil effects of its excessive use are everywhere apparent.

281. Uses of Alcohol. — Alcohol is largely used in the chemical laboratory, in pharmacy, and in the arts. It affords a smokeless fuel and is an indispensable solvent for many substances (such as resins and oils) that are insoluble in water. It is largely used in the preparation of varnishes, perfumes, and medicinal tinctures, and is the fundamental principle of all fermented and distilled liquors.

282. Other Alcohols. — Most of the alcohols that contain a greater number of carbon atoms to the molecule than does ethyl alcohol are of little commercial importance, glycerine being the chief exception. Most of them are liquids that increase in density and in temperature of boiling with the increase in the number of carbon atoms. The highest in the series are solids.

283. Ethers. — As the abstraction of water from the hydroxides of the metals yields metallic oxides, so does the abstraction of water from the alcohols, which are hydroxides of the univalent carbon radicals, yield oxides that are called ethers. Thus methyl alcohol yields methyl ether, and ethyl alcohol yields ethyl ether.

$$2CH_3OH = (CH_3) - O - (CH_3) + H_2O.$$

$$2C_2H_5OH = (C_2H_5) - O - (C_2H_5) + H_2O.$$

This abstraction of water is most readily effected by treatment of the alcohol with strong sulphuric acid.

284. Common Ether. — Ether [" sulphuric ether," ethyl ether, ethyl oxide $(C_2H_5)_2O$] is prepared by distilling a mixture of strong sulphuric acid and alcohol. The distillate, which is a mixture of ether and water, is condensed in a cold receiver and separates into two layers, water below and ether above. The ether is drawn off and wholly freed from water by allowing it to stand over quicklime, and then redistilling it.

Properties of Ether.

CAUTION. — Owing to the danger arising from the extreme volatility and inflammability of ether, the pupil should deal with only minute quantities of this compound.

Experiment 205. — Put 10 or 12 drops of common alcohol and an equal quantity of sulphuric acid into a test-tube and heat gently. The peculiar odor of ether may be recognized.

Experiment 206. — Pour a small quantity of ether into the palm of the hand and notice its rapid evaporation and absorption of sensible heat.

Experiment 207. — Put a few drops of ether into a tumbler, cover loosely and, after the lapse of a minute, bring a flame to the edge of the tumbler. The heavy ether vapor will ignite with a sudden flash.

285. Properties. — Ether is a colorless, volatile, inflammable liquid, having a density of 0.72. It is almost insoluble in water and has a strong and peculiar odor. It is largely used as an anæsthetic in surgical operations. Its common name, "sulphuric ether," comes from the method of its preparation, and is a misnomer; ether contains no sulphur.

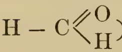
NOTE. — The relations of C_2H_6O and $(C_2H_5)_2O$ to each other and to their common compound radical, ethyl, may be made more evident by the following typical formulas:

Water type.	*Alcohol.*	*Ether.*
$\left.\begin{array}{r}H\\H\end{array}\right\}O$	$\left.\begin{array}{r}(C_2H_5)'\\H\end{array}\right\}O$	$\left.\begin{array}{r}(C_2H_5)'\\(C_2H_5)'\end{array}\right\}O$

Aldehyde.

Experiment 208. — Place a few pieces of potassium dichromate (a good oxidizing agent) in a small flask and pour upon it a few cubic centimeters of strong sulphuric acid. Then add slowly a like quantity of ordinary alcohol and notice the odor.

286. Aldehydes. — This is the general name of a class of compounds intermediate between the alcohols and the hydrocarbon acids. They are derived from their corresponding primary alcohols by the oxidation and removal of two atoms of hydrogen, as is signified by the etymology of the name. By the addition of an atom of oxygen, an aldehyde is converted into an acid.

287. Formic Aldehyde. — Formic aldehyde (CH_2O or  $H-C\begin{smallmatrix}\diagup\!\!\!\diagup O\\ \diagdown H\end{smallmatrix}$) is made by oxidizing methyl alcohol.

$$2CH_4O + O_2 = 2CH_2O + 2H_2O.$$

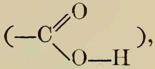
Its solution in water is called formalin. Formalin is a powerful and useful disinfectant.

288. Acetic Aldehyde. — Acetic aldehyde (ordinary aldehyde, ethaldehyde, acetaldehyde, C_2H_4O) is produced by the oxidation of ordinary alcohol (i.e., ethyl alcohol).

$$C_2H_6O + O = C_2H_4O + H_2O.$$

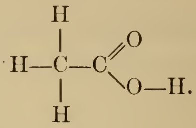
It is a volatile liquid with a characteristic pungent odor. It is easily converted into paraldehyde, a substance of the same percentage composition. Paraldehyde is used in medicine; its vapor-density shows (§ 134) that it is represented by the formula, $C_6H_{12}O_3$.

289. Chloral. — Chloral (C_2Cl_3HO) is a colorless liquid formed by the action of chlorine upon alcohol. With water it forms chloral hydrate (C_2Cl_3HO, H_2O), an easily soluble crystalline compound used in medicine. Just as chloroform may be regarded as a trichlorine substitution product derived from marsh-gas, so chloral may be regarded as a like product derived from aldehyde.

290. Hydrocarbon Acids. — When one or more of the hydrogen atoms of a hydrocarbon molecule are replaced by the hypothetical compound radical carboxyl  $\left(-C\begin{matrix} /\!\!/ O \\ \diagdown O-H\end{matrix}\right)$, an acid is produced. As only the hydrogen of the carboxyl is replaceable by a basic element or group, the basicity of the acid depends upon the number of these carboxyl groups.

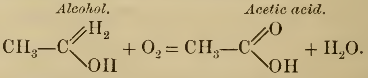
291. Formic Acid. — This acid (CH_2O_2) is of greater theoretical than commercial importance. It is a colorless liquid and occurs in nature in red ants (whence its name), in stinging nettles, and elsewhere. It may be regarded as formic aldehyde (CH_2O) to which an atom of oxygen has been added (§ 286), or as a compound of hydrogen and carboxyl ($H-COOH$). It is the first member of an homologous series called fatty acids, having the general formula $C_nH_{2n}O_2$.

292. Acetic Acid. — This acid ("pyroligneous acid," wood vinegar, $C_2H_4O_2$), when pure, is a colorless liquid having a penetrating odor and an intense acid taste. It is extremely corrosive, causing blisters when brought into contact with the skin. In its pure state, at temperatures below 16°, it is a crystalline solid, known as glacial or crystalline acetic acid. Acetic acid is the second member of the series of fatty acids, and may be regarded as acetic aldehyde to which one atom of oxygen has been added (§ 286), or methane in which one hydrogen atom has been replaced by carboxyl (§ 290).



As it has only one replaceable hydrogen atom, viz., the one in the group COOH, the acid is monobasic. It is this acid that gives the sour taste and peculiar odor to vinegar. Vinegar is a dilute solution of acetic acid with coloring matter and other soluble impurities derived from the juice of the fruit from which it is generally made.

(*a*) If the remaining part of the fermented liquid of Experiment 189 has stood a few days, it may be found to have a sour taste. If it stands long enough, it will be changed to vinegar. By oxidation, the alcohol is changed to acetic acid and water, two hydrogen atoms of the alcohol being replaced by one oxygen atom.



(*b*) Large quantities of acetic acid are also obtained by the destructive distillation of wood in large iron retorts. The liquid portion of the distillate is made, by further treatment, to yield acetic acid. This method of preparation is the origin of the alternative names above recorded.

293. Acetates. — Acetic acid forms a very large and important class of salts called acetates. Lead acetate [$Pb(C_2H_3O_2)_2$], unfortunately called sugar of lead because it is sweet, is a dangerous poison used in medicine. Another well-known salt of acetic acid is copper acetate [$Cu(C_2H_3O_2)_2$], a variety of which is called verdigris.

294. Vinegar. — Vinegar may be made by allowing wine or cider or some dilute alcohol mixed with a little old vinegar to stand in casks with free access of air. The alcohol, under the influence of a peculiar ferment, takes up oxygen, changing first to aldehyde and afterward to acetic acid. By this mode, only a small surface is exposed for oxidation, perhaps one square yard to one hundred gallons. The process will, therefore, be slow. If the same volume of the liquid is exposed in wide, shallow vessels, the oxidation will be more rapid. It will be still better to allow the liquid to trickle over shavings placed in a vessel that allows a free access of air to its interior, giving a surface of exposure of one hundred square yards to a gallon of liquid. The process of oxidation will then go on more rapidly. Vinegar of excellent quality may be thus prepared in a few hours. The process would otherwise require months.

(*a*) Figure 73 shows the plan of a vessel, *AB*. About a foot from the top is a disk, *b b*, perforated with holes one-quarter inch in diameter and about an inch apart. Into these holes cotton wicks, knotted at the top, are placed to conduct the liquid at a proper rate to the space below. Near the bottom another perforated disk

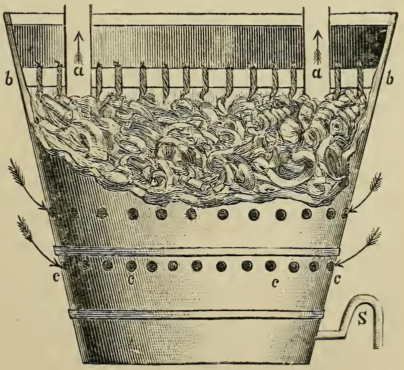


FIG. 73.

is placed. Between these disks the vessel is filled with shavings, upon which the liquid from the space above trickles. Oxidizing air is admitted through holes in the side of the vessel and passes upward, escaping through the tubes or chimneys, *a a*, as shown by the arrows. Old vinegar is first allowed to trickle over the shavings until a gelatinous coating is formed upon them. This coating acts as a ferment. Charcoal in pieces as large as a walnut is said to be better than shavings, serving the double purpose of giving greater surface and of condensing the oxygen of the air in its pores, thus favoring oxidation without the ferment. The vinegar settles slowly to the bottom and is drawn off through a siphon or a stop-cock at *s*.

(*b*) Vinegar is also made in large quantities from dilute alcohol made from corn. This naturally colorless product is usually colored with burned sugar to give it the appearance of fruit vinegar.

(*c*) The peculiar ferment known as "mother of vinegar" is a microscopic fungus which appears on the surface of the liquid, where it absorbs oxygen from the air and subsequently gives it to the alcohol.

295. Other Fatty Acids. — The most important of the higher members of this $C_nH_{2n}O_2$ series are propionic acid ($C_3H_6O_2$), butyric acid ($C_4H_8O_2$), palmitic acid ($C_{16}H_{32}O_2$), and stearic acid ($C_{18}H_{36}O_2$). For reasons that will soon appear it is convenient to mention here a member of the $C_nH_{2n-2}O_2$ series, namely, oleic acid ($C_{18}H_{34}O_2$). The principal vegetable and animal fats and oils are palmitates, stearates, and oleates.

EXERCISES.

1. Write the graphic formula for iodoform.

2. Write the formula for ethaldehyde and paraldehyde. What is the name of the law that justifies the statement that there are three times as many atoms in a liter of the vapor of the latter as in a liter of the vapor of the former?

3. Formic acid is the first member of an homologous series of acids. What one word distinguishes these from other acids?

4. Why is acetic acid monobasic?

5. Write two graphic formulas showing that chloroform may be looked upon as a derivative from marsh-gas.

6. Symbolize the alcohols of the first five members of the paraffin series.

7. What generic term is applied to the hydroxides of the hydrocarbon radicals?

8. Write two graphic formulas showing that wood-spirit may be looked upon (*a*) as a derivative of marsh-gas; (*b*) as a derivative of water.

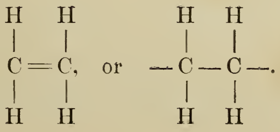
9. Symbolize the acetates of K, Pb″, Cu″, and Ca″.

10. Show that an ether is a dehydrated alcohol.

296. Analogous Hydroxides. — Just as the hydroxide of an univalent hydrocarbon radical is called an alcohol, so the hydroxide of a bivalent hydrocarbon radical is called a glycol, and the hydroxide of a trivalent hydrocarbon radical is called a glycerol. In other words, an alcohol contains one hydroxyl group joined to a carbon atom, a glycol contains two hydroxyl groups united to different carbon atoms, and a glycerol contains three hydroxyl groups united to three carbon atoms.

(*a*) Glycols and glycerols are sometimes spoken of as more complex alcohols.

297. Glycols. — In our study of the marsh-gas series, we have had to do with a series of univalent compound radicals (§ 257, *c*) that bore a very simple relation to the paraffins themselves. In the ethelyne or olefiant-gas series, the successive homologues may act either as saturated molecules, i.e., in the free state, or as bivalent compound radicals.

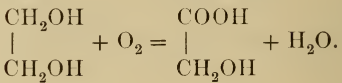


$$\begin{array}{ccc} H & & H \\ | & & | \\ C & = & C \\ | & & | \\ H & & H \end{array}, \quad \text{or} \quad \begin{array}{ccccc} & H & & H & \\ & | & & | & \\ - & C & - & C & - \\ & | & & | & \\ & H & & H & \end{array}.$$

From these bivalent radicals are built up, in a now familiar way, series of glycols, acids, etc., many of them with numerous isomeric forms. As common alcohol is ethyl hydroxide, C_2H_5-OH, so ordinary glycol is ethylene dihydroxide, $C_2H_4(OH)_2$. By this process of adding $(OH)_2$ to the formulas for the successive members of the ethylene series, we obtain the formulas for a series of glycols, analogous to the series of alcohols.

298. Oxalic Acid. — The oxidation of the glycols gives a series of hydrocarbon acids, at least one member of which is of industrial importance. If ordinary glycol is gently oxidized, glycolic acid is produced.

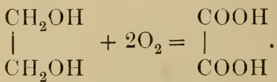
Glycol. *Glycolic acid.*



$$\begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array} + O_2 = \begin{array}{l} COOH \\ | \\ CH_2OH \end{array} + H_2O.$$

As the familiar carbonyl group herein appears but once, glycolic acid is monobasic (§ 290). If the glycol is more completely oxidized, oxalic acid is produced.

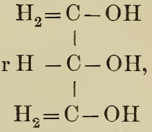
Glycol. *Oxalic acid.*



$$\begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array} + 2O_2 = \begin{array}{l} COOH \\ | \\ COOH \end{array} .$$

Evidently this acid, $C_2H_2O_4$, is dibasic. Both of these acids are found in nature. Oxalic acid is an active poison. It is used in calico-printing, in straw-bleaching, in cleaning brass and other metals, in removing ink-stains from cloths, etc. It is prepared on the small scale by the action of nitric acid upon granulated sugar, and on the large scale by heating wood shavings or sawdust with sodium and potassium hydroxides. As it forms harmless salts with calcium and magnesium, its best antidote is chalk or magnesia. If neither of these is at hand, the whitewash scraped from a wall may be used.

299. Other Vegetable Acids. — Lactic acid ($C_3H_6O_3$) is made by the lactic fermentation of sugar (§ 278, *a*). Malic acid ($C_4H_6O_5$) occurs in many fruits, such as apples, cherries, etc. Tartaric acid ($C_4H_6O_6$) is widely distributed in fruits such as grapes, cucumbers, potatoes, berries of the mountain-ash, etc. It is prepared from argol, an acid potassium tartrate ($KHC_4H_4O_6$) that is deposited in crusts from fermenting wines. Purified argol is called cream of tartar. Tartaric acid is dibasic. It is largely used in dyeing, in calico-printing, and in the manufacture of baking-powders. Sodium-potassium tartrate is called Rochelle salt. Tartar emetic is a tartrate of potassium and antimony. Citric acid ($C_6H_8O_7$) also occurs in many fruits, especially lemons, from the juice of which it is prepared.

300. Glycerin. — Glycerin, $C_3H_5(OH)_3$, or 

$$\begin{array}{rcl} H_2= & C & -OH \\ & | & \\ H\ - & C & -OH, \\ & | & \\ H_2= & C & -OH \end{array}$$

is produced in small quantities in the fermentation of sugar, nearly three per cent of the products being glycerin. It is also a by-product of soap-making and of the manufacture of stearic acid.

(*a*) Glycerin may be regarded as a hydroxide of the trivalent compound radical glyceryl, C_3H_5. Being the hydroxide of a trivalent hydrocarbon radical (§ 296), it is a glycerol, an analogue of alcohol and glycol.

301. Properties of Glycerin. — Glycerin is a sweet liquid of syrupy consistency, and without odor or color. It is non-volatile under ordinary conditions. At $-40°$, it solidifies to a fine crystalline mass. Glycerin is soluble in water and in alcohol in all proportions. It absorbs moisture from the atmosphere and ranks next to water as a solvent.

302. Uses. — Glycerin is used in the manufacture of nitroglycerin and dynamite. On account of its oily and non-volatile properties, it is used as a lubricant for watch- and clock-work. The same properties and its antiseptic nature make it useful as an application to the skin to keep it soft and pliable and to prevent chapping.

303. Natural Fatty Bodies. — Nearly all the fats, oils, and waxes of the animal and vegetable kingdoms are compounds of the hydrocarbon acids. The most important of these fats and oils are palmitin, stearin, and olein. Palmitin and stearin predominate in the composition of the solid fats, and olein in that of the oils.

(*a*) Palmitin, stearin, and olein may be regarded as salts formed by substituting the trivalent radical glyceryl (C_3H_5) for three atoms of hydrogen in three molecules of their respective acids (§ 295). Thus palmitin is glyceryl palmitate [$C_3H_5(C_{16}H_{31}O_2)_3$], stearin is glyceryl stearate [$C_3H_5(C_{18}H_{35}O_2)_3$], and olein is glyceryl oleate [$C_3H_5(C_{18}H_{33}O_2)_3$].

Soap-making.

Experiment 209. — In an iron pot boil for about an hour 115 grams (a quarter of a pound) of lard with a solution of 40 grams of caustic soda in 250 cu. cm. of water. When the liquid is cooled, add a strong solution of common salt. Soap will rise to the surface and become solid when cold.

304. Soaps. — *Soaps are salts formed by the substitution of the alkali metals for the glyceryl in the fats*, i.e., *they are the alkali salts of the fatty acids*, especially palmitic and stearic acids. The following shows the reaction:

$$\overset{\textit{Stearin.}}{C_3H_5(C_{18}H_{35}O_2)_3} + \overset{\substack{\textit{Sodium}\\ \textit{hydroxide.}}}{3NaOH} = \overset{\textit{Sodium stearate.}}{3Na(C_{18}H_{35}O_2)} + \overset{\textit{Glycerin.}}{C_3H_5(OH)_3}.$$

Common soap may be prepared by boiling tallow in a weak solution of sodium hydroxide. As saponification proceeds, stronger solutions are to be added until all the grease disappears. If the fat was boiled in a strong lye at first, a coating of soap would be formed around it, protecting it from further action of the lye, soap being insoluble in a strong alkali solution. The soap, when formed, is in solution in the water and glycerin that are present. From this solution it may be separated by adding common salt to form a brine in which the soap is insoluble. The soap will rise and become a solid at the surface; the glycerin will remain in solution.

(*a*) Soft soap is potassium palmitate and stearate; hard soap is sodium palmitate and stearate.

Experiment 210. — Pass carbon dioxide through half a liter of dilute lime-water until the precipitate that is formed is dissolved. Rub a bit of soap between the hands wet with this hard water.

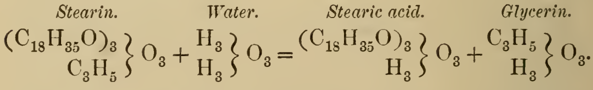
Experiment 211. — Repeat Experiment 210, using a hard water made by shaking some powdered gypsum with a liter of soft water.

305. Properties. — Soap is soluble in water or in alcohol. If a large quantity of water is added to a solution of soap, some of the soap is decomposed, setting a portion of the alkali free in solution and precipitating an insoluble acid sodium stearate in pearly scales. It is this property that renders soap useful as a cleansing agent. The large amount of water used decomposes the soap, the alkali enters into composition with the grease of the dirt, and renders it soluble in the water. The fatty acid is carried away in the lather formed.

When soap is added to a hard water, insoluble calcium or magnesium salts of palmitic and stearic acids are formed. All of these insoluble salts must be precipitated before the soap can have any cleansing action.

(*a*) Many soaps contain adulterants such as soluble silicates, resin, sand, pipe-clay, etc. When the genuine article can be had, Castile soap made of olive-oil is the best of all soaps.

306. Saponification. — Any process by which the fatty acids and the glycerin are separated and set free is called saponification. Soap-making is but one process. Glycerin may be separated from the fatty acids by means of superheated water, the latter behaving, at a high temperature, much as do the alkalies.



Stearin. *Water.* *Stearic acid.* *Glycerin.*

$$\left.\begin{matrix}(C_{18}H_{35}O)_3\\ C_3H_5\end{matrix}\right\}O_3 + \left.\begin{matrix}H_3\\ H_3\end{matrix}\right\}O_3 = \left.\begin{matrix}(C_{18}H_{35}O)_3\\ H_3\end{matrix}\right\}O_3 + \left.\begin{matrix}C_3H_5\\ H_3\end{matrix}\right\}O_3.$$

307. Common Fats. — The common fats are mixtures of the natural fats mentioned above. Tallow is composed mostly of stearin. Olein predominates in lard. Butter is distinguished from the other fats by containing butyrin, the glycerin salt of butyric acid. It is to this salt that the pleasant odor and flavor of fresh butter are due. In rancid butter, some of the butyric acid has been set free, imparting its disagreeable odor. The acid may be removed and the butter made sweet by sufficient washing with water. In trade parlance, such butter is said to be "renovated." When the fatty part of beef suet is separated from the fibrous matter and then melted in tanks surrounded with water of a temperature of 50°, a clear yellow oil is obtained. This oil is allowed to solidify, and is then subjected to pressure at a temperature of 32°. From the oil that flows away, great quantities of artificial butter are now made. This is done by mixing this oil with lard and cotton-seed oil, and churning the mixture with milk to give it the taste and odor of true butter. The product is called butterine or oleomargarine, and differs but slightly in chemical composition from true butter. The stearic acid separated from fats is a white solid largely used in the manufacture of candles.

308. Oils.—Oils are liquid fats that exist ready formed in nature. Most of them are fluid at ordinary temperatures. They are insoluble in water but completely soluble in ether. Most of them are only sparingly soluble in alcohol. Oils are classified as fixed oils and essential oils. The fixed oils leave a permanent stain on paper and can not be distilled without decomposition. They are glyceryl salts and form soaps with alkaline bases, as already illustrated. They are grouped according to their origin, as vegetable oils and animal oils. The essential oils are volatile and not capable of saponification.

(*a*) The vegetable oils occur chiefly in the seeds of plants or in the pulp about the seeds. They are usually divided into two groups, the drying oils and the non-drying oils. The drying oils, like linseed-oil, absorb oxygen on exposure to the air, sometimes with the evolution of so much heat that spontaneous combustion takes place. They are extensively used in making varnishes and mixing paints. Castoroil is a connecting link between the drying and the non-drying oils. The non-drying oils like olive- (sweet-) oil and cotton-seed oil become rancid on exposure to the air.

(*b*) The animal oils are glyceryl salts of the fatty acids, and so rich in oleic acid that they remain liquid at ordinary temperatures. Sperm-oil, train-oil, cod liver oil, neat's-foot oil, and lard oil are familiar members of this group. They have a characteristic and persistent odor which in some of the fish oils is peculiarly offensive.

(*c*) The essential or volatile oils are generally obtained by distilling the parts of plants in which they occur. They are soluble in alcohol or ether. Some of them, like the oils of lemon and of orange, are so abundant in the leaves and the skin of the fruit that they may be separated by mechanical pressure. Most of them are isomeric or polymeric with oil of turpentine ($C_{10}H_{16}$), and absorb oxygen rapidly. By such absorption the oil of turpentine acquires the properties of ozone and often bleaches the inner end of the cork of the bottle that contains it. Essences are prepared from the essential oils by distillation with water or by the addition of water in sufficient quantity to hold the oils in emulsion.

309. Aniline Dyes. — The fact that many hydrocarbons, including benzene, toluene, naphthalene, anthracene, and carbolic acid, are obtained from coal-tar, and that some of these serve as starting-points in the preparation of many other hydrocarbons, has already been stated (§§ 268, *c*, and 265). Thus, when benzene is treated with nitric acid, the products of the reaction are nitrobenzene ($C_6H_5NO_2$) and water. Nitrobenzene is a yellow liquid with an odor much like that of oil of bitter almonds. When nitrobenzene is treated with a solution that yields nascent hydrogen, its oxygen is replaced thus:

$$C_6H_5NO_2 + 6H = C_6H_5NH_2 + 2H_2O.$$

This product, $C_6H_5NH_2$, is a colorless liquid known as aniline. By treating aniline and a similar substance known as toluidine with mercuric chloride or arsenic acid, the dye called magenta is produced. Most of the aniline dyes, of which there are many and some of which are very beautiful, are prepared from magenta.

310. Other Aromatic Compounds. — As many of these coal-tar products have a pleasant aromatic odor, they are often called aromatic compounds. By oxidizing toluene (C_7H_8), which it will be remembered is found in coal-tar, benzoic acid ($C_7H_6O_2$) is produced. This acid also occurs in gum benzoin and in the balsams of Peru and Tolu. By the removal of an atom of oxygen from the formula for benzoic acid, we have the formula for the oil of bitter almonds (C_7H_6O). Thus, the oil of bitter almonds is benzoic aldehyde (see § 286). The oil of bitter almonds occurs in bitter almonds, laurel-leaves, cherry-stones, etc. The preparation of this "organic" compound from coal-tar, and its use in turn in the preparation of artificial indigo, constitute one of the historic victories by which modern chemistry broke down the ancient wall between organic and inorganic chemistry.

(*a*) Anthracene, another constituent of coal-tar, is largely used in the preparation of alizarin. This well-known dye was formerly obtained from madder-root. Now the artificial alizarin is almost exclusively used for dyeing Turkey red.

311. Carbolic Acid. — This familiar substance, sometimes called phenol (C_6H_6O or C_6H_5OH), may be considered as benzene in which hydroxyl has replaced one of the hydrogen atoms. It is extracted from coal-tar. It is not properly an acid, but it has some acid properties. It is extremely corrosive and poisonous, and is extensively used as a disinfectant.

EXERCISES.

1. Give the name and valence of C_3H_5 and write its graphic formula.

2. Why was salt added at the end of Experiment 209?

3. What is the difference between the composition of soft soap and that of hard soap?

4. Can you detect in the name carboxyl a suggestion of the names of two or more simple compound radicals of which we may suppose that carboxyl is made up?

5. Propionic acid is the third member of an homologous series of which the first is formic acid. Write the formula for propionic acid. Write the general formula for the series.

6. Give the formula and name of the eighteenth member of this acid series.

7. What is the general name for the hydroxide of a trivalent hydrocarbon radical?

8. By the progressive oxidation of ordinary glycol, two different acids are formed one of which is monobasic, the other dibasic. Give their names and the name of the atomic group that determines their basicity.

9. Outline in succession the changes in the condition of a particle of carbon as it completes the cycle of a constituent of the atmosphere, of vegetable matter, of animal matter, and of the atmosphere again.

10. (*a*) How much soap may be made by the use of 10 pounds of pure stearin? (*b*) How much sodium hydroxide must be taken?

11. How much glycerin is there in 100 kilograms of tallow, supposing the latter to be pure stearin?

12. Write the formula of a lead soap and of a calcium soap.

13. When soap is dissolved in water containing $CaSO_4$, a reaction takes place giving an insoluble calcium soap. Write the reaction.

14. If an excess of H_2SO_4 is added to a small quantity of CH_2O_2 in a test-tube, and a gentle heat is applied, a regular disengagement of gas takes place. The gas comes from the decomposition of the fatty acid and burns with a blue flame. Water is formed at the same time. Write the reaction.

15. (*a*) What is the name of $CH_3 — CH_2 — CH_2 — CH_3$? (*b*) Write its full structural formula.

16. Show that chlorine is diatomic.

17. Write the reaction for the production of nitrobenzene from benzene.

18. Write the reaction for the preparation of aniline from nitrobenzene. What peculiar condition of the gas used is necessary to the reaction?

19. From the formula for olein (glyceryl oleate) determine the basicity of oleic acid. Write a structural formula for oleic acid that shall indicate its basicity by the number of its carboxyl groups.

20. Show by graphic formulas that a valuable disinfectant may be provided by oxidizing methyl hydroxide and dissolving the product in water. Give the name of this disinfectant.

VII. THE CARBOHYDRATES.

312. Carbohydrates. — The carbon compounds of this class include the most abundant substances found in the vegetable kingdom. Each of them consists of hydrogen and oxygen in the proportions to form water, and combined with six atoms of carbon or some multiple of six atoms of carbon for each molecule of the carbohydrate. As they enter largely into the economy of plant and animal organisms, they are of great physiological importance.

There are three general classes as follows:

1. $C_{12}H_{22}O_{11}$; as sucrose.
2. $C_6H_{12}O_6$; as dextrose and levulose.
3. $C_6H_{10}O_5$; as starch, inulin, dextrin, and cellulose.

The members of the first two groups are called sugars; they are soluble in water, and are more or less sweet in taste. The third group is composed of compounds, many of which are insoluble in water, and are capable of being converted to some of the members of the second group. The members of the first group may all be converted to those of the second, but no method of changing the inferior sugars of the second class to the more valuable cane-sugar of the first has yet been discovered.

313. Sucrose. — Sucrose (cane-sugar, $C_{12}H_{22}O_{11}$) is found in the juice of certain plants, as sugar-cane, sugar-maple, sugar-beet, sorghum, and many other plants. In the manufacture of cane-sugar from sugar-cane, the juice is pressed from the canes by passing them between rollers. The juice is treated with milk of lime and heated. The lime neutralizes the acids and the heat coagulates the albumen in the juice. The coagulated albumen rises and mechanically carries with it many of the impurities, some of which have combined with the lime. The scum thus formed is removed, and the liquid evaporated until it is of such a consistency that sugar crystals will form when the liquid is cooled. The crystals, when drained, are "brown" or "muscovado" sugar. The liquid remaining is molasses.

(*a*) Brown sugar is refined by dissolving it in water, filtering the solution through layers of animal charcoal, and evaporating the water from the filtrate. When sucrose is boiled, part of it is changed to a mixture of dextrose and levulose, the proportion thus changed depending upon the temperature and time of boiling. To lessen this loss of sucrose, the filtered solution is evaporated in large vacuum-pans from which the air and steam are exhausted. The degree of concentration desired is thus secured more quickly and at a lower temperature, lessening the loss and obviating the risk of burning. When the "mother-liquor" drains from the crystals in molds, loaf-sugar is left; when it is driven off by a centrifugal machine, granulated sugar is left.

(*b*) Formerly, sugar was made almost wholly from the sugar-cane and, as this grows only in a warm climate, nearly all of the sugar came from warm countries. More recently, large and increasing quantities of sugar are made from the sugar-beet. As this plant grows in a temperate climate, France, Austria, Russia, and the United States have become important sugar-producing countries. When in the seventeenth century, sugar was first found to be a constituent of the beet, the beets contained only about 2 per cent of sugar. By skillful and long-continued cultivation, this percentage has been increased to 18 or 20. At the sugar factory, the beets are washed and cut into small, thin strips. These strips are put into large iron vats with warm water which dissolves out some of the sugar. This first water is then replaced by a fresh supply, and the process repeated until all the sugar is extracted. This process of removing the sugar from the pulp is called the diffusion method, and is now largely used with sugar-cane also. The juice thus obtained is purified by lime, bleached by sulphurous oxide, and evaporated in vacuum-pans as in the other method of refining.

(*c*) The sugar from the sap of the sugar-maple or from the juice of the sugar-beet is identical with cane-sugar. As the impurities of maple-sugar are agreeable to the taste of many persons, the sugar is not refined. Beet-sugar is always refined, as its impurities are offensive to all.

(*d*) Sugar of milk or lactose ($C_{12}H_{22}O_{11} + H_2O$) occurs in the milk of mammals. It is made from the whey of milk after the fat or butter, and the casein or cheese have been removed. It is less sweet and less easily soluble in water than cane-sugar. It may be used as a food by invalids and children who can not digest ordinary sugar. About 4 per cent of milk is lactose.

(*e*) Maltose ($C_{12}H_{22}O_{11}$) is formed by diastase from starch in the process of brewing.

(*f*) When sugar is heated to about 210° or 220°, it loses water and is converted into caramel.

314. Dextrose and Levulose. — When a solution of sucrose is boiled with an acid or subjected to the action of yeast, it is converted into two isomeric varieties of sugar, dextrose (glucose, grape-sugar, starch-sugar, $C_6H_{12}O_6$), and levulose (fruit-sugar, $C_6H_{12}O_6$).

$$\underset{\textit{Sucrose.}}{C_{12}H_{22}O_{11}} + H_2O = \underset{\textit{Dextrose.}}{C_6H_{12}O_6} + \underset{\textit{Levulose.}}{C_6H_{12}O_6}.$$

This mixture of dextrose and levulose is called invert-sugar.

(*a*) Dextrose is found in many ripe fruits. The "candied" sugar of raisins and other dried fruits is dextrose. It crystallizes with difficulty and is generally found in a syrupy condition. It is prepared by boiling starch ($C_6H_{10}O_5$) in water acidulated with sulphuric acid. It has less sweetening power than sucrose. Large quantities of glucose are now made from Indian corn. The corn-starch or potato-starch is boiled with dilute sulphuric acid for several hours. When it has cooled, the acid is neutralized with lime, and the solution is filtered. It is then evaporated to a syrup and sold as glucose or corn-syrup, or evaporated further to crystallization, and sold as grape-sugar. Large quantities of both varieties are used in the manufacture of candies and syrups of all kinds and in the manufacture of alcoholic liquors. In the reaction, the acid does not enter into any combination, but facilitates the taking up of water by the starch.

$$C_6H_{10}O_5 + H_2O = C_6H_{12}O_6.$$

(*b*) Levulose is found with dextrose in many ripe fruits, in honey, molasses, etc. It does not crystallize. It has less sweetening power than sucrose.

(*c*) Dextrose and levulose may be fermented (Experiment 189); sucrose can not be fermented until after its conversion into dextrose and levulose.

Starch.

Experiment 212. — Grate a large potato on a fine grater, and stir the potato particles into about a quart of water. Allow the coarser particles to settle, and decant the still white, milky liquid into another vessel. Let this stand for several hours, or until the liquid clears. Then pour off the water and dry the remaining starch. Boil a little of the dry starch in water. Largely dilute a little of the paste thus formed and test it with iodine as in Experiment 131. Successively dilute the remaining paste, testing a little of it after each dilution, and see how small a quantity of starch you can thus detect.

Experiment 213. — Place a particle of the starch on a glass, add a drop of water, cover it with a thin cover-glass, and examine it with a microscope that magnifies about three hundred diameters. Observe the shape and markings of the granules. Make similar observations with corn-starch, wheat-flour, buckwheat-flour, tapioca, and sago. Compare the form and appearance of the several granules until you are able thus to identify the source of each. By sufficiently magnifying, the source of most kinds of starch may be positively identified.

315. Starch. — Starch ($C_6H_{10}O_5$) is a familiar substance found in grain (e.g., wheat and Indian corn), in the tuber of the potato plant and in the root, stem, or fruit of many other plants. It is composed of microscopic granules which, when heated in water nearly to the boiling-point, swell and burst, forming a pasty mass. This starch paste forms a blue color with iodine.

(*a*) Tapioca, arrow-root, sago, and inulin are varieties of starch. The finest flour contains about 70 per cent of starch, and about 10 per cent of gluten, a substance that in many respects resembles the white of eggs.

316. Dextrin. — When a starch is heated to about 210°, it is changed to an isomeric compound called dextrin. Unlike starch, dextrin is soluble in cold water, forming a mucilaginous liquid. The adhesive compound on postage-stamps is largely dextrin. When starch is boiled in dilute sulphuric acid, it is converted first into dextrin and then into glucose.

317. Bread-making. — In making bread, the water that is added to the flour forms a dough. The addition of yeast causes the starch to go to sugar, and fermentation to begin. As the fermentation proceeds, the carbon dioxide produced tends to escape through the tenacious dough, causing the latter to "rise." In the subsequent process of kneading, the half-fermented "sponge" is evenly distributed through the loaf and the large bubbles of gas imprisoned in the dough are broken up into smaller ones and the bread thus made finer grained. After kneading, the molded loaves are allowed to ferment again until they rise properly, when they are placed in a hot oven. The heat stops the fermentation, vaporizes the alcohol, and expands the vapor and the carbon dioxide. As these aëriform substances escape through the loaf, the loaf increases in size and "lightness." If the process has been satisfactorily conducted, by the time that the escape of gas and vapor has ceased, the walls of the bread cells will be strong enough to retain their form. If the dough is allowed to stand too long before baking, the gas will escape, the still plastic walls of the bread cells will collapse, and the bread "fall." If the oven is not hot enough or if the dough is too wet, a similar result will ensue and the bread will be "slack-baked." If the oven is too hot, a crust will form too quickly, the gas, being prevented from escaping, will collect at the center and the loaf be hollow. At the surface of the loaf, a substance much like caramel is formed; this is the crust. The crust also contains dextrin. When the crust is moistened and the loaf returned to the oven, the dissolved dextrin left by evaporation gives to the crust a smooth, shining surface.

The temperature at which the dough is kept during the fermentation is important. The yeast-plant grows best at a temperature of about 21° or 22°. If the sponge or dough becomes a few degrees cooler than this, the growth of the yeast is checked and the bread-rising stops. If the temperature is a few degrees higher, the growth of the germs of the acetic acid ferment is favored and that of the yeast-germs hindered, so that the dough becomes sour; then the bread will be sour and heavy. Success demands fresh, healthy yeast-plants to start the fermentation, and the maintenance of the temperature most favorable to their growth while the bread is rising.

Vegetable Parchment.

Experiment 214. — Dilute 25 cu. cm. of sulphuric acid with 10 or 12 cu. cm. of water. When the mixture is cold, immerse in it, for 15 or 20 seconds, a piece of filter-paper. Rinse the paper in water and then in dilute ammonia-water, to remove all traces of the acid. Finally, rinse the paper again in pure water. The paper will have acquired greater toughness and rigidity and will resemble parchment in other respects. It has been changed to vegetable parchment or parchment-paper. It may be necessary to repeat the experiment, varying the time of immersion, to get good results.

318. Cellulose. — Cellulose ($C_6H_{10}O_5$) constitutes the outer wall of every vegetable cell and is, therefore, found in every part of every plant. It may be said to form the framework of every vegetable tissue. It is insoluble in water or in alcohol, but may be dissolved in concentrated sulphuric acid. By diluting and boiling this solution, the cellulose may be converted into dextrose and dextrin. Rags, paper, wood, and other forms of cellulose may thus be used in the preparation of glucose and alcohol. Linen and cotton are nearly pure cellulose.

(*a*) Paper consists almost wholly of cellulose. The various forms of vegetable fiber used in its manufacture (linen and cotton rags, wood, straw, etc., according to the kind of product desired) are reduced to pulp partly by mechanical means and partly by boiling with caustic soda. This pulp diluted with the necessary amount of water is poured over an apron upon a steadily moving cloth made of fine brass wire specially woven for this purpose. The water drains from the pulp through this wire cloth. The paper gains in strength by the gradual loss of water, until the web is strong enough to be led without breaking from the wire cloth to the press rolls, the drying cylinders, etc.

(*b*) By treating cellulose with a mixture of nitric and sulphuric acids, it is changed to gun-cotton (nitrocellulose, pyroxylin), an explosive substance that burns in the air with a sudden flash and no smoke (see § 83). Gun-cotton may be considered to be cellulose with some of its hydrogen atoms replaced by the compound radical NO_2. A solution of gun-cotton in a mixture of ether and alcohol, known as collodion solution, is much used in photography. Celluloid is an intimate mixture of gun-cotton and camphor. When heated, it is so plastic that it can easily be molded. It hardens as it cools.

Albumin.

Experiment 215. — Place a teaspoonful of the white of an egg in a test-tube; add 25 cu. cm. of C_2H_6O. Notice the coagulation.

Experiment 216. — Place the remainder of the white of the egg in a test-tube; place the test-tube and a thermometer in a vessel of water; heat the water; notice that at the temperature of about 60° the white of the egg coagulates.

319. Albuminoids. — Albumin is composed of carbon, hydrogen, oxygen, nitrogen, and sulphur — a very complicated structure. It is typical of a group of bodies (histogenetic) that are essential to the building up of the animal organism, of which group the leading members are albumin, fibrin, and casein. These differ but little, if any, in their chemical composition, but widely in their properties. They all exist in two conditions, — the soluble and the insoluble.

(*a*) The white of the eggs of birds is the most familiar instance of albumin. It is soluble in water and coagulated by heat or alcohol. The albumin of plants is found chiefly in the seed.

(*b*) Soluble fibrin is found in the blood. It hardens on exposure to the air and, entangling the corpuscles of the blood, forms the clot. By washing the clot with water, fibrin is left as a white, stringy mass. Insoluble fibrin constitutes muscular fiber.

(*c*) Casein is found in the milk of animals. It is not coagulated by heat, but is coagulable by rennet, the inner membrane of the stomach of the calf. This property is utilized in cheese-making. Cheese contains from 10 to 40 per cent of fat and from 20 to 40 per cent of casein, most of the remainder being water.

(*d*) All of the albuminoids are amorphous, and may be kept, when dry, for any length of time; when moist, they rapidly putrefy and produce a sickening odor.

Gelatin.

Experiment 217. — Dilute a quantity of hydrochloric acid with about six times its volume of water. Place a clean bone (e.g., the femur of a chicken) in the dilute acid, and allow it to remain for three or four days. The mineral part of the bone will gradually dissolve, and there will be left a flexible substance that preserves the shape of the bone.

Experiment 218. — Place the flexible substance left from the last experiment in water and boil it for three or four hours. It will dissolve and, when the liquid cools, will assume a jelly-like condition.

320. Gelatin. — The bones and skins of animals contain a substance called ossein. The product of Experiment 217 was ossein. When this substance is boiled in water, gelatin is produced. The product of Experiment 218 was gelatin. Glue is an inferior quality of gelatin.

321. Food of Animals. — The substances just considered, i.e., the sugars, starch, cellulose, albumin, and gelatin, constitute almost wholly the food of animals. The necessity for such food is threefold, — to build new tissue, to repair wasted or injured tissue, and to furnish heat. As almost all animal tissues are nitrogen-containing substances, the tissue-forming food-stuffs are of the albumin class (albuminoids or proteids). The heat supply is chiefly met by the fats and the carbohydrates, starch and sugar (amyloids). Only ruminant animals with special stomachs can digest cellulose freely.

(*a*) Much the larger part of the needed food is required for heating purposes. Consequently, only a small proportion of the food necessary consists of meat and other nitrogenous foods except in the case of rapidly growing persons. Milk contains from 3 to 7 per cent of fat, about 4 per cent each of sugar and casein, and 0.7 per cent of mineral matter. It is a well-proportioned food for growing persons, but is rather too high in nitrogenous constituents for persons whose tissues do not need heavy growth or repair.

EXERCISES.

1. Why does it require more sugar to sweeten fruits when the sugar is added before cooking than it does when the sugar is added after cooking?

2. Write the formula for dextrin.

3. Name the compounds symbolized as follows: BaO, BaO_2, Hg_2O, HgO, N_2O, NO, N_2O_3, N_2O_5, NO_2.

4. How many liters of chlorine are required for the combustion of 10 liters of olefiant gas? $C_2H_4 + 2Cl_2 = 4HCl + C_2$.

5. (*a*) Give a reaction for the preparation of carbon dioxide. (*b*) How may this gas be distinguished from every other gas? (*c*) How much of it is produced by burning 10 liters of marsh-gas?

6. In the analysis of a certain compound, the following data were obtained:

Carbon . .	= 62.07 per cent.	Oxygen . .	= 27.58 per cent.
Hydrogen .	= 10.35 " "	Vapor-density	= 58 " "

What is the molecular formula of the compound? What is the general formula of the acid series to which it belongs?

7. (*a*) Find the percentage composition of marsh-gas. (*b*) Of olefiant gas.

8. What weight of $KClO_3$ is necessary to the preparation of 35,000 cu. cm. of oxygen?

9. On completely decomposing, by heat, a certain weight of potassium chlorate, I obtained 20.246 grams of potassium chloride. (*a*) What weight of $KClO_3$ did I use? (*b*) What volume of oxygen did I obtain?

10. To inflate a certain balloon properly requires 132.74 kilograms of hydrogen. What weight of zinc will be needed to prepare this quantity of hydrogen?

11. Explain the statement that in burning acetylene the heat given out by the combustion of its constituents is increased by the decomposition heat of the C_2H_2.

12. When a fat is heated with a stronger base than glycerin, the fatty acids leave the glycerin and combine with the metallic base. What is the name of the compound thus formed?

13. State two ways in which albumin may be coagulated.

14. Sketch in outline the several steps in the preparation of alcohol from cotton cloth.

15. State in general terms the composition of carbohydrate molecules.

16. In what way are alcohols and glycols analogous?

17. How is carboxyl related to the basicity of a hydrocarbon acid?

18. What is the cause of the chemical changes involved in fermentation?

19. Of what is ordinary alcohol the hydroxide?

20. Of what hydrocarbon is chloroform a substitution product?

VIII. OTHER ELEMENTS OF THE CARBON FAMILY.

322. Rare Elements of this Family. — Titanium, zirconium, cerium, and thorium are rare metals not found native. Their most common oxides are analogous to the dioxides of carbon and silicon. At 100° titanium decomposes water, and at high temperatures it has the rare power of uniting directly with free nitrogen. When, as a metallic powder, titanium or cerium is sifted into a flame, it burns with dazzling brilliance. Zirconium dioxide is a white, infusible powder, and gives out an intense white light when heated. Like cerium dioxide, it forms a small constituent of the mantles used in gas-lighting by the Welsbach system. From ninety-eight to ninety-nine per cent of the Welsbach mantles consist of thorium oxide (ThO_2). A fine-meshed cotton cloth of the desired shape is saturated with nitrate of thorium and small proportions of the nitrates of zirconium and of cerium. When this is burned, the nitrates are decomposed and mantles of the oxides of the metals result. The combustion of the gas heats these mantles to such a degree of incandescence that they emit several times as much light as would the mere combustion of the same quantity of the gas.

EXERCISES.

1. Describe the preparation and state the principal properties of H_2S, HCN, CH_4, and C_2H_6O.

2. Write the symbols representing chloroform, glycerin, ether, acetic acid, cane-sugar, and starch.

3. (*a*) Name the products of the combustion of common alcohol. (*b*) Describe briefly the process of preparing coal-gas, and tell its composition.

4. Name the substances symbolized as follows: KNO_2, KNO_3, KCl, $KClO$, $KClO_2$, $KClO_3$, $KClO_4$.

5. (*a*) Find the weight of 20 liters of oxygen. (*b*) Of 50 liters of chlorine. (*c*) Of 250 liters of NH_3.

6. What materials and what quantities would you need to prepare 50 liters of each of the oxides of carbon?

7. By heating MnO_2 with H_2SO_4 the following reaction takes place:

$$2MnO_2 + 2H_2SO_4 = 2MnSO_4 + 2H_2O + O_2.$$

(*a*) What weight and (*b*) what volume of oxygen can be thus obtained from 50 grams of manganese dioxide?

8. (*a*) Give the ordinary methods of preparing oxygen, hydrogen, and hydrochloric acid. (*b*) In what do they differ, and in what do they agree? (*c*) Find the amount of chlorine, by weight and by measure, in 2 kilograms of hydrochloric acid.

9. If 100 liters of CO_2 are required, by what means would you obtain it, from what materials, and what quantity of each material?

10. A taper is burned in a glass cylinder, at the bottom of which is a little lime-water. Explain the observed formation of a crust on the surface of the liquid.

11. Show by a graphic formula that the compound radical carboxyl (CO_2H) is univalent.

12. What is the molecular weight of ammonia gas? Determine from that weight the density of the gas.

13. Increase threefold the number of each kind of atoms in a molecule of acetic acid. The molecular formula thus produced symbolizes two isomeric carbohydrates. Give the names of the two substances thus symbolized.

IX. THE SILICON FAMILY.

SILICON: symbol, Si; density (of crystals), 2.5; atomic weight, 28; valence, 4.

323. Silicon. — Although this element does not occur free in nature, it is the most abundant and widely diffused of the elements except oxygen. In combination as silica or as metallic silicates, it forms a large part of the earth's crust.

(*a*) Free silicon may be prepared in several ways, but the processes are difficult and the element is rare.

(*b*) Silicon exists, like carbon, in three allotropic forms; as a soft brown, amorphous powder that burns easily in air or oxygen forming SiO_2; as hexagonal plates, corresponding to graphite in luster and electric conductivity; as needle-shaped octahedral crystals that are hard enough to scratch glass.

(*c*) There is a compound of hydrogen and silicon known as hydrogen silicide (SiH_4) that is somewhat analogous to CH_4. Similar compounds are formed with members of the halogen group, as $SiCl_4$, etc.

324. Silicon Dioxide. — Silicon has only one oxide (silica, silicic anhydride, SiO_2). It is very abundant in nature. There are extensive mountain ranges that consist almost wholly of silicon dioxide. Its purest form is quartz or rock-crystal, which is found in beautiful hexagonal prisms terminated by hexagonal pyramids. Quartz has a density of 2.6, and is hard enough to scratch glass.

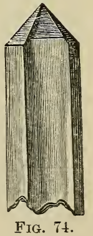


FIG. 74.

(*a*) Amethyst, cairngorm stone, and rose-quartz are nearly pure crystallized silica. Agate, carnelian, chalcedony, flint, jasper, and onyx are nearly pure amorphous silica colored by traces of other oxides, as those of iron and manganese. White sand and sandstone are generally nearly pure silica. Siliceous sand and sandstone are often colored yellow by an iron oxide.

(*b*) Silica is insoluble in water or in any acid except hydrofluoric.

$$SiO_2 + 4HF = SiF_4 + 2H_2O.$$

The silicon fluoride thus formed is gaseous. Silica can also be slowly dissolved in a boiling solution of potassium or sodium hydroxide. It is dissolved in the waters of some thermal springs. The geysers of Iceland contain dissolved silica which is deposited by the cooling waters upon objects immersed in them. Silica melts in the oxyhydrogen flame to a colorless glass that remains transparent when cold.

Silicic Acid.

Experiment 219.—Place a few cubic centimeters of concentrated soluble glass in a small evaporating-dish and add strong hydrochloric acid until the mixture shows an acid reaction. A thick jelly-like mass will be formed in the liquid. Place the dish on a water-bath and evaporate its contents to dryness. Heat this solid residue gently over the lamp. It will diminish in volume. Add water and filter. The insoluble powder left upon the filter is precipitated SiO_2, one of the lightest known powders. The jelly-like mass formed in this experiment is principally silicic acid.

Experiment 220. — Add some hydrochloric acid to a dilute solution of water-glass. Sodium chloride or potassium chloride will be formed with silicic acid. Pour the liquid mixture into a dialyser, made of parchment-paper stretched over a wooden ring and floated on the surface of pure water. The chloride solution passes through the membrane while the silicic acid remains dissolved in the dialyser. Crystallizable substances, like sodium and potassium chlorides, are sometimes called crystalloids, and uncrystallizable substances, colloids. Crystalloids and colloids may be separated as in this experiment. The process is called dialysis.

325. Silicic Acid. — Normal silicic acid has the formula H_4SiO_4. It is so unstable that when it is set free from its salts, it at once breaks down to ordinary silicic acid, H_2SiO_3, the analogue of carbonic acid.

$$H_4SiO_4 = H_2SiO_3 + H_2O.$$

Most of the ordinary silicates are derivatives of this acid. Like carbonic acid, it is easily converted into the dioxide and water.

$$H_2SiO_3 + \text{heat} = SiO_2 + H_2O.$$

(*a*) By heating ordinary silicic acid, what are known as polysilicic acids may be formed.

$$2H_2SiO_3 + \text{heat} = H_2Si_2O_5 + H_2O.$$

$$3H_2SiO_3 + \text{heat} = H_4Si_3O_8 + H_2O.$$

Of these polysilicic acids, some of which are found in nature, opal is the best known example.

326. Natural Silicates. — Silica unites with many metallic oxides to form silicates. The natural silicates are very numerous and many of them are of a very complex composition. Thus, clay is a silicate of aluminum ; feldspar is a double silicate of aluminum and potassium; mica is a triple silicate of aluminum, potassium, and iron. There are mountain ranges made up of these silicates.

327. Artificial Silicates. — Sodium and potassium silicates (water-glass or soluble glass) are soluble in water; they are largely used in the arts. The most important of the artificial silicates are glass and Portland cement. Glass is a mixture of a silicate of sodium or of potassium, or of both, with a silicate of one or more other metals. The composition is determined by the desired infusibility, insolubility, transparency, or color of the glass.

(*a*) Bohemian glass is a silicate of potassium and calcium. It is fusible only with difficulty and is but little acted upon by chemical reagents. It is free from color and is largely used in chemical apparatus.

(*b*) Window-, crown, or plate glass is a silicate of sodium and calcium. It is harder than Bohemian glass, but more easily fusible and more readily acted upon by chemical reagents.

(*c*) Bottle-glass, or common green glass, is a silicate of sodium, calcium, aluminum, and iron. Its color is due to the iron oxide present as an impurity in the cheap materials used. It is harder and more infusible than window-glass, but more easily acted upon by acids.

(*d*) Flint-glass is a silicate of potassium and lead. It has a high density and great refracting power. It is the most easily fusible variety of glass and is easily acted upon by chemical reagents. "Crystal" is a pure flint-glass used for optical purposes. "Strass" is a flint-glass very rich in lead and having a very high refractive power. It forms the basis of the artificial gems and precious stones known as "paste."

(*e*) Glass softens at a red heat and can then be readily worked and welded (see Appendix, § 5). At higher temperatures it becomes still softer and finally melts. On cooling, it passes from a thin, mobile liquid through all degrees of viscosity to a hard solid.

(*f*) Glass is acted upon readily by hydrofluoric acid (see Experiment 124). Etched glass is much used instead of the more expensive cut glass.

(*g*) When glass, heated almost to redness, is dipped into oil heated to 300° and then allowed to cool gradually, it becomes toughened. Table glass thus toughened is not readily broken by falling or being thrown, but, when it is thrown with sufficient force to break it, it is shattered into minute pieces.

(*h*) Glass is easily colored by the addition of the proper materials to the fused mass. Thus, a green color is produced by the addition of a ferrous or cupric oxide; blue, by a cobalt oxide; violet, by manganese dioxide; ruby, by gold, etc.

(*i*) Portland cement is an artificial silicate made by strongly heating together a very intimate mixture of nearly pure calcium carbonate, as limestone or marl, with a siliceous clay. The calcium unites chemically with the silica and alumina of the clay, producing silicates and aluminates of such a character that, when very finely ground and mixed with the proper proportion of water, they set to a solid stone more hard and durable than the best sandstone. It is a variety of "hydraulic" cement; i.e., it "sets" or hardens even under water. See § 180 (*b*).

NOTE. — Carbon and silicon closely resemble each other in the composition of some of their simplest compounds.

Carbon dioxide	CO_2	Silicon dioxide	SiO_2
Carbonic acid	H_2CO_3	Silicic acid	H_2SiO_3
Marsh-gas	CH_4	Silicon hydride	SiH_4
Carbon tetrachloride	CCl_4	Silicon tetrachloride	$SiCl_4$

Their points of difference are also well marked.

328. Germanium. — The discovery of this element, which was made in 1886 by Winkler, was predicted in 1871 by Mendeleef, from its place in the periodic system. It is a steel-colored metal with many properties analogous to those of tin.

TIN: symbol, Sn; density, 7.29; atomic weight, 118; valence, 2, 4.

329. Source. — The principal tin ore is a dioxide called casserite or tinstone. It is found in but few localities, the principal ones being Cornwall in England, the island of Banca, and the Malay Peninsula. It has also been found in Australia, New Hampshire, Alabama, and California. Native tin has been found in small quantities.

330. Preparation. — Tin is prepared by pulverizing, roasting, and washing the ore, and then smelting it with charcoal or anthracite. After the reduction is complete, the tin is drawn off and cast in bars.

Properties of Tin.

Experiment 221. — The familiar, so-called "tinware" is only tinned ware, iron coated with tin. Heat a piece of tinned iron over the lamp until the tin has melted; thrust the plate into cold water to harden the tin quickly; remove the smooth surface of the metal by rubbing it first with a bit of paper moistened with dilute aqua regia, and then with paper wet with soda-lye. Notice the crystalline figures thus produced, resembling frost upon a window pane.

Experiment 222. — If you have a cake of tin, wash one surface of it with dilute aqua regia until the crystalline forms, above mentioned, appear.

Experiment 223. — Hold a bar of tin near the ear and bend the bar. Notice the peculiar crackling sound. Continue the bending and notice that the bar becomes heated. The phenomena noticed seem to be caused by the friction of the crystalline particles.

331. Properties. — Tin is a lustrous, soft, white metal, that melts at about 230°. It is highly malleable, slightly tenacious, ductile at 100°, and brittle at 200°. It has a marked tendency to crystallize on cooling from a melted condition. It unites readily with oxygen, chlorine, sulphur, and phosphorus when heated with them. It is not easily tarnished by even moist air but is easily acted upon by acids. Heated in the air, it burns to the dioxide. It forms two series of compounds, the stannous and the stannic.

332. Uses. — Tin is largely employed in the form of foil, and as a coating for other metals; e.g., copper used for bath-tubs or cooking utensils, sheet-iron for "tin-plate" and iron tacks, and as a lining for lead water-pipes. It is largely used in making numerous alloys.

(*a*) Bronze and bell-metal are alloys of copper and tin. Plumber's solder and pewter are alloys of lead and tin. Britannia metal is an alloy of copper, antimony, and tin. A common "silvering" of mirrors is an amalgam of mercury and tin.

(*b*) The tin of tinned ware is sometimes adulterated with lead, which is less costly. This alloy of lead and tin will oxidize much more readily than tin will. This lead oxide is easily dissolved by the $C_2H_4O_2$ of vinegar forming the dangerous poison, lead acetate or "sugar of lead." The various acids of our common fruits unite with the lead oxide to form salts, and all of the soluble lead salts are poisonous.

333. Tin Compounds. — Tin forms two oxides, the monoxide (stannous oxide, SnO) and the dioxide (stannic oxide, SnO_2). The former is basic; the latter is both a basic and an acid-forming oxide. Their compounds are designated as stannous and stannic salts. Stannic acid (H_2SnO_3) is a white solid. Stannous chloride ($SnCl_2$) is prepared by dissolving tin in warm hydrochloric acid. Tin tetrachloride (stannic chloride, $SnCl_4$) can be prepared by passing chlorine over tin-foil or over fused tin in a retort. If a quick stream of chlorine is forced through melted tin, heat and light are evolved. Stannic chloride is a colorless liquid which, when treated with one-third its weight of water, forms a crystalline mass called "butter of tin." When a solution of stannic chloride in water is boiled, stannic acid (H_2SnO_3) is formed as a precipitate. Although insoluble in water, this acid is easily soluble in hydrochloric, nitric, and sulphuric acids. When tin is treated with concentrated nitric acid, a white powder known as metastannic acid is formed. These two tin acids seem to have the same composition, but as the latter is insoluble in acids as well as in water, the two can not be identical.

LEAD: symbol, Pb; density, 11.37; atomic weight, 206; valence, 2, 4.

334. Source of Lead. — Lead is seldom found free in nature, but its sulphide (galena, galenite, PbS) is quite abundant, and is, by far, its commonest ore. Galena is generally associated with silver sulphide. The United States produces more lead than any other country.

335. Preparation. — The smelting of lead from its ores is carried out in a reverberatory or in a blast-furnace.

In the former case, the ore is first heated in an open furnace, in which part of the sulphide is oxidized, yielding lead oxide, sulphur dioxide, and lead sulphate. The furnace is then closed and heated to a higher temperature when the oxide and sulphate just formed act each upon a part of the still undecomposed ore, yielding metallic lead and sulphur dioxide.

$$\begin{aligned} 2PbS + 3O_2 &= 2PbO + 2SO_2 \\ PbS + 2O_2 &= PbSO_4 \\ PbS + 2PbO &= 3Pb + SO_2 \\ PbS + PbSO_4 &= 2Pb + 2SO_2. \end{aligned}$$

In the blast-furnace process, lead ore, limestone, and some iron ore are mixed with coal and fused with an air-blast. The heat from the combustion of the coal melts the charge, while the lead sulphide burns to lead and sulphur dioxide, the silica and other impurities uniting with the calcium and iron to form a slag.

The Lead Tree.

Experiment 224. — To a solution of 5 grams of lead nitrate in a liter of water add two or three drops of nitric acid. Using this liquid instead of the solution of lead acetate, repeat Experiment 161.

336. Properties. — Lead is a metal so soft as to be easily cut with a knife or indented with a finger-nail and to leave a streak when rubbed upon paper. It has considerable malleability and little ductility. Repeated fusion renders it hard and brittle, probably by oxidation. When freshly cut, it has a bluish-gray color and a bright luster that is quickly dulled by oxidation. It melts at about 330°, and may be crystallized by slowly cooling a large quantity of the melted metal and pouring out the still liquid portion. It is very slightly acted upon by cold sulphuric or hydrochloric acid; its best solvent is nitric acid. It is precipitated in metallic form from a solution of one of its salts by metallic zinc.

(*a*) Many potable waters and especially well-waters containing ammoniacal salts, often due to decaying organic matter, act upon lead with the formation of compounds that act as cumulative poisons. In many cases, the use of lead water-pipes is very dangerous for this reason. If, upon examining the inner surface of a lead pipe that has been thus used, it is found to be bright it may be known that dangerous soluble salts have been formed and carried away with the water.

(*b*) In the presence of air and moisture, lead is attacked by even feeble acids like acetic or carbonic acid. Hence, the use of cooking utensils that are made of lead or that contain lead even in the form of solder or as an adulteration of otherwise harmless substances sometimes leads to the formation of poisonous lead compounds. When these are taken into the system, they unite with certain tissues of the body and are not readily eliminated. Thus the lead may accumulate until the quantity is sufficient to produce poisoning. For this reason, lead is called a cumulative poison.

337. Uses. — Lead is largely used for many purposes on account of its softness, pliability, easy fusibility, and its comparative freedom from chemical action with water and most of the acids.

338. Lead Oxides. — Lead suboxide (Pb_2O) is also called plumbous oxide. Lead monoxide (PbO) is also called plumbic oxide, but more frequently litharge. It is prepared on the large scale by highly heating melted lead in a current of air. It is used in the manufacture of glass. Red lead or minium (Pb_3O_4) is largely used as a paint and in the manufacture of flint-glass. Lead dioxide (PbO_2)

or plumbic peroxide is most easily produced by treating red lead with nitric acid.

$$Pb_3O_4 + 4HNO_3 = PbO_2 + 2Pb(NO_3)_2 + 2H_2O.$$

The valence of lead in red lead is explained by the theory that red lead is a union of the dyad and the tetrad oxides.

$$2PbO + PbO_2 = Pb_3O_4.$$

339. Lead Sulphide. — Lead sulphide (PbS) occurs native as galenite or galena and may be prepared artificially by passing hydrogen sulphide into any solution of a lead salt, or by adding a soluble sulphide to such a solution. The precipitate thus formed is of a deep but varying color. This color, together with the insolubility of the precipitate, is of use in detecting the presence of lead.

340. Soluble Lead Salts. — Lead nitrate [$Pb(NO_3)_2$] is readily formed by acting upon metallic lead with dilute nitric acid. Lead acetate [$Pb(C_2H_3O_2)_2$] is formed by dissolving litharge in acetic acid. It has a sweet, astringent taste, whence its common name, "sugar of lead." The soluble lead salts are intensely poisonous.

Insoluble Lead Salts.

Experiment 225. — Add some hydrochloric acid to a dilute solution of lead nitrate or of lead acetate. A precipitate will be formed. Heat the liquid, and thus dissolve the precipitate. As the liquid cools, crystals of lead chloride will appear.

341. Insoluble Lead Salts. — Lead chloride ($PbCl_2$), lead sulphate ($PbSO_4$), or lead chromate ($PbCrO_4$) is formed by adding a soluble chloride, sulphide, or chromate to a solution of a lead salt. Lead chloride is easily soluble in hot, but not in cold, water. Lead chromate is known as chrome yellow. Lead carbonate ($PbCO_3$) is formed as a white precipitate by adding ammonium carbonate to a cold solution of lead acetate or nitrate. It occurs in nature as cerusite. White lead is a compound of varying proportions of lead carbonate and lead hydroxide. When ground with linseed-oil, it forms the basis of ordinary white paint, although zinc white is used for the same purpose.

342. Lead Poisoning. — While metallic lead is not poisonous, all of its soluble salts are so in a very high degree. Lead acetate, given in doses of from three-tenths to six-tenths of a gram, produces symptoms of acute lead poisoning which often end fatally. Small doses of the oxides and carbonates frequently repeated often produce chronic lead poisoning. Painter's colic is a form of chronic poisoning by lead carbonate. Soluble sulphates, e.g., Epsom salt, are antidotes for lead poisons.

343. Tests. — The sweet taste and poisonous character of the soluble lead salts render their detection a matter of great importance.

(*a*) Any lead compound when heated on charcoal in the blowpipe-flame gives a bead of malleable lead. This bead is readily soluble in warm nitric acid; and this acid solution yields a precipitate with sulphuric acid.

(*b*) Potable waters suspected of containing lead compounds may be tested by slightly acidulating with hydrochloric acid and charging with hydrogen sulphide. If a black precipitate is formed, lead is probably present. The probability is sufficient to call for the services of a chemical expert. If lead salts are present in not too minute quantities, the addition of hydrochloric acid will yield a white crystalline precipitate of lead chloride which is soluble in an excess of boiling water. If the solution of the lead salt is tolerably strong, the addition of potassium iodide will generally yield a yellow precipitate of lead iodide, while the addition of potassium chromate gives a fine yellow precipitate of lead chromate or chrome yellow.

EXERCISES.

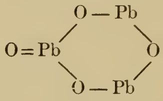
1. (*a*) Write the reaction for the formation of lead oxide in the first stage of lead smelting. (*b*) For the formation of lead sulphate in the same stage.

2. (*a*) Express the reaction between the lead oxide and galenite in the second stage of lead smelting. (*b*) For the reaction between lead sulphate and the ore in the same stage.

3. Why are lead compounds called cumulative poisons?

4. Define normal, acid, basic, and double salts. Illustrate each.

5. (*a*) What substance is represented by the formula



?

(*b*) What does this formula indicate concerning the valence of the lead atoms?

6. What volume of CO_2 is produced by burning 1 liter of CH_4?

7. What is the volume of 1 kilogram of oxygen?

8. Write the symbol for lead acetate.

9. What is common washing-soda? Baking-soda? Why is the latter better for baking than the former?

10. What name is given to a solution of calcium hydroxide in water?

11. What is the percentage of carbon dioxide contained in calcium carbonate?

12. Complete the following equation: $Ca(OH)_2 + CO_2 =$.

13. A molecule of a certain oxide contains one atom of tin and has a weight of 150. What is its formula?

14. How many liters of marsh-gas will weigh as much as 25 liters of ethene?

15. A certain compound has a molecular weight of 60. Its centesimal composition is as follows: 40 of C, 53.4 of O, and 6.6 of H. What is the compound?

16. What weight of lead may be precipitated from a solution of lead acetate by 65 decigrams of zinc? (See Experiment 161, and § 293.)

17. What is the valence of tin in stannous compounds? In stannic compounds?

CHAPTER XV.

THE FIFTH GROUP—PENTADS.

344. The Nitrogen Family. — This family consists of nitrogen, vanadium, columbium, praseodymium (see § 373), and tantalum. (See the table on page 145.) Nitrogen and its compounds have been considered in earlier chapters. The other members of this family are rare elements with properties that closely relate them to nitrogen. Some of these analogies are apparent in the formulas of some of their compounds:

Nitrogen	N_2O	NO	N_2O_3	NO_2	N_2O_5	HNO_3	Gas
Vanadium	V_2O	VO	V_2O_3	VO_2	V_2O_5		Metal
Columbium	—	CbO	—	CbO_2	Cb_2O_5	$HCbO_3$	Metal
Praseodymium	—	—	Pr_2O_3	PrO_2	Pr_2O_5	—	Metal
Tantalum	—	—	—	TaO_2	Ta_2O_5	$HTaO_3$	Metal

Their symbols and atomic weights are given in the list of chemical elements printed in the Appendix.

345. The Phosphorus Family. — This family consists of phosphorus, arsenic, antimony, and bismuth. Their characteristics show striking resemblances, as will soon appear. They are individually important.

PHOSPHORUS: symbol, P; density, 1.8; atomic weight, 31; valence, 3, 5.

346. Phosphorus. — This element does not occur free in nature, but its compounds with oxygen and some metal (chiefly calcium) are found in large quantities. Calcium phosphate is found as the native minerals apatite and phosphorite; it forms, also, the greater part of the mineral constituent of animal bone.

(*a*) The ultimate source of phosphorus is the granitic rocks, by the disintegration of which the fertile soil has been produced. All fruitful soils contain phosphates. These salts are diffused in such small quantities that their direct collection by the manufacturing chemist would be very costly. Plants collect the phosphates from the soil; herbivorous animals obtain them by consuming the plants; from the bones of animals, the chemist derives the phosphates from which phosphorus is prepared. The process is devious and complicated, but the greater part of it is inexpensive.

NOTE. — The name comes from two Greek words that mean a bearer of light, phosphorus being luminous in the dark. The alchemists used to call it "Son of Satan." Phosphides were formerly called phosphurets.

Preparation of Phosphorus.

See the Caution on page 15. Phosphorus burns are very difficult to heal.

Experiment 226. — Mix intimately 25 grams of aluminum powder with 60 grams of sodium metaphosphate and 20 grams of powdered silica. Place the mixture in a good-sized combustion-tube (about a meter in length), the mouth of which is bent to dip beneath water.

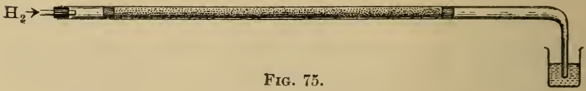


FIG. 75.

Slowly heat the mixture to a moderate red heat, at the same time passing a slow current of hydrogen through the tube. Phosphorus will collect in the front part of the tube and may be expelled by heat into the water.

$$6NaPO_3 + 10Al + 3SiO_2 = 3Na_2SiO_3 + 5Al_2O_3 + 6P.$$

347. Preparation. — In the preparation of phosphorus, animal bones are burned and powdered. This powdered bone-ash is treated with sulphuric acid. This treatment yields an insoluble calcium sulphate (gypsum, $CaSO_4$) and a soluble salt, calcium acid phosphate, called "super-phosphate of lime." The insoluble sulphate is removed by filtration. The clear solution is then evaporated to a syrupy liquid, mixed with powdered charcoal, dried, heated, and finally distilled in earthen retorts, the necks of which dip under water. The liberated phosphorus condenses under the water. After purification, it is melted under hot water and run into cylindrical molds placed in cold water.

(*a*) In the process just described, the following reactions take place. When the acid acts on the calcium phosphate of the bones:

$$Ca_3(PO_4)_2 + 2H_2SO_4 = CaH_4(PO_4)_2 + 2CaSO_4.$$

When the acid phosphate solution with charcoal is dried and heated, calcium metaphosphate is produced:

$$CaH_4(PO_4)_2 = Ca(PO_3)_2 + 2H_2O.$$

When the mixture is heated white-hot in the distillation retorts, calcium phosphate, carbon monoxide, and phosphorus are produced:

$$3Ca(PO_3)_2 + 10C = Ca_3(PO_4)_2 + 10CO + P_4.$$

(*b*) Large quantities of phosphorus are now made by heating calcium phosphate with carbon and silica to the intense heat of the electric furnace. The silica acts in the place of the H_2SO_4 of the older process, liberating phosphoric acid which is reduced by the carbon:

$$2Ca_3(PO_4)_2 + 10C + 6SiO_2 = 6CaSiO_3 + 10CO + P_4.$$

Either mineral phosphates or the phosphates derived from bones may be used in this process.

348. Physical Properties. — Pure phosphorus is an almost colorless, translucent solid. The ordinary commercial article has a feeble yellow tinge. When freshly cut, it has a garlic-like odor, often hidden by the odor of ozone which is generally present when moist phosphorus is exposed to the air. It is insoluble in water, sparingly soluble in turpentine, petroleum, and other oils, and easily soluble in carbon disulphide. It is soft and waxlike in warm weather but brittle at low temperatures. Under water, it melts at 44°, forming a viscid, oily liquid that boils at 290°, yielding a colorless vapor. At 500° the vapor is sixty-two times as heavy as hydrogen. Consequently, its molecular weight is 124, or four times its atomic weight. From this we conclude that the phosphorus molecule contains four atoms and that each atom occupies half the space taken up by a hydrogen atom.

Chemical Properties of Phosphorus.

Experiment 227. — Bury a piece of phosphorus, the size of a grain of wheat, in a teaspoonful of lampblack or powdered bone-black that has been freshly prepared or recently heated. The oxygen condensed within the pores of the carbon unites with the vapor of the phosphorus, developing enough heat to melt and finally to ignite the phosphorus.

Experiment 228. — Dissolve a small piece of phosphorus in carbon disulphide. Pour some of the solution upon a piece of filter-paper placed upon the ring of a retort-stand. The volatile CS_2 soon evaporates, leaving the phosphorus in a finely divided state exposing a large surface to the oxidizing influence of the air. The phosphorus soon bursts into flame, which only partly consumes the paper. The burning phosphorus quickly covers the paper with a coat of incombustible and protecting varnish. If the experiment is performed in a dark room, the phosphorescence will be very marked.

Experiment 229. — Rub a piece of dry phosphorus the size of a pinhead between two bits of board. The heat developed by the friction is sufficient to ignite it. Read the description of Experiment 6.

Experiment 230. — Heat a small piece of phosphorus in a dry tube with a mere trace of iodine. Combination promptly takes place, a small quantity of volatile phosphoric iodide is formed and the rest of the phosphorus is changed to an allotropic form known as red phosphorus. Try to repeat Experiment 229 with red phosphorus.

Experiment 231. — Close one end of a piece of narrow glass tubing about 30 cm. long by fusing it in a flame. In the ignition-tube thus made place a small bit of red phosphorus and heat it gently in the lamp-flame. A yellow coating is quickly deposited upon the cool walls of the tube not far from the heated end. Allow the tube to cool, and cut off the end just below the yellow sublimate. Scratch this yellow deposit with a wire; it will take fire, as it is ordinary, yellow phosphorus. By heating the red phosphorus, a part of it burned, thus removing the oxygen from the lower part of the tube. The inert nitrogen remaining there, enveloped and protected the rest of the phosphorus from combustion and thus permitted its reconversion into the ordinary variety.

Experiment 232. — Touch a slice of phosphorus with a test-tube containing boiling water. The phosphorus will be ignited.

Experiment 233. — Place a piece of phosphorus under water warm enough to melt it. Bring a current of oxygen from the gas-holder into contact with the melted phosphorus. The phosphorus will take fire and burn brilliantly under water.

Experiment 234. — Upon a thin slice of phosphorus place a crystal of iodine. The two elements promptly unite with great energy, leading to the combustion of the excess of phosphorus.

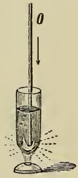


FIG. 76.

349. Chemical Properties. — Phosphorus combines readily with many of the elements, especially oxygen. It undergoes slow combustion at ordinary temperatures (forming P_2O_3) and oxidizes with great energy at a temperature not much above its melting-point (forming P_2O_5). On account of this easy inflammability, phosphorus should be kept and cut under water and *never handled with dry fingers.* Owing to its slow combustion, it is feebly luminous in the dark. In distillation, the oxygen in the retort must be replaced by some inert gas like hydrogen, nitrogen, or carbon dioxide. Heated for several hours to about 240°, out of contact with oxygen or any other substance capable of entering into chemical union with it, it is changed to the remarkable allotropic modification known as red phosphorus.

(*a*) The differences between the ordinary yellow and the red varieties of phosphorus are shown in the following table:

Pale yellow	Chocolate red.
Strong odor	Odorless.
Density = 1.83	Density = 2.14.
Phosphorescent	Not phosphorescent.
Translucent	Opaque.
Soluble in carbon disulphide	Insoluble in carbon disulphide.
Subject to slow combustion	Exempt from slow combustion.
Melts at 44°	Melts at 255°.
Changes to red at 240°	Changes to yellow at 300°.
Soft	Hard.
Flexible	Brittle.
Poisonous	Not poisonous.
Chemically active	Chemically inactive.

350. Uses. — Phosphorus is extensively used in the manufacture of friction-matches, the match-tips generally being a mixture of phosphorus, glue, and potassium chlorate. Safety-matches are tipped with antimonious sulphide and potassium chlorate. These ignite, not by simple friction, but by rubbing on a prepared surface containing red phosphorus, manganese dioxide, and sand. Ordinary phosphorus mixed with flour paste is a rat poison that has probably led to the burning of many houses. Phosphorus is used in medicine; many of the phosphates are important remedial agents. Phosphorus fumes produce, in the workmen in match factories, phosphorus-necrosis, a disease in which the bones of the jaw are destroyed. Taken internally, yellow phosphorus is extremely poisonous, a very small quantity causing death. There is no good antidote; the best treatment is promptly to give an emetic.

EXERCISES.

1. Symbolize two molecules of pentad phosphorus.

2. (*a*) What is a binary molecule? (*b*) A ternary molecule? (*c*) How are binary molecules named? Illustrate.

3. How much phosphorus is contained in 120 kilograms of bone-ash, of which 88.5 per cent is $Ca_3(PO_4)_2$ and the rest is $CaCO_3$?

4. (*a*) Find the percentage composition of carbon monoxide. (*b*) Find the formula of a gas having the composition 27.27 per cent carbon; 72.73 per cent oxygen, and weighing 1.9712 grams to the liter.

5. What elementary solid should never be handled with dry fingers? What one should never be handled with wet fingers?

6. What is the meaning of the following:

If from $\left.\begin{matrix}(HO)-(NO_2)\\(HO)-(NO_2)\end{matrix}\right\}$ we take H_2O, $O\left\langle\begin{matrix}(NO_2)\\(NO_2)\end{matrix}\right.$ will remain.

7. What reason have we for thinking that phosphorus is tetratomic?

8. How may the formula for acetic acid be derived from the formula for marsh-gas?

9. What are the products of the slow oxidation of alcohol? Of the quick oxidation?

10. Write the formula for potassium formate.

Hydrogen Phosphide.

Experiment 235. — Dissolve 20 grams of potassium hydroxide (caustic potash) in 50 cu. cm. of water. When the solution is cool, place it in a flask of not more than 100 cu. cm. capacity; add half a gram of phosphorus in thin slices, and 5 or 6 drops of ether; close the flask with a cork carrying a long glass delivery-tube that terminates beneath water. The ether is added that its heavy vapor may force the oxygen of the air from the flask; when possible, it is better to use a current of illuminating-gas for this purpose. When the contents of the flask are boiled, gas escapes from the delivery-tube and bubbles up through the water. As each bubble of gas comes into contact with the air, it bursts into flame with a bright light. If the air of the room is still, beautiful expanding rings of white smoke (P_2O_5) will rise, with vortex motion, to the ceiling. At the end of the experiment, be careful that air is not sucked back into the phosphine in the flask.

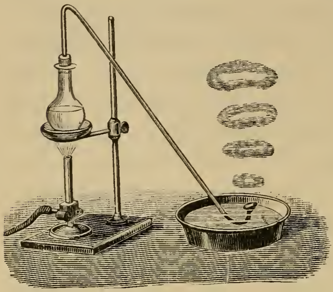


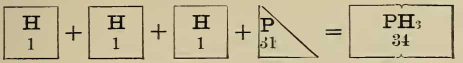
FIG. 77.

351. Hydrogen Phosphide. — This colorless, poisonous, ill-smelling gas (phosphureted hydrogen, phosphorus trihydride, phosphine, PH_3) is generally prepared by heating phosphorus in a strong alkaline solution. The reaction is complicated.

(*a*) PH_3 is easily formed by placing calcium phosphide in water. Two other compounds of hydrogen and phosphorus are known of which one is liquid and the other solid at the ordinary temperature. Their proper formulas have not been definitely ascertained.

(*b*) Pure PH_3 is not spontaneously combustible in the air. The combustion above noticed is due to the presence of a small quantity of the liquid phosphide just mentioned. If the gas, as it comes from the flask (Fig. 77), is passed through a tube chilled by a freezing mixture, this liquid (probably P_2H_4) will be condensed. The escaping PH_3 will not take fire as it subsequently bubbles through the water and comes into contact with the air.

(*c*) The composition of PH_3 may be represented thus:



In this case, the weight of half a unit volume is the atomic weight. The unit volume, being half the molecular volume, would include two phosphorus atoms. Compare the above diagram with the one given for ammonia.

Phosphorus Oxide.

Experiment 236. — Place a piece of thoroughly dry phosphorus weighing not more than a gram in a small, dry capsule; place the capsule upon a large, dry plate; ignite the phosphorus with a hot wire and quickly cover it with a dry bell-glass or wide-mouthed bottle of 2 or 3 liters' capacity. The capsule, plate, and bell-glass should be warmed to insure their being dry. A white, fleecy powder will be deposited within the bell-glass.

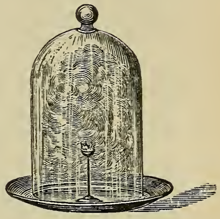


FIG. 78.

352. Phosphorus Oxides. — Phosphorus has two well-known oxides, the phosphorous and the phosphoric oxide.

(*a*) Phosphorous oxide (phosphorus anhydride, phosphorus trioxide, P_2O_3) is formed by the slow combustion of phosphorus in a limited current of dry air. It is a white, amorphous substance, very soluble in water and burns in the air to phosphoric oxide. It is said that its vapor-density indicates the formula P_4O_6.

(*b*) Phosphoric oxide (phosphoric anhydride, phosphorus pentoxide, P_2O_5) is formed by the combustion of phosphorus in an excess of oxygen. Its attraction for water is so great that it forms the most efficient known means of drying gases. If left in the air, it deliquesces completely in a few minutes; if thrown into water, it hisses like a hot iron and dissolves with the evolution of much heat. It may be kept in dry tubes sealed by fusion. It is said that its vapor-density indicates the formula P_4O_{10}.

353. Phosphorus Acids. — Phosphorus combines with oxygen and hydrogen to form a remarkable series of acids, as follows:

$$H_3PO_2\text{, hypophosphorous acid.}$$

$$P_2O_3 + 3H_2O = 2H_3PO_3\text{, phosphorous acid.}$$

$$P_2O_5 + \begin{cases} 3H_2O = 2H_3PO_4\text{, phosphoric acid (ordinary or tribasic).} \\ 2H_2O = H_4P_2O_7\text{, pyrophosphoric acid.} \\ H_2O = 2HPO_3\text{, metaphosphoric acid.} \end{cases}$$

(*a*) H_3PO_2 gives a series of salts known as hypophosphites; e.g., sodium hypophosphite, NaH_2PO_2. When heated, it decomposes into H_3PO_4 and PH_3. It is monobasic. Its anhydride (P_2O) has been claimed by some.

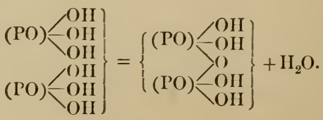
(*b*) H_3PO_3 may be formed by the action of water on P_2O_3, by the slow oxidation of phosphorus in moist air, or by the decomposition of phosphorus trichloride by water: $PCl_3 + 3H_2O = H_3PO_3 + 3HCl$. When heated, it decomposes into H_3PO_4 and H_3P. Although it is dibasic, it is possible to displace its third atom of hydrogen to produce such compounds as sodium phosphite, Na_3PO_3, and triethyl phosphite $(C_2H_5)'_3PO_3$.

(*c*) H_3PO_4 may be prepared by the direct union of P_2O_5 and boiling water, but the usual process is to oxidize phosphorus with nitric acid. When heated, it changes to $H_4P_2O_7$ or HPO_3, as explained below. It is tribasic, and yields normal, double, and acid phosphates in great variety. It is sometimes called orthophosphoric acid. It and its salts are the most important of the phosphoric series. (See Exercise 3, p. 324.)

(*d*) $H_4P_2O_7$ is formed by heating H_3PO_4 to 215°, thus depriving it of water:

$$2H_3PO_4 + \text{heat} = H_4P_2O_7 + H_2O.$$

It is tetrabasic and yields normal, double, and acid pyrophosphates in great variety. The group, PO (phosphoryl), acts as a trivalent compound radical.



$$\left.\begin{array}{l} (PO)\begin{cases} OH \\ OH \\ OH \end{cases} \\ (PO)\begin{cases} OH \\ OH \\ OH \end{cases} \end{array}\right\} = \left\{\begin{array}{l} (PO)\begin{cases} OH \\ OH \end{cases} \\ \quad > O \\ (PO)\begin{cases} OH \\ OH \end{cases} \end{array}\right\} + H_2O.$$

(*e*) HPO_3 is formed by the direct union of P_2O_5 and cold water, or by heating H_3PO_4 to redness, thus depriving it of water:

$$H_3PO_4 = HPO_3 + H_2O.$$

It is monobasic and yields only normal metaphosphates. It is sometimes called glacial phosphoric acid. It is said that its vapor-density indicates the formula $H_2P_2O_6$. If its aqueous solution is boiled, it yields H_3PO_4.

354. Tests. — With a solution of silver nitrate, a soluble phosphate gives a brown precipitate that is soluble in dilute nitric acid. With a nitric acid solution of molybdic acid containing ammonium nitrate, phosphates give bright yellow precipitates that are insoluble in dilute acids but soluble in ammonia.

355. Plant Foods. — Plants derive all of their carbon from the air, but their mineral constituents and their nitrogen come from the soil. The chief mineral constituents necessary for plant growth are silicon, calcium, magnesium, iron, sodium, potassium, and phosphorus. Silicon, calcium, iron, and sodium are present in most soils in quantities that can not be exhausted by plant growth. But by the continued cultivation of crops, the supply of available potassium, nitrogen, and phosphorus in the soil becomes exhausted unless the loss is made good. That they may become plant-food, these elements must be supplied in a form soluble in the plant juices so that they may be taken up by the plant roots. Most of the natural compounds of potassium and nitrogen are thus soluble, but the natural phosphates are insoluble and require chemical treatment to make them available as plant-food.

356. Fertilizers. — The principal sources of phosphorus for fertilizers are rock phosphate [$Ca_3(PO_4)_2$] and the bones of animals. These are insoluble in water or in plant juices. They are, therefore, ground and treated with sulphuric acid, forming calcium sulphate and calcium acid phosphate.

$$Ca_3(PO_4)_2 + 2H_2SO_4 = 2CaSO_4 + CaH_4(PO_4)_2.$$

This mixture is called by the trade name of "superphosphate" and, with some salt of potassium and a nitrate (or an ammonia compound), constitutes the basis of most commercial fertilizers.

EXERCISES.

1. What is the valence of phosphorus in P_2O_5? Represent this molecule by its graphic formula.

2. (*a*) What is the name of $Ca''_3(PO_4)_2$? (*b*) Why may not the formula be written $CaPO_4$?

3. Choose between $HNa'PO_4$ and HNa_2PO_4. Give a reason for your choice.

4. Write the empirical and the graphic formulas for the oxide of P'''.

5. The formula for "microcosmic salt" is $HNa(NH_4)PO_4$. (*a*) What is the systematic name of the salt? (*b*) Is it a normal salt? Why? (*c*) Write the formula of the corresponding acid? (*d*) What is the basicity of that acid?

6. Symbolize disodium hydrogen phosphate, sodium dihydrogen phosphate, and normal sodium pyrophosphate.

7. What is the systematic name of the sodium salt of monobasic phosphoric acid?

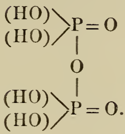
8. If 2 liters of PH_3 are decomposed, what volume of phosphorus vapor will it yield?

9. Why is it that, while an atom of phosphorus is only 31 times as heavy as an atom of hydrogen, a liter of phosphorus vapor is 62 times as heavy as a liter of hydrogen?

10. (*a*) Is Na'_3PO_4 an acid salt? Why? (*b*) Is it a double salt? Why? (*c*) Is it a normal salt? Why? (*d*) Is it a salt at all? Why?

11. Can you write the formula for sodium hydrogen metaphosphate?

12. Give the empirical formula for the compound graphically symbolized as follows:



13. What does this last graphic formula intimate concerning the valence of the phosphorus?

14. If one atom of oxygen in a molecule of metaphosphoric acid is replaced by two of hydrogen, what will result?

15. What is represented by $O = P \equiv$?

16. Write the reaction for the combustion of one molecule of phosphorus in an excess of oxygen.

17. $Ca''_3P_2 + 6HCl = 3CaCl_2 + 2 \qquad .$ Complete the equation.

18. Write the reaction for the decomposition of H_3PO_2 by heat.

19. What is the difference between a phosphide and a phosphuret?

20. (*a*) What is the valence of phosphorus in H_3PO_3? (*b*) In H_3PO_4?

21. The tube represented in Fig. 79 has a fine opening at *a*, burning phosphorus at *c*, and a tube, *e*, connected with an aspirator so that a current of air may be drawn through the apparatus. What is the product of the combustion?

Fig. 79.

22. I have a substance insoluble in carbon disulphide; it causes HNO_3 to give off red fumes, and forms with it H_3PO_4. What is the substance? What are the red fumes?

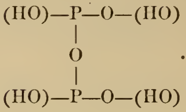
23. (*a*) If from the imaginary double molecule, $2H_5PO_5$, we take $2H_2O$, what will remain? (*b*) What, if we take $3H_2O$? (*c*) What, if we take $4H_2O$? (*d*) What, if we take $5H_2O$?

24. (*a*) If in a molecule of tribasic phosphoric acid one of the univalent hydroxyl groups is replaced by an atom of hydrogen, what will result? (*b*) What, if two such groups are replaced by H_2?

25. If a liter of PH_3 is decomposed by the passage of a series of electric sparks, what volume of hydrogen will it yield?

26. Write the formulas for phosphorus trihydrate and phosphoryl trihydrate.

27. Give the name of the compound graphically symbolized as follows:



$$\begin{array}{rcl}(HO)- & P & -O-(HO)\\ & | & \\ & O & \\ & | & \\ (HO)- & P & -O-(HO)\end{array}.$$

28. What does the above graphic formula intimate concerning the valence of the phosphorus?

ARSENIC: symbol, As; density, 5.6 to 5.9; atomic weight, 75; valence, 3, 5.

357. Arsenic. — Arsenic is widely distributed in small quantities. It is sometimes found free in nature but more frequently combined with iron, sulphur, and other elements. It is generally prepared from arsenical pyrite (mispickel, FeAsS) by sublimation, or from its oxide by reduction with charcoal.

358. Properties and Uses. — Arsenic has a metallic luster and a steel-gray color. Its vapor is 150 times as heavy as hydrogen. In its physical properties, it closely resembles a metal; in its chemical properties, it more closely resembles a non-metal. It has been called "the connecting link" between the metallic and the non-metallic elements, being closely connected with antimony and bismuth on the one hand, and with phosphorus and nitrogen on the other. Like phosphorus, its molecule contains four atoms, as is shown by its vapor-density (§ 136, *a*). Most of its soluble compounds are active poisons. Heated in the air, it burns, forming the trioxide. It is used in the manufacture of shot and of fireworks.

NOTE. — The "arsenic" or "white arsenic" of the druggist is arsenic trioxide (As_2O_3). The arsenides were formerly called arseniurets.

359. Hydrogen Arsenide. — This very poisonous gas (arsine, arseniureted hydrogen, AsH_3) may be formed by the action of dilute sulphuric acid upon zinc and any arsenic-containing compound, because all arsenical compounds are reduced to the hydride by nascent hydrogen. In its preparation, great care must be taken not to breathe any of the gas or to allow it to escape into the room, as it is extremely poisonous. Very small quantities have been known to produce death. When burned in the air, it yields water and arsenic trioxide. When heated without access of air, it is dissociated into arsenic and hydrogen. Its volumetric composition is similar to that of hydrogen phosphide.

(*a*) NH_3 has strong basic properties; PH_3 has weak basic properties; AsH_3 has no basic properties.

Arsenic Trioxide.

Experiment 237. — Place a small quantity of arsenic trioxide in a tube of hard glass about 10 cm. long, and hold the tube in a sloping position in a lamp-flame until the powder is volatilized. With a magnifying lens, examine the walls of the tube where the trioxide has condensed; the oxide will be seen to be crystalline.

Experiment 238. — Make the tube used in the last experiment into an ignition-tube by fusing and sealing one end of it in the lamp-flame. In the bottom of the tube thus formed, place a little (a few milligrams only) of arsenic trioxide and above it a small piece of charcoal, as shown at *c*. Holding the tube horizontal, heat the charcoal splinter to redness; then gradually bring the tube into a nearly vertical position, keeping the charcoal red-hot and heating the tip of

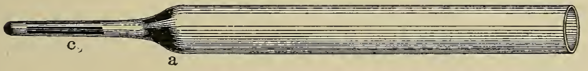


FIG. 80.

the tube until the trioxide is vaporized. The vapor will be reduced by the glowing charcoal and a brilliant ring of metallic arsenic will appear at *a*.

360. Arsenic Oxides and Sulphides. — Arsenic trioxide (arsenious oxide, arsenious anhydride, white arsenic, As_2O_3) is prepared on the large scale by roasting arsenical ores with free access of air. The arsenic thus oxidized and volatilized appears as white fumes that are led into large chambers where they are condensed to a white powder. Arsenic trioxide occurs in three varieties, the amorphous or vitreous, and two different crystalline forms, rhombic and octahedral. It is feebly soluble in water, but dissolves more readily in boiling hydrochloric acid, and freely in alkaline solutions. Heated in contact with air, it volatilizes without change. Heated in contact with carbon, it gives up its oxygen and is reduced to metallic arsenic. As a poison it is very dangerous, because it has no warning odor and scarcely any taste, and because very small quantities produce death. Its best antidote is *freshly* prepared ferric hydroxide which forms with it an insoluble salt and thus prevents the poison from entering the system. When these can not be quickly obtained, an emetic should be promptly administered. Arsenic trioxide is largely used in the manufacture of pigments and of glass, as a mordant in cotton printing, and as an insecticide. As the vapor-density of this substance is 198, its molecular formula is sometimes written with apparent propriety, As_4O_6.

(*a*) Arsenic pentoxide (arsenic anhydride, As_2O_5) may be obtained by oxidizing the trioxide with nitric acid, evaporating to dryness, and heating nearly to redness. It is less powerfully poisonous than the trioxide.

(*b*) Two native sulphides of arsenic are found. The red sulphide (As_2S_2) is called realgar; it is used in making fireworks. The yellow sulphide (As_2S_3) is called orpiment; it is used as a pigment. In addition to the disulphide and the trisulphide, a pentasulphide (As_2S_5) is obtained by fusing the trisulphide with sulphur.

361. Arsenic Acids. — Arsenic forms a series of acids that presents remarkable analogies to the phosphorus acid series.

$$As_2O_3 + 3H_2O = 2H_3AsO_3, \text{ arsenious acid.}$$

$$As_2O_5 + \begin{cases} 3H_2O = 2H_3AsO_4, \text{ tribasic arsenic acid.} \\ 2H_2O = H_4As_2O_7, \text{ pyroarsenic acid.} \\ H_2O = 2HAsO_3, \text{ metaarsenic acid.} \end{cases}$$

(*a*) When As_2O_3 is dissolved in water, the solution gives a feebly acid reaction and is supposed to contain H_3AsO_3. The corresponding salts are called arsenites; e.g., silver arsenite, Ag_3AsO_3.

(*b*) H_3AsO_4 is generally prepared by treating As_2O_3 with nitric acid. The commercial form is a liquid, from which transparent crystals may be obtained by cooling. As it is tribasic, it yields three series of arsenates which closely resemble the corresponding phosphates in composition and crystalline form. Heated to 180° it loses water and becomes $H_4As_2O_7$. Heated to 200° it loses another molecule of water and becomes $HAsO_3$.

Marsh's Test for Arsenic.

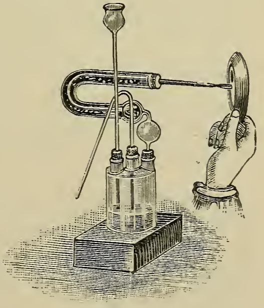


FIG. 81.

Experiment 239. — Arrange the apparatus for the preparation of dry hydrogen, using a cold mixture of 1 part of sulphuric acid and 3 parts of water. It is well to keep the generating flask cool by placing it in a cold water-bath. When the air has been expelled from the apparatus, ignite the jet. Hold a piece of cold porcelain in the flame, and notice that no colored stain is produced. (If a stain should appear, it would show that the materials used in the generating flask were impure.) *Keep the jet* *burning* and add, through the funnel-tube, a few drops of a hot aqueous solution of As_2O_3. Notice the change in the appearance of the flame. Hold the cold porcelain in the flame. A stain having a metallic luster will be produced. The stain is metallic arsenic, freed from combination in AsH_3 by the heat of the flame and deposited, just as soot would be by a candle-flame. Do not let the porcelain become hot enough to vaporize the arsenic and to cause the stain to disappear. Keep the jet burning until the apparatus is placed in the ventilating closet or out of doors, to prevent the escape of AsH_3 into the room.

Experiment 240. — Clean the generating flask and repeat the experiment, using "Paris green" instead of the As_2O_3.

Experiment 241. — Boil a green-paper label with hydrochloric acid in a test-tube. Test this solution for the presence of arsenic, as in Experiment 239. Try the same with green wall-paper or with green paint scraped from woodwork.

NOTE. — Formerly, cloth and paper were often colored green by arsenic-containing coloring matters. These dangerously poisonous substances have now been largely (but not wholly) replaced by coal-tar dyes free from arsenic. Arsenical green paints are still common.

Experiment 242. — After passing the AsH_3 through a drying-tube containing potassium hydroxide and calcium chloride, as shown in Fig. 81, heat the delivery-tube to a red heat. The gas will be decomposed, the arsenic being deposited as a dark band ("mirror of arsenic") upon the cool part of the tube and the hydrogen burning with its characteristic flame at the jet. Little or no deposit will then be made on the cold porcelain.

Experiment 243. — To show that the stains produced in Experiments 239 and 240 are arsenic and not antimony, *which might imitate them*, touch one of the stains with a glass rod dipped into a solution of chloride of lime. If the metal dissolves, it is arsenic.

362. Marsh's Test. — The preceding experiments rudely illustrate Marsh's test for arsenic. The test is so delicate that a hundredth of a milligram ($\frac{1}{7000}$ of a grain) of the poison may be recognized with certainty. In examinations of great importance, as in trials for murder by arsenical poisoning, the purity of all materials used and the nature of the metallic deposit are carefully determined by confirmatory tests.

EXERCISES.

1. Write the equation representing the combustion of hydrogen arsenide.

2. What is the weight of $10As_2O_3$?

3. Name the following: H_3AsO_4; NaH_2AsO_4; Na_2HAsO_4; Na_3AsO_4.

4. Write a graphic formula for $H_3P'''O_3$.

5. When AsH_3 is prepared from Zn_3As_2 and dilute sulphuric acid, zinc sulphate is produced. How much AsH_3, by weight and by volume, can be prepared from 50 grams of Zn_3As_2?

6. Why is As_2O_3 said to be dimorphous?

7. What is a dyad? A monobasic acid?

8. You are given a mixture of ordinary and red phosphorus. How will you separate the two varieties?

9. Name two elements that are thought to be tetratomic, and give a reason for such belief.

10. What volume of steam will result from the burning of 100 grams of hydrogen?

11. Write the formula for sodium acetate. Remember that sodium is a monad.

12. Write the formula for copper acetate. Copper is a dyad.

13. Write the reaction for Experiment 238.

14. Write the reaction for the preparation of arsenic from arsenical pyrite.

15. Is tartaric acid monobasic? If so, why? If not, why not?

16. Rochelle salt is sodium-potassium tartrate with four equivalents of water of crystallization. Write the formula for Rochelle salt.

ANTIMONY: symbol, Sb; density, 6.7; atomic weight, 119; valence, 3, 5.

363. Antimony. — The antimony of commerce is obtained from the mineral stibnite, which is an antimony trisulphide (gray antimony, antimony glance, Sb_2S_3). Antimony is, however, found native and in combination with other elements than sulphur. The stibnite is first melted to remove earthy impurities, and is then fused with about half its weight of iron ($Sb_2S_3 + Fe_3 = 3FeS + Sb_2$), or roasted in a reverberatory furnace and reduced with coal. It may also be prepared by the electrolysis of its salts.

Properties of Antimony.

Experiment 244. — With the blowpipe heat a small piece of metallic antimony on charcoal. Similarly heat a small piece of arsenic. Notice the effect in each case, and see if in this way you can distinguish between arsenic and antimony.

Experiment 245. — Repeat Experiment 239, using a solution of tartar emetic instead of the solution of arsenic trioxide. Note in what respects the antimony spot differs from the arsenic spot.

Experiment 246. — Make two molds by boring conical cavities in a block of plaster of Paris. See that each mold terminates below in a sharp point. Make two or three clean-cut grooves in the sides of the molds. Into one mold, pour melted lead; into the other, melted type-metal. Remove the casts, and notice that the lead cone is blunted at the apex while the type-metal is pointed; that the ridges on the sides of the lead cone are ill defined, while those on the sides of the type-metal are well defined. The lead contracts as it cools and thus shrinks from the mold. The type-metal is composed of about 70 parts of lead, 10 parts of tin, and 20 parts of antimony. The tin gives it toughness, and the antimony hardness. The antimony tends to crystallize as it cools, thus causing the type-metal to expand, to force itself into every part of the mold, and to make a sharply defined cast.

364. Properties and Uses. — Antimony is a bluish-white metal. It is so brittle that it may be powdered in a mortar. Its crystalline tendency is so strong that, when it is cooling from the melted condition, beautiful fernlike figures are formed on the free surface of the metal. These figures may be seen on one surface of almost every cake of antimony found in commerce. Antimony melts at

450°. It is not acted upon by the air at ordinary temperatures, but when melted in contact with the air it rapidly oxidizes. At a red heat, it burns with a white flame, forming antimony trioxide (Sb_2O_3). It is a constituent of tartar emetic, and is largely used in the arts as a constituent of type-metal, britannia and bearing metals, pewter, and other valuable alloys.

(*a*) Antimony is strongly attacked by chlorine (Experiment 90), forming $SbCl_3$. It is not acted upon by dilute hydrochloric or sulphuric acid, but it is easily dissolved by aqua regia. Nitric acid acts upon it, forming insoluble Sb_2O_5.

(*b*) Antimony is an acid-forming and a base-forming element, as are nitrogen and phosphorus. Some of its basic compounds in neutralizing acids form salts in which the basic hydrogen of the acids is replaced by antimony. Neither nitrogen nor phosphorus can thus replace the hydrogen of an acid.

365. Antimony Compounds. — The compounds of antimony correspond closely to those of arsenic.

(*a*) Hydrogen antimonide (stibine, antimoniureted hydrogen, SbH_3) is formed when a soluble compound of antimony is acted upon by *nascent* hydrogen. It is analogous to arsine, but its metallic deposit is easily distinguished from that of the latter compound by its darker color, smoky appearance, non-volatility, and other tests. Its combustion yields H_2O and Sb_2O_3.

(*b*) There are three known oxides of antimony, represented by the formulas Sb_2O_3, Sb_2O_4, and Sb_2O_5. The tetroxide may be considered a mixture of the other two: $Sb_2O_3 + Sb_2O_5 = 2Sb_2O_4$. These oxides form acids that resemble the phosphorus acids. There are also two sulphides (Sb_2S_3 and Sb_2S_5) and two chlorides ($SbCl_3$ and $SbCl_5$). The trichloride is a soft solid, known as butter of antimony; the pentachloride is a strongly fuming liquid.

BISMUTH: symbol, Bi; density, 9.8; atomic weight, 207; valence, 3, 5.

366. Bismuth. — Bismuth is found in nature free, and in combination with oxygen (Bi_2O_3), or with sulphur

(Bi_2S_3). In its preparation, bismuth ores are roasted and then smelted in a pot with iron, carbon, and slag. The crude bismuth is drawn off in a melted condition from the bottom of the smelting pot after the layer of less easily fusible "cobalt-speiss" above has solidified. Most of the bismuth of commerce comes from Saxony and Bohemia.

Crystallization of Bismuth.

Experiment 247. — Melt 2 or 3 kilograms of bismuth in a crucible. Perforate the covering crust that forms on cooling and pour out the still molten liquid within. When cool, break the crucible to obtain a view of the beautiful bismuth crystals thus formed.

367. Properties and Uses. — Bismuth is a brittle, brilliant, pinkish-white metal that, except in color, looks like antimony. Of all known substances, it is the most diamagnetic. In cooling from fusion, it crystallizes more readily than any other metal. Its crystals are nearly cubical rhombohedrons, often beautifully iridescent from the film of oxide formed when the crystals were still hot. It melts at 264° and expands in solidifying. In dry air at ordinary temperatures it is unaltered, but, when strongly heated, it burns with a bluish-white flame forming yellow bismuth trioxide (Bi_2O_3). It is used in forming alloys and in the construction of thermoelectric piles.

(*a*) Bismuth is acted upon readily by chlorine. Cold hydrochloric and sulphuric acids have no action upon it. Its best solvents are nitric acid and aqua regia. It has four oxides, viz., Bi_2O_2, Bi_2O_3, Bi_2O_4, Bi_2O_5. When the metal is dissolved in nitric acid and the solution is evaporated to dryness, bismuth nitrate [$Bi(NO_3)_3$] is obtained. Such salts, in which bismuth acts as a trivalent metal, are called bismuth salts. In another class of compounds, called bismuthyl salts, the group BiO (bismuthyl) acts as an univalent compound radical, as in bismuthyl nitrate. When bismuth nitrate is decomposed by heat or by water, basic nitrates or "subnitrates" of bismuth are formed. These are of varying composition, but all of them are the products of the incomplete neutralization of the basic compound, $Bi(OH)_3$.

Fusible Alloys.

Experiment 248. — Place 30 grams of bismuth, 15 grams of lead, and 15 grams of tin in boiling water. Let the metals remain there until you are convinced that none of them can be thus melted. Then place them in an iron spoon, melt them together and pour the molten mass into cold water. Immerse the alloy thus formed in boiling water and notice that it melts. Pour the liquid alloy into a small test-tube and allow it to cool. Notice that, after several minutes, the cooling and expanding metal bursts the glass walls that confine it.

368. Fusible Metals. — Bismuth forms, with certain other metals, alloys that melt at a temperature far below the melting-point of any of their constituents. The composition and melting-points of some of these are given in the following table:

	NEWTON'S METAL.	ROSE'S METAL.	LICHTENBERG'S METAL.	WOOD'S METAL.
Bismuth . . .	8 parts	2	5	4
Lead	5 "	1	3	2
Tin	3 "	1	2	1
Cadmium . .	0 "	0	0	1
Melting-point .	94.5°	93.75°	91.6°	60.5°

These melting-points may be still further reduced by the addition of mercury. It will be noticed that any of these fusible metals will melt in boiling water. If any of them is melted and poured into a glass vessel, the expansion will burst the glass when the metal cools.

These alloys are used in obtaining casts of woodcuts, etc., the cast being made when the metal has so far cooled as to be viscid. Lead, tin, and bismuth are mixed in such proportions that the alloy melts at some particular temperature above 100° for the making of safety-plugs for steam-boilers. As soon as the steam reaches the pressure corresponding to the melting-point of the alloy, the plug melts and the steam escapes. These alloys are also used in the automatic sprinkling devices for extinguishing fires in buildings. The rooms to be protected are supplied with pipes and sprinkling devices containing water under pressure. These pipes are closed with a fusible metal alloy. When a fire occurs, the heat melts the easily fusible alloy causing the room to be flooded with water from the sprinklers.

369. The Pentad Group. — The members of this group, and especially the members of each family of this group, have certain well-marked resemblances. Thus the hydrides of nitrogen and of phosphorus have strong analogies that override family lines, while the resemblances of the oxides and the acids of nitrogen and of phosphorus are far from complete. But between phosphorus, arsenic, and antimony, and between antimony and bismuth, the resemblances are very close. There is an increase in density, atomic weight, and metallic characteristics from nitrogen to bismuth, and (in a general way) an increase in chemical activity from bismuth to nitrogen. In the phosphorus family, each of the elements crystallizes in two forms; i.e., each is dimorphous. In the case of each of the four members of this family, these two crystal forms are the same; i.e., these four elements are isomorphous. The atomic weight of arsenic differs but little from the arithmetical mean of the atomic weights of phosphorus and antimony, and the atomic weight of antimony bears a similar relation to the atomic weights of phosphorus and bismuth. These relations have a significance confirmatory of the theory that the properties of the chemical elements are really periodic functions of their atomic weights (see § 148).

EXERCISES.

1. Write the reaction for Experiment 90.

2. What is meant by the statement that As_2O_3 and Sb_2O_3 are isodimorphous?

3. When a current of hydrogen disulphide is passed through a solution of $SbCl_3$, Sb_2S_3 and an acid are formed. Write the reaction.

4. Write a graphic formula for tribasic phosphoric acid, representing it as a compound of pentad phosphorus.

5. Write a graphic formula for hypophosphorous acid representing it as a compound of trivalent phosphorus.

6. (*a*) How is P_2O_5 made? (*b*) How many distinct phosphoric acids can be formed? Give their names and formulas.

7. Write the formula for bismuthyl nitrate.

8. When iodine and red phosphorus act upon each other in the presence of water, the reaction may be represented thus:

$$P + 5I + 4H_2O = 5HI + H_3PO_3.$$

What weight and what volume of the binary acid gas can be obtained by using 10 grams of phosphorus?

9. Write the structural formula for bismuth hydroxide.

10. Write the formula for antimoniureted hydrogen. How does it differ from that of stibine?

11. What is a chemical compound? How do you find the combining weights of compounds? Illustrate by potassium chlorate.

12. Give the formulas and names of two common compounds of sodium with one chemical and one physical property of each.

13. How much potassium nitrate would be decomposed by 650 grams of sulphuric acid, and how much nitric acid would be formed?

CHAPTER XVI.

THE SIXTH GROUP—HEXADS.

I. THE CHROMIUM FAMILY.

NOTE.—In the classification of elements according to the periodic law (p. 145), oxygen appears as a member of this family. This element has already been considered.

CHROMIUM: symbol, Cr; density, 4.78; atomic weight, 52; valence, 2, 3, 6.

370. Chromium.—Chromium is a rather rare, almost silver-white metal, and is not found free in nature. Its chief ore is chromite or chrome iron ore ($FeCr_2O_4$). It forms the green coloring matter of emerald and some other minerals. The fused metal is almost as hard as the diamond and melts less easily than platinum. At a white heat, it combines directly with oxygen or with nitrogen, forming, with the latter, a brown chromium nitride. It is a good conductor of electricity and is magnetic. The presence of from five-tenths to three per cent of this metal renders steel ("chromium steel") harder than carbon alone can do. Several chromium compounds are somewhat extensively used in the arts.

371. Chromic Oxides and Acids.—Chromium forms three oxides: the monoxide (chromous oxide, CrO); the sesquioxide (chromic oxide, green oxide of chromium, Cr_2O_3); and the trioxide (chromic anhydride, CrO_3).

(*a*) Chromic trioxide may be obtained by treating potassium dichromate with sulphuric acid. The red crystals thus formed may be dissolved in water forming chromic acid (H_2CrO_4). Dichromic acid ($H_2Cr_2O_7$) may be regarded as chromic acid from which water has been abstracted.

Chromium Salts.

Experiment 249. — To a solution of about 20 grams of potassium dichromate slowly add potassium hydroxide until the solution is of a pure yellow color. Evaporate two-thirds of the solution to crystallization. The red dichromate has been changed to the yellow chromate.

$$K_2Cr_2O_7 + 2KOH = 2K_2CrO_4 + H_2O.$$

Experiment 250. — Concentrate the remaining third of the yellow solution obtained in the last experiment and slowly add nitric acid until the color indicates a change of yellow potassium chromate back to red potassium dichromate.

Experiment 251. — Place a small quantity of potassium chromate in a test-tube and add a little concentrated hydrochloric acid. An easily recognizable gas will be evolved. From the equation

$$K_2CrO_4 + 8HCl = 2KCl + CrCl_3 + 4H_2O + 3Cl,$$

show that potassium chromate is a good oxidizing agent.

Experiment 252. — Repeat the last experiment substituting potassium dichromate for the chromate. From the equation

$$K_2Cr_2O_7 + 14HCl = 2KCl + 2CrCl_3 + 7H_2O + 3Cl_2,$$

show that potassium dichromate is a good oxidizing agent.

Experiment 253. — Dissolve 15 grams of pulverized $K_2Cr_2O_7$ in 100 cu. cm. of warm water. When the solution has cooled, add 15 cu. cm. of strong sulphuric acid, and pour it into a porcelain dish placed in cold water. When the liquid is cool, slowly stir in 8 cu. cm. of alcohol and set the whole aside for a day. At the end of that time, crystals of chrome alum will cover the bottom of the dish.

372. Chromates, etc. — Potassium chromate (yellow chromate of potash, K_2CrO_4) is used in the arts, but the potassium dichromate (bichromate of potash, $K_2Cr_2O_7$) is, by far, the most important of the chromium compounds, as it serves as the starting-point in the preparation of nearly all of the others. It crystallizes in beautiful garnet-red prisms and is prepared in large quantities from chrome iron ore ($FeCr_2O_4$).

(*a*) Chrome yellow is a lead chromate ($PbCrO_4$) insoluble in water. It is largely used as a pigment. Chrome alum [K_2SO_4, $Cr_2(SO_4)_3$, $24H_2O$] is a crystallizable double salt used in dyeing, calico-printing, and tanning.

373. The Chromium Family. — The other members of this family are the rare metals, molybdenum, neodymium, tungsten, and uranium. None of them are found free in nature. Molybdenum has a silver-white color and is highly infusible. In 1885, Welsbach separated the supposed element "didymium" into two substances, neodymium and praseodymium. Some chemists think that the so-called didymium consists of a group of nine or more elements. Steel that has been hardened by the addition of tungsten is used for tools for cutting other hard metals. The chief ore of uranium is an impure oxide known as pitchblende. The metal is hard and malleable and in color resembles nickel; it is feebly radioactive. The uranous salts are green; the uranic salts are yellow. Most of the latter have a remarkable power of fluorescence. Uranium yellow ($Na_2U_2O_7$) is largely used to give the beautiful yellowish green color to the variety of glass known as uranium glass. The uranyl group, UO_2, also acts as a bivalent compound radical in such compounds as uranyl nitrate and uranyl sulphate.

(*a*) The symbols and atomic weights of these elements are given in the table of chemical elements printed in the Appendix. Some of the family resemblances appear in the table herewith given.

Chromium	CrO	Cr_2O_3	—	CrO_3	H_2CrO_4	$K_2Cr_2O_7$
Molybdenum	MoO	Mo_2O_3	MoO_2	MoO_3	H_2MoO_4	—
Neodymium	—	Nd_2O_3	—	NdO_3	—	—
Tungsten	—	—	WO_2	WO_3	H_2WO_4	—
Uranium	—	U_2O_3	UO_2	UO_3	—	$Na_2U_2O_7$

EXERCISES.

1. Write the graphic formula for $K_2\overset{VI}{Cr}O_4$.

2. The constituents of air are free. Is air a chemical compound?

3. Is the manufacture of gunpowder a chemical or a physical process? Why? The combustion of gunpowder? Why?

4. From the formula for chrome iron ore (chromic iron) derive the formula for an hypothetical acid of which this ore may be regarded as a salt.

5. If 20 grams of hydrogen are exploded with oxygen, how many grams of oxygen are necessary? How many grams of dry steam will be produced?

6. You have been given the formula for potassium dichromate. Write the formula for dichromic acid.

7. Write an equation that shows that dichromic acid may be regarded as partly dehydrated chromic acid.

8. When potassium chromate is treated with nitric acid, potassium nitrate, potassium dichromate, and water are formed. Write the reaction.

9. Write the formula for some binary compound of trivalent chromium.

10. Why is "chromium steel" used for burglar-proof safes?

11. Write in tabular form the name, the atomic and molecular symbols, and the atomic weights of 20 elements.

12. Write the formula for normal sodium phosphate; for monosodium phosphate; for disodium phosphate; for potassium-hydrogen sulphate.

II. THE SULPHUR FAMILY.

SULPHUR: symbol S; density, 1.96 to 2.07; atomic weight, 32; valence, 2, 4, 6.

374. Sulphur. — Sulphur is found in nature free, and in combination principally with iron, zinc, and copper. Free sulphur is found in the volcanic regions of Italy and Sicily, and in Louisiana, Texas, and some of the Western states. It occurs sometimes in the form of transparent yellow crystals, but generally mixed with earthy materials. It is found in combination with hydrogen or with the metals, as sulphides, and with oxygen and many metals, as sulphates.

(*a*) Among the native sulphides are hydrogen sulphide (sulphureted hydrogen, H_2S), a gaseous constituent of the waters of "sulphur springs," lead sulphide (galena, PbS), zinc sulphide (blende, ZnS), copper sulphide (chalcocite, CuS), and iron disulphide (pyrite, FeS_2), etc. Sulphides were formerly called sulphurets.

(*b*) Among the native sulphates are calcium sulphate (gypsum, $CaSO_4$), barium sulphate (barite or heavy spar, $BaSO_4$), and sodium sulphate (Glauber salt, Na_2SO_4).

(*c*) Sulphur is a constituent of bone, and of some animal and vegetable tissues.

(*d*) A large part of the sulphur of commerce comes from Sicily. Some of the native crystals there found are from 5 to 7 cm. in thickness.

375. Preparation. — Native sulphur is freed from most of its earthy impurities near the place where it is found and thus fitted for purposes of commerce. The process is one of fusion or of distillation. Sulphur may also be obtained from pyrite by heat.

(*a*) One method of obtaining crude sulphur from the native earthy material is represented in Fig. 82. The earthy material is transferred through an opened slide from the preliminary heater, *D*, into the cast-iron pot, *A*, which is then closed with an iron cover and heated by a fire beneath. The sulphur thus vaporized in *A* passes over into closed vessels where it condenses to a liquid. From each condenser, *B*, the liquid sulphur runs out into wooden vessels, *K*, partly filled with water. The crude ore in the chamber, *D*, is warmed by the heated gases from the fire under *A*.

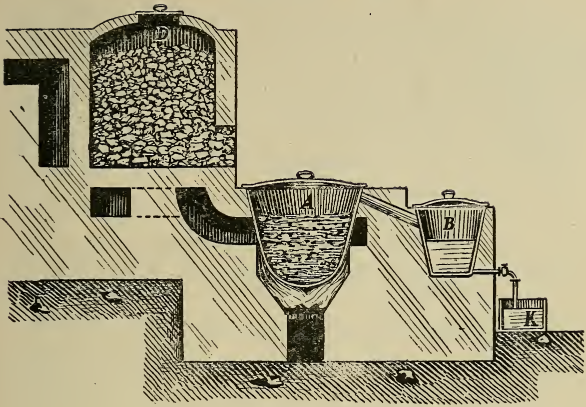


FIG. 82.

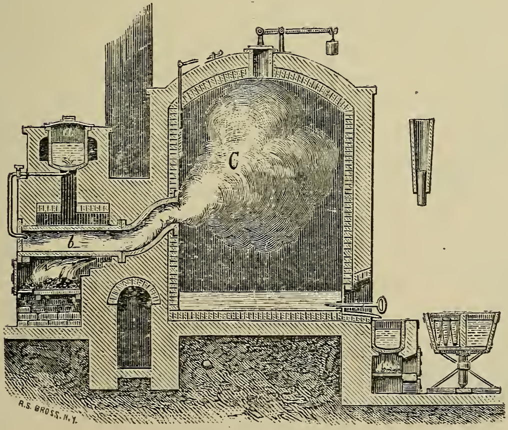


FIG. 83.

(*b*) The crude sulphur, provided by the foregoing or some other process, is further purified by distillation. It is melted in a tank, *a* (Fig. 83), runs through a pipe into the iron retort, *b*, where it is vaporized. The vapor passes from *b* into the large brick chamber, *C*, where it condenses. When the walls of *C* are cold, the sulphur condenses in the form of a light powder known as "flowers of sulphur"; when the walls of *C* are hot, the sulphur condenses to a liquid, and collects on the floor of the chamber, whence it is drawn off and run into molds to form "roll brimstone."

Physical Properties of Sulphur.

Experiment 254.—Put 30 grams of small pieces of dry sulphur into a test-tube of about 30 cu. cm. capacity. Hold the test-tube just above the lamp-flame (rotating it meanwhile) so that the sulphur melts, forming a limpid liquid of light yellow color. Heat it hotter and notice that it becomes viscid and dark colored. Heat it hotter and notice that it becomes almost black. Invert the test-tube and notice that the sulphur has become so viscid that it will not run out from the tube. Heat it hotter and notice that it again becomes fluid. Heat it until it boils and notice that it is converted into a light yellow vapor.

Experiment 255. — Pour half of the boiling sulphur of the last experiment, in a fine stream, into a large vessel nearly full of cold water, keeping the tube in motion so as to string out the sulphur; or invert a glass funnel in the water and pour the melted sulphur round and round, so as to lay a string of sulphur spirally upon the body of the funnel. The sulphur when taken from the water will be found to have no crystalline structure, to be soft, nearly black, and plastic. With filter-paper carefully dry a good sample of the plastic sulphur without pressing it into a compact mass. Carefully weigh the sample and lay it aside for a day. Then examine it for change of structure and weight. In the meantime, allow the boiling sulphur remaining in the test-tube to cool slowly and quietly, under close observation. Notice that it repasses through the viscid and limpid states and finally crystallizes as it solidifies.

Fig. 84.

Experiment 256. — Melt 200 grams of sulphur in a clay crucible. Allow it to cool until a crust forms over the top. Through a hole pierced in this crust, pour out the remaining liquid sulphur. When the crucible is cool, break it open. It will be found lined with needle-shaped crystals. The crucible may be saved by pouring the melted sulphur into a box of pasteboard or of folded paper. (Compare Experiment 247.)

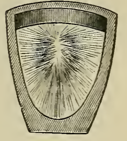


FIG. 85.

Experiment 257. — Dissolve a piece of sulphur in carbon disulphide (CS_2). The disulphide will quickly evaporate, leaving behind crystals of sulphur that resemble the native crystals. Carbon disulphide is very volatile, and its vapor is very inflammable. In experimenting with it, see that there is no flame near.

376. Physical Properties. — Sulphur manifests remarkable changes when heated. It melts at 115°, becomes dark colored and viscid at 230°, regains its fluidity at above 250°, and boils a little below 450°. On cooling, these changes occur in inverse order. Its vapor-density has been the subject of careful investigation for the sake of determining the constitution of its molecule. The early determinations of a vapor-density of 96 signifying a molecule consisting of six atoms, were accepted until recent times. In 1860 it was found that above 860° the vapor-density is only 32, signifying a molecule consisting of two atoms. More recently it was found that the molecule of sulphur in solution consists of eight atoms, and it was inferred that the same molecule exists in sulphur vapor just above its boiling-point. The latest investigations indicate that there are only two sulphur molecules (S_8 and S_2) and that, at the boiling-point, the molecule with eight atoms begins to decompose into molecules of two atoms. This decomposition is progressive, being complete at about

850°. Sulphur is odorless and tasteless, and exists in three distinct forms, orthorhombic, monoclinic, and amorphous.

(*a*) The crystals of sulphur formed by fusion are monoclinic; the native crystals and those formed by solution and evaporation are orthorhombic. Substances which, like sulphur, crystallize under two systems are called dimorphous (two-formed). Sulphur is not only thus dimorphous, but the plastic variety is amorphous (without crystalline form).

(*b*) The orthorhombic form of sulphur is brittle and soluble in carbon disulphide, petroleum, or turpentine; it is the stable form from low temperatures up to 96°. The monoclinic form is brittle; it is the stable form from 96° to 120°. The form of the crystal seems to depend upon the region of stability in which the sulphur happens to be. The amorphous form is plastic and insoluble in carbon disulphide. Exposed to the air, it gradually assumes the brittle form at ordinary temperatures; heated to 100°, it changes, and evolves enough heat to raise its temperature to 110°.

Chemical Properties of Sulphur.

Experiment 258. — Ignite a small piece of sulphur on the bottom of an inverted saucer and notice the peculiar blue flame. Cautiously observe the odor of the gaseous product. This odor is commonly called sulphurous, but it is the odor not of the sulphur but of its dioxide (SO_2). Wet a piece of blue litmus-paper, stick it on the inner surface of the bottom of a beaker, invert the beaker over the burning sulphur, and notice the effect of the gas on the litmus.

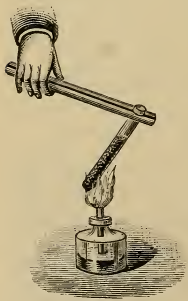


Fig. 86.

Experiment 259. — Mix intimately 4 grams of flowers of sulphur and 8 grams of copper filings. Heat the mixture in an ignition-tube until the elements unite with a vivid combustion to form copper sulphide (CuS).

Experiment 260. — In a mortar thoroughly mix 3.2 grams of flowers of sulphur and 6.5 grams of zinc-dust. Take a small portion of the mixture on the tip of a spatula-blade and, at arm's length, thrust it into a gas-flame. The chemical union of the mixed substances produces zinc sulphide. Repeat the experiment using 5.6 grams of iron-dust instead of the zinc-dust, and name the product. Compare the weights of the sulphur, zinc, and iron used in this experiment with the atomic weights of these elements.

377. Chemical Properties. — Sulphur unites with oxygen at the comparatively low temperature of about 250°. It enters energetically into union with most of the elements, in many cases with the evolution of light.

378. Uses. — Sulphur is largely used in the manufacture of sulphuric acid, vulcanized india-rubber, friction matches, gunpowder, and sulphur dioxide.

379. Tests. — Free sulphur is easily recognized by its color, and by the odor of the oxide that is formed when it is burned. Combined sulphur may be detected by mixing the compound with pure sodium carbonate and fusing the mixture before the blowpipe on charcoal. The carbon of the charcoal unites with the oxygen of the sulphate (for example) forming gaseous carbon dioxide (CO_2) and leaving the sodium and the sulphur combined as sodium sulphide.

$$Na_2SO_4 + 2C = Na_2S + 2CO_2.$$

When the fused mass is placed on a silver coin and water added, a brown stain of silver sulphide is formed on the coin.

EXERCISES.

1. Why are the ends of friction matches generally dipped in melted sulphur or in paraffin?

2. When sulphur is prepared from pyrite, Fe_3S_4 is formed. Write the reaction.

3. By bringing bromine and phosphorus together in the presence of water, both phosphoric (H_3PO_4) and hydrobromic acids are formed. (*a*) What weight of bromine is necessary to yield 5 grams of the colorless gas, HBr? (*b*) What weight of bromine is necessary to yield 10 liters of HBr?

4. Iodine acts upon $KClO_3$, forming potassium iodate and setting chlorine free:

$$2KClO_3 + I_2 = 2KIO_3 + Cl_2.$$

(*a*) How much chlorine by weight may thus be freed by 10 grams of iodine? (*b*) How much by volume?

5. (*a*) How many grams of hydrogen may be prepared by the use of 260 grams of zinc? (*b*) How many liters? (*c*) How many grams of HCl are necessary?

6. Can S_2 and S_8 exist at the same temperature? Explain.

7. (*a*) One cubic centimeter of water will yield by electrolysis how many grams of free gases? (*b*) How many cubic centimeters of oxygen? (*c*) How many cubic centimeters of hydrogen? (*d*) The explosion of these gases will yield how many cubic centimeters of dry steam?

8. (*a*) If ozone could be produced from $KClO_3$, how many grams of the former could be produced from 10 grams of the latter? (*b*) How many liters of the former?

9. Determine the formula of a compound that has a vapor-density of 49, and that contains 2.04 per cent of hydrogen, 32.65 per cent of sulphur, and 65.31 per cent of oxygen.

10. Calomel and corrosive sublimate are each composed of mercury and chlorine atoms. Why do the two substances differ, their atoms being of the same kind?

11. Complete the following equation by inserting the proper figures, and correct any error that you find:

$$K_2ClO_3 + HCl = KCl + H_2O + Cl_2.$$

12. Write with mathematical propriety the names and the molecular (or the multimolecular) weights of $2HNO_3$, $3CaCO_3$, K_2CrO_4, $2H_3PO_4$, and SiO_2, following this model:

$3H_2O_2$; $3[2(1) + 2(16)] = 102$, the weight of 3 molecules of hydrogen dioxide.

380. Hydrogen Sulphide. — Hydrogen sulphide (hydrosulphuric acid, H_2S) occurs free in certain volcanic gases, and is the characteristic constituent of the waters of "sulphur springs." It is generated by the putrefaction of animal matter, causes the peculiar odor of rotten eggs, and is a constant constituent of sewer gases.

Preparation of Hydrogen Sulphide.

Experiment 261. — Into a gas-bottle, arranged as for the preparation of hydrogen, put about 10 grams of iron sulphide (FeS), replace the cork snugly, add enough water to seal the lower end of the funnel-tube, and place the bottle in the ventilating chamber, out of doors, or in a good draft of air to carry off any of the offensive H_2S that may escape. Let the delivery-tube dip 5 or 6 cm. under cold water contained in another bottle, *e*. Add a few cubic centimeters of sulphuric or of hydrochloric acid. Bubbles of gas appear in *e* and are absorbed by the water. Add acid in small quantities, as in the preparation of hydrogen, until the water in *e* smells strongly of the gas. Remove the gas-bottle and cork it tightly.

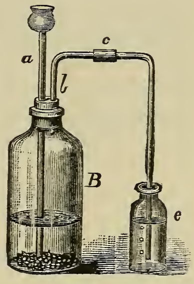


FIG. 87.

381. Preparation. — Hydrogen sulphide may be prepared by the direct union of its constituents, but it is generally prepared by the action of dilute sulphuric or of hydrochloric acid upon iron sulphide (ferrous sulphide, FeS). The gas may be collected over warm water.

$$FeS + H_2SO_4 = FeSO_4 + H_2S, \text{ or}$$
$$FeS + 2HCl = FeCl_2 + H_2S.$$

382. Physical Properties. — Hydrogen sulphide is a colorless gas, having a sweetish taste and the offensive odor of rotten eggs. At the ordinary atmospheric pressure, and at a temperature of $-74°$, it condenses to a colorless liquid that boils at − 63.5°, and that solidifies at − 91° to a white crystalline mass. Its density is 17, it being thus a little heavier than air. At ordinary temperatures, water dissolves a little more than three times its volume of the gas. The solution has the peculiar odor of the gas and a slightly acid reaction.

Chemical Properties of Hydrogen Sulphide.

Experiment 262. — Bring a flame to the open mouth of a jar of H_2S. The gas will burn with a pale blue flame, forming water and sulphur dioxide, and depositing a slight incrustation of sulphur on the inside of the jar.

Experiment 263. — Attach a drying-tube, containing calcium chloride, to the delivery-tube of the gas-bottle. Provide the drying-tube with a jet made of glass tubing. When all of the air has been expelled from the apparatus, *and not till then*, hold a lighted match to the jet. (A mixture of H_2S and air is explosive.) The gas will burn with a blue flame. Hold a dry bottle over the flame. Moisture will condense on the sides of the bottle. This liquid will redden blue litmus-paper.

$$2H_2S + 3O_2 = 2H_2O + 2SO_2.$$

Experiment 264. — Burn a jet of H_2S, using the apparatus arranged as described in Experiment 28. With blue litmus-paper test the liquid that accumulates in the cup.

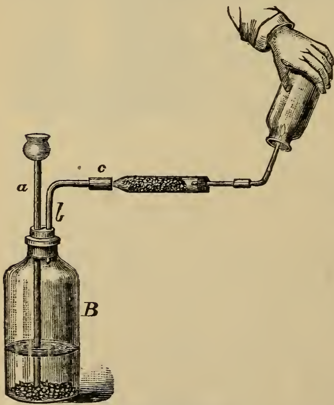


Fig. 88.

Experiment 265. — Heat the glass tube between the drying-tube and the jet. The H_2S will be decomposed and the sulphur deposited on the cold part of the tube. The product that now accumulates in the cup will not redden blue litmus-paper. The analysis of H_2S is here followed by the synthesis of water.

Experiment 266. — Moisten a bright silver or copper coin and hold it in a stream of H_2S. The coin will be quickly blackened by the formation of a metallic sulphide. The same effect will follow the dipping of the bright coin into a water solution of H_2S.

Experiment 267. — Write your name in a colorless, water solution of lead acetate (sugar of lead). Hold the autograph, before drying, in a stream of H_2S. The lead sulphide formed renders the invisible writing legible.

Experiment 268. — Make a sketch in the same colorless liquid and allow it to dry. At any convenient time, float the paper containing the invisible design upon a solution of H_2S. The figure will "come out" promptly.

Experiment 269. — In separate test-tubes place warm solutions of the following substances:

1. Lead acetate [$Pb(C_2H_3O_2)_2$], diluted.
2. Mercuric chloride ($HgCl_2$).
3. Cadmium nitrate [$Cd(NO_3)_2$].
4. Sodium arsenite (Na_3AsO_3) and dilute hydrochloric acid.
5. Antimony chloride ($SbCl_3$).
6. Zinc acetate [$Zn(C_2H_3O_2)_2$].

To each tube add a few cubic centimeters of a saturated solution of H_2S. The following precipitates will be found:

1. Lead sulphide (PbS); black.
2. Mercuric sulphide (HgS); red, then black.
3. Cadmium sulphide (CdS); yellow.
4. Arsenious sulphide (As_2S_3); yellow.
5. Antimonious sulphide (Sb_2S_3); orange.
6. Zinc sulphide (ZnS); white.

Write the equation for each of these reactions. Add a dilute acid to the contents of each test-tube, and notice what precipitates are dissolved. Then treat a dilute solution of zinc sulphate with H_2S, write the reaction, and explain why there is no precipitate. Add a few drops of ammonia-water, and explain why the zinc sulphide is precipitated.

Experiment 270. — Dissolve about a gram of potassium iodide (KI) and a few small crystals of iodine in about 10 cu. cm. of water in a test-tube. Pass a slow current of H_2S through the solution until the latter is decolorized. Hydriodic acid is formed and sulphur is set free.

$$H_2S + I_2 = 2HI + S.$$

The potassium iodide is used because, while iodine is only slightly soluble in water, it is readily soluble in a solution of an iodide.

383. Chemical Properties. — Hydrogen sulphide is easily combustible, the products of its combustion being water and sulphur dioxide, provided there is an excess of oxygen.

$$2H_2S + 3O_2 = 2H_2O + 2SO_2.$$

If the supply of oxygen is insufficient, only water and free sulphur will be formed, hydrogen having a stronger attraction for oxygen than sulphur has.

$$2H_2S + O_2 = 2H_2O + 2S.$$

Hydrogen sulphide is readily decomposed by many metals with liberation of hydrogen and formation of a metallic sulphide.

$$2Ag + H_2S = Ag_2S + H_2.$$

It is this reaction that causes silverware to tarnish, the hydrogen sulphide generally coming from illuminating gas and from the products of the combustion of coal. Almost all oxidizing agents decompose hydrogen sulphide with formation of oxygen-sulphur compounds. It precipitates metallic sulphides from solutions of the compounds of many metals. Its solution reddens blue litmus. The gas is very poisonous when breathed, and even when much diluted its respiration is very injurious. Under such circumstances, the best antidote is the free inhalation of pure oxygen preceded by the inhalation of dilute ammonia.

(*a*) With hydroxides of the metals, hydrogen sulphide yields two classes of salts, — sulphides and sulphydrates.

$$2KOH + H_2S = K_2S + 2H_2O$$
$$KOH + H_2S = KHS + H_2O.$$

The salts that appear in the products of these illustrative reactions are potassium sulphide (K_2S) and potassium hydrosulphate (KHS).

384. Volumetric Composition. — The composition of hydrogen sulphide may be ascertained by heating metallic tin in a known volume of the gas. The gas will be decomposed, the sulphur combining with the tin as tin sulphide and the hydrogen being set free. The volume of hydrogen will be the same as that of the hydrogen sulphide decomposed. When a platinum-wire spiral is electrically heated to redness in a known volume of hydrogen sulphide, the gas is decomposed. The volume of the hydrogen will again be the same as that of the hydrogen sulphide. Careful analyses have proved that the composition of this gas may be expressed by the following diagram:

$$\boxed{\begin{matrix}H\\1\end{matrix}} + \boxed{\begin{matrix}H\\1\end{matrix}} + \boxed{\begin{matrix}S\\32\end{matrix}} = \boxed{\begin{matrix}H_2S\\34\end{matrix}}$$

385. Uses and Tests. — Hydrogen sulphide is very extensively used in the chemical laboratory as a reagent, forming sulphides that are characteristic (in color, solubility, or some other easily recognized property) for certain metals or groups of metals. It is easily detected by its odor, or by holding in it a strip of paper wet with an aqueous solution of lead acetate.

NOTE. — Hydrogen sulphide was formerly called sulphureted hydrogen. Hydrogen persulphide (H_2S_2) has been prepared as a yellow, transparent, oily liquid.

386. Carbon Disulphide. — Carbon disulphide (CS_2) is prepared synthetically on a large scale by passing sulphur vapor over glowing coke or charcoal.

$$C_2 + 2S_2 = 2CS_2.$$

CAUTION. — In performing experiments with CS_2, see that there is no flame near.

Properties of Carbon Disulphide.

Experiment 271. — Put a few drops of CS_2 into each of four small test-tubes. Into the first tube put a little powdered sulphur; into the second, a few crystals of iodine; into the third, a very small piece of phosphorus; into the fourth, a little water. Notice the solubility of the sulphur, iodine, and phosphorus in CS_2, and the insolubility of CS_2 in water.

Experiment 272. — Wet a block of wood and place a watch-crystal upon it. A film of water may be seen under the central part of the glass. Half fill the crystal with CS_2 and rapidly evaporate it by blowing over its surface a stream of air from the lungs or from a small bellows. So much heat is rendered latent in the vaporization that the glass is firmly frozen to the wooden block.

Experiment 273. — Into a glass cylinder pour a few drops of CS_2. In a few moments the cylinder will be filled with a heavy vapor. Thrust into the cylinder the end of a glass rod, heated not quite to redness. The vapor will be ignited.

FIG. 89.

$$3O_2 + CS_2 = CO_2 + 2SO_2.$$

387. Properties. — Ordinary carbon disulphide is a liquid of light yellow color and offensive odor. Its vapor is injurious to animal and vegetable life and exceedingly inflammable. As it is heavier than water and insoluble therein, it is easily preserved under water. It is diathermanous, has a highly refractive effect upon light, evaporates rapidly at ordinary temperatures, and boils at about 46°, yielding a heavy vapor that ignites at about 150°, and that forms an explosive mixture with air. Pure carbon disulphide is colorless and has an agreeable odor resembling that of chloroform.

388. Uses. — Carbon disulphide is used as a solvent for phosphorus, iodine, sulphur, and many resins and oils. It is used in the extraction of fats and oils, in the cold process of vulcanizing caoutchouc, and largely for the extermination of vermin, and as a solvent for rubber in making rubber cement.

EXERCISES.

1. Write the reaction for Experiment 261.

2. When metallic tin is heated in H_2S, the gas is decomposed. The sulphur unites with the tin. (*a*) Name the solid and gaseous products. (*b*) How will the volume of this gaseous product compare with that of the decomposed gas?

3. When a spiral of platinum wire is heated in an atmosphere of H_2S, the gas is decomposed with the deposition of solid sulphur. What volume of hydrogen can thus be set free from a liter of H_2S?

4. The reaction resulting from passing a current of H_2S through an aqueous solution of bromine is as follows:

$$H_2S + Br_2 = 2HBr + S.$$

(*a*) What volume of H_2S is needed to yield 4 liters of HBr? (*b*) What weight of bromine will thus combine with 10 grams of H_2S?

5. Why was 6H instead of $3H_2$ written into the equation near the bottom of page 262?

6. (*a*) How many liters of oxygen will unite with 20 liters of NO to form NO_2? (*b*) How many each of oxygen and NO to form 30 liters of NO_2?

7. Arsenic vapor is 150 times as heavy as hydrogen. (*a*) What is the molecular weight of arsenic? Explain. (*b*) The atomic weight of arsenic is 75. How many atoms are there in an arsenic molecule?

8. (*a*) What name would you apply to a substance that has only one kind of atoms? (*b*) One that has two kinds? (*c*) One that has three kinds?

9. State Avogadro's law. Define chemistry.

10. What weight of sulphur in 10 liters of sulphur vapor under normal pressure at 500°? At 1050°?

11. How much zinc sulphide will be formed by the precipitation of 10 grams of zinc chloride by hydrogen sulphide?

12. What volume of hydrogen sulphide, at 0° and 760 mm., will be required for the precipitation mentioned in Exercise 11?

13. An analysis of acetic acid shows that it contains about 40 per cent of carbon, 6.67 per cent of hydrogen, and 53.33 per cent of oxygen. The vapor-density of the acid is found to be about 30. Determine from these data the formula for acetic acid.

14. What is the valence of sulphur in hydrogen sulphide?

15. Write in tabular form the names, molecular symbols, and molecular weights of 10 binary compounds that you have studied.

389. Sulphur Oxides. — Sulphur and oxygen unite to produce two acid-forming oxides (or anhydrides) symbolized as SO_2 and SO_3. These unite with water to form the acids symbolized as H_2SO_3 and H_2SO_4.

(*a*) In addition to these, we have sulphur sesquioxide (S_2O_3), which has no corresponding known acid; hyposulphurous acid (H_2SO_2), which has no corresponding known oxide; sulphur peroxide (S_2O_7); and the thionic acids (§ 403). Sulphur sesquioxide is a rare compound, and easily decomposes into sulphur dioxide and sulphur.

390. Sulphur Dioxide. — This oxide of sulphur (SO_2) is known by the various names of sulphurous oxide, sulphurous anhydride, sulphurous acid gas, and sulphuryl.

Preparation of Sulphur Dioxide.

Experiment 274. — Put 20 or 30 grams of small bits of copper (Cu) and 60 cu. cm. of strong sulphuric acid into a flask and apply heat. The gas that is evolved may be purified by passing it through water in a wash-bottle, *b* (Fig. 90), and then collected by downward displacement or over mercury. It may be recognized by its familiar odor. A solution of copper sulphate (blue vitriol, $CuSO_4$) remains in the flask.

$$2H_2SO_4 + Cu = CuSO_4 + 2H_2O + SO_2.$$

Experiment 275. — When an aqueous solution of the gas is desired, the above experiment may be modified by substituting charcoal for the copper, and absorbing the gas in water as shown at *c*.

$$2H_2SO_4 + C = 2SO_2 + 2H_2O + CO_2.$$

If these mixed gases are passed through water in a series of Woulffe bottles (Fig. 29), most of the sulphur dioxide and very little of the carbon dioxide will be absorbed. Such a solution is often wanted in the laboratory.

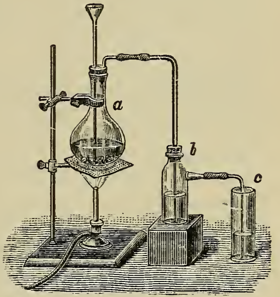


FIG. 90.

391. Preparation. — For industrial purposes, sulphur dioxide is generally prepared by burning sulphur or some sulphide in the air. When thus prepared, it is mixed with nitrogen from the air. When the pure anhydride is wanted, it is generally prepared from strong sulphuric acid by heating it with copper, mercury, or carbon, as illustrated by the preceding experiments.

Properties of Sulphur Dioxide.

Experiment 276. — From the generating flask, *a* (Fig. 90), pass the SO_2 through a bottle or tube packed in ice; then dry the cool gas with sulphuric acid or calcium chloride; then pass the dry gas through a U-tube packed in salt and pounded ice. The SO_2 will condense to a liquid at the low temperature thus produced. If the U-tube has good glass stop-cocks, as shown in the figure, the liquid SO_2 may be sealed and preserved. If the two arms of a common U-tube have been previously drawn out to make a narrow neck upon each, the expensive stop-cocks may be dispensed with; after the condensation of the SO_2, these necks may be fused with the blowpipe flame and the liquid thus sealed for preservation.

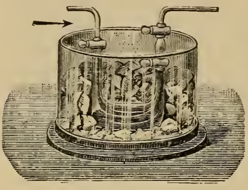


FIG. 91.

Experiment 277. — Add a few drops of the aqueous solution of SO_2 to a weak solution of potassium permanganate. The red color of the latter will disappear, owing to its reduction by SO_2.

Experiment 278. — Burn some sulphur under a bell-glass within which are some moist, bright-colored flowers. The flowers will be bleached. The color may be partly restored by dipping some of the flowers into dilute sulphuric acid and others into ammonia-water.

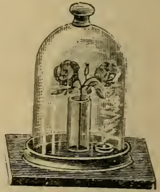


FIG. 92.

Experiment 279. — Partly fill each of two glasses with a fresh infusion of purple cabbage. Add a little of the aqueous solution of SO_2. The bleaching action is not very manifest. To each, add cautiously, drop by drop, a solution of potassium hydroxide (caustic potash, KOH); the color will disappear. To the contents of one glass, add a little strong sulphuric acid; a red color appears. To the other add more of the solution of the hydroxide; a green color appears.

Experiment 280. — Lower a lighted taper into a jar of SO_2. Does this gas support combustion?

CAUTION. — The next three experiments should be performed under a ventilating hood with a good draft.

Experiment 281. — Pour some of the liquid SO_2 upon the surface of mercury contained in a capsule, and, by means of a bellows, blow a current of air over it. The mercury will be frozen.

Experiment 282. — If you have a thick, platinum crucible, heat it red-hot and pour some of the liquid SO_2 into it. The dioxide will assume the "spheroidal state," like that of the globules of water sometimes seen upon the top of a hot stove, the temperature of the liquid being below its boiling-point. If, now, a little water is poured in, the SO_2 will be instantly vaporized by the heat taken from the water, which therefore at once becomes ice. By some dexterity, the lump of ice may be thrown out of the red-hot crucible.

Experiment 283. — Wrap the bulb of an alcohol thermometer in cotton-wool and pour some of the liquid SO_2 upon it. The change of sensible into latent heat effected by the vaporization of the dioxide produces a diminution of temperature and the thermometer falls, perhaps as low as $-60°$.

392. Properties. — Sulphur dioxide is a transparent, colorless, irrespirable, suffocating gas. Under ordinary conditions, it is neither combustible nor a supporter of combustion. It has a density of 32, being more than twice as heavy as air. It bleaches many colors, not by destroying the coloring matter, as chlorine does, but by uniting with it to form unstable, colorless compounds. When, by the action of chemical agents, the sulphur dioxide is set free from the colorless compounds thus formed, the color reappears. This oxide condenses to a liquid at $-16°$ under the ordinary atmospheric pressure, or at the ordinary temperature under a pressure of three atmospheres. The liquid has a density of 1.43, boils at $-8°$, and vaporizes rapidly in the air at the ordinary temperature, producing great cold. It solidifies when cooled below $-76°$.

(*a*) Sulphur dioxide has a strong affinity for oxygen. If these dry gases are conducted over hot platinum-sponge or platinized asbestos, sulphur trioxide is formed.

$$2SO_2 + O_2 = 2SO_3.$$

The Winckler or "contact" method, by which large quantities of sulphuric acid are made, is based on this reaction.

(*b*) An aqueous solution of SO_2 slowly absorbs oxygen from the air, yielding sulphuric acid (H_2SO_4). Write the reaction in complete molecules. Some other agents effect a similar change more promptly, thus:

$$SO_2 + 2H_2O + I_2 = H_2SO_4 + 2HI.$$

(*c*) The composition of sulphurous anhydride is represented by the following diagram:

$$\boxed{\begin{matrix} \text{O} \\ 16 \end{matrix}} + \boxed{\begin{matrix} \text{O} \\ 16 \end{matrix}} + \boxed{\begin{matrix} \text{S} \\ 32 \end{matrix}} = \boxed{\begin{matrix} \text{SO}_2 \\ 64 \end{matrix}}$$

393. Uses and Tests. — Sulphur dioxide is largely used in the manufacture of sulphuric acid and for bleaching straw, silk, woolen goods, and wood-pulp for the manufacture of paper. It is also used as an antichlor for the purpose of removing the excess of chlorine present in the bleached rags from which paper is made, and as an antiseptic. When free, it is easily detected by its familiar odor and by its blackening a paper wet with a solution of mercurous nitrate.

394. Sulphur Trioxide. — When dry oxygen and dry sulphurous anhydride are mixed and passed over heated platinum-sponge or platinized asbestos, they combine, forming dense fumes of sulphur trioxide (sulphuric oxide, sulphuric anhydride, SO_3). When these fumes are condensed in a dry, cool receiver, they form white, silky, fiber-like crystals resembling asbestos. Sulphur trioxide may be prepared more easily by gently heating Nordhausen acid (§ 401) and condensing the vapor given off, as in the method above described. When perfectly dry, it does not exhibit any acid properties and may be molded with the fingers without injury to the skin. It has so great an attraction for water that it can be preserved only in vessels hermetically sealed. It unites with water with a hissing sound and the evolution of much heat, forming sulphuric acid.

$$SO_3 + H_2O = H_2SO_4.$$

395. Sulphurous Acid. — Sulphur dioxide is freely soluble in water, forming sulphurous acid (hydrogen sulphite, H_2SO_3). At 40° this liquid is decomposed into water and sulphur dioxide; when it is cooled below 5°, it yields a crystalline hydrate of sulphurous acid with a composition of H_2SO_3, $14H_2O$. On standing, it absorbs oxygen from the air and changes to sulphuric acid (H_2SO_4). As it is dibasic, it gives rise to two series of sulphites (§ 94). The term "sulphurous acid" is frequently applied to sulphur dioxide, but such use of the term is incorrect.

396. Sulphuric Acid. — Sulphuric acid (hydrogen sulphate, oil of vitriol, H_2SO_4) seldom occurs free in nature, but its salts, especially those of calcium and barium, are abundant. Sulphuric acid is to the chemical arts what iron is to the mechanical arts; it enters, directly or indirectly, into the preparation of nearly every substance with which the chemist deals. It has been said that the commercial prosperity of any country may be well measured by the quantity of sulphuric acid that it uses.

397. Preparation. — Sulphuric acid is formed by the addition of water to sulphur trioxide. The water may be added at the time of the formation of the anhydride or subsequently. For this purpose, the sulphuric anhydride is formed by the oxidation of sulphurous anhydride by means of nitrogen oxides or acids, or by the method of oxidation described in § 394.

(*a*) In a bottle having a capacity of 1 liter or more, burn a bit of sulphur. In the atmosphere of SO_2 thus formed, place a stick (or a glass rod carrying a tuft of guncotton) that has been dipped in strong nitric acid. Red fumes of nitrogen dioxide will appear. The red fumes show that the nitric acid has been robbed of part of its oxygen.

$$2HNO_3 + SO_2 = H_2SO_4 + 2NO_2.$$

In the presence of moisture, SO_2 is able to reduce (i.e., to take oxygen from) HNO_2, HNO_3, N_2O_3, or NO_2. In the process just described, the SO_2 reduced the acid; the acid oxidized the SO_2.

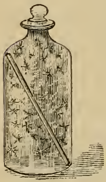


FIG. 93.

(*b*) The manufacture of H_2SO_4 may be prettily represented by the following lecture-table process: A large glass globe or flask is filled with air or oxygen and provided with five tubes. One tube connects it with a flask that furnishes a current of SO_2; another connects it with a second flask or bottle, that furnishes a current of nitric oxide; the third connects it with a flask that furnishes a current of steam; by the tube, *d*, a supply of air or oxygen is admitted, from time to time, into the globe. The fifth tube, *e*, allows the escape of the waste products of the reaction; it may be connected with an aspirator.

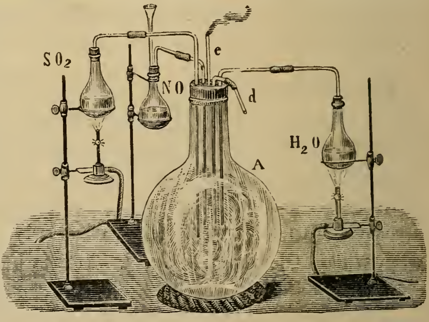


FIG. 94.

(1) Nitric oxide enters the globe and takes oxygen from the air. The ruddy fumes of nitrogen peroxide are seen.

(2) On admitting a current of SO_2, the red fumes of nitrogen peroxide disappear and white "leaden-chamber crystals" form on the walls of the globe. The NO_2 has been reduced and the SO_2 oxidized.

(3) On admitting steam, the crystals disappear, and dilute H_2SO_4 collects at the bottom of the globe.

(4) If air is admitted, red fumes again appear and the process may be repeated.

(*c*) In the manufacture of this acid on the commercial scale, SO_2 and nitrogen oxides are generally formed by burning crude sulphur, pyrite (FeS_2), or blende (ZnS) in kilns provided for that purpose, as shown at *S* in Fig. 95. The quantity of air admitted is carefully regulated. From the kilns the SO_2 and other gases are drawn through the apparatus by the draft of a large chimney. They are carried first into the leaden Glover tower, *G*, which is filled with coke that is drenched with nitrosyl-sulphuric acid from the Gay-Lussac tower, *L*. If the nitro-

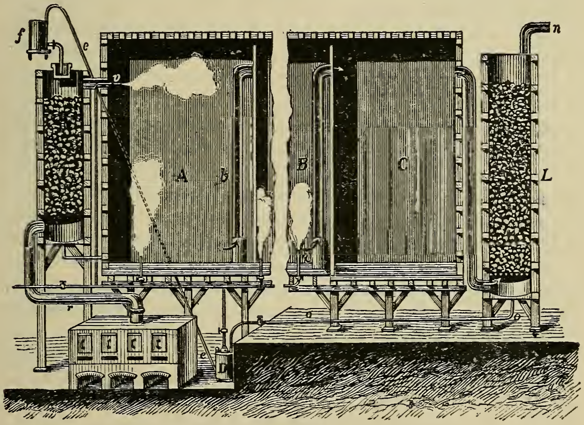


FIG. 95.

gen oxides are not supplied in sufficient quantity by the reaction of sodium nitrate and H_2SO_4 in the furnaces, liquid nitric acid is allowed to trickle down over the coke in *G*. The H_2SO_4 formed in this Glover tower is drawn off below, while nitrogen trioxide, air, and an excess of SO_2 pass on to the lead-lined chambers, *A*, *B*, and *C*, in succession. In each of these chambers the gases meet steam, and the oxidation and the union with water continue. These lead chambers are sometimes 30 meters long, 6 or 7 meters wide, and about 5 meters high, having thus a capacity of about a thousand cubic meters. They are supported by a wooden framework, carried by pillars of brick or iron. The H_2SO_4 formed in the chambers accumulates on the floor. The process is conducted so that this "chamber acid" has a density of 1.55, as a stronger acid absorbs the nitrogen oxides. After leaving the lead chambers, the excess of nitrogen oxides is absorbed by concentrated H_2SO_4 in the Gay-Lussac tower, while the nitrogen escapes. The "chamber acid," which contains 64 per cent of H_2SO_4, is then concentrated in the "denitrating," or Glover tower, where it is mixed with the "nitrated acid" from the Gay-Lussac tower and exposed to the influence of the hot gases as they pass from the kilns into the chambers. If not yet sufficiently concentrated, the acid from the Glover tower is evaporated in leaden pans until it has a density of 1.7 and contains 78 per cent of H_2SO_4. If concentrated beyond this point, the hot acid attacks the lead of the pans. Lead is used for this apparatus because it is the cheapest metal not attacked by dilute sulphuric acid. In this form the acid is technically called brown oil of vitriol, as it is slightly colored by organic impurities. It is largely sold for a great variety of purposes. Further concentration and purification are carried on in glass retorts of from 75 to 150 liters capacity, or in large platinum stills until the liquid contains 98 per cent of H_2SO_4 and has a density of upwards of 1.8. The strongest acid may be concentrated in cast-iron stills, as when its density is greater than 1.8 it has little action on iron.

(*d*) Although we have no reason to think that some of the reactions in the manufacture of H_2SO_4 are not simultaneous, we may, with propriety, trace them as if they were really consecutive. Several such explanatory series of reactions have been written out. One of these is herewith given, not as a didactic statement of what actually takes place, but as a theoretical exposition of what may take place.

(1) $4FeS_2 + 11O_2 = 8SO_2 + 2Fe_2O_3$, or $S + O_2 = SO_2$.

(2) $2HNO_3 + 2SO_2 + H_2O = 2H_2SO_4 + N_2O_3$.

(3) $SO_2 + N_2O_3 = SO_3 + 2NO$.

(4) $SO_3 + H_2O = H_2SO_4$.

(5) $2NO + O_2 = 2NO_2$, or $4NO + O_2 = 2N_2O_3$.

The NO_2 and the N_2O_3 formed by these reactions are absorbed by the concentrated H_2SO_4 in the Gay-Lussac tower, combining chemically to form nitrosyl-sulphuric acid.

$$2H_2SO_4 + N_2O_3 = 2H(NO)SO_4 + H_2O.$$

This nitrosyl-sulphuric acid is pumped back to the Glover tower, where it comes into contact with steam, whereby H_2SO_4 and N_2O_3 are formed.

$$2H(NO)SO_4 + H_2O = 2H_2SO_4 + N_2O_3.$$

(*e*) It is thus seen that most of the oxygen used for the oxidation of the SO_2 comes from the air admitted to the chambers through the kiln. The part taken in the process by the nitrogen oxide is very interesting, it acting as a carrier of oxygen from the air to the SO_2. Theoretically, but not practically, a single molecule of HNO_3 or of NO would be sufficient for the manufacture of an unlimited amount of H_2SO_4, as may be seen by repeating the equations above (omitting the second) in a series continued to any extent desired. But, since air is used instead of pure oxygen, the nitrogen thus introduced into the chambers has to be removed, and, in its passage out, sweeps away some of the nitrogen oxides, which then have to be supplied anew.

(*f*) The lead chambers for this method of manufacturing H_2SO_4 are expensive, as is the niter used. The Winckler method previously mentioned (§ 392, *a*) requires a considerable investment for platinum-sponge, but it requires no niter and yields a concentrated acid, pure without distillation. It is gradually replacing the chamber process where the strongest acid is required.

Properties of Sulphuric Acid.

Experiment 284. — Place 27 cu. cm. of water in a graduated tube. Slowly add 73 cu. cm. of H_2SO_4. When the mixture has cooled, notice that its volume is about 92 cu. cm. instead of 100 cu. cm.

CAUTION. — In mixing H_2O and H_2SO_4, pour the acid into the water, not the water into the acid. If the lighter liquid is poured on top of the heavier, it will float there and great heat will be developed at the level where they come into contact. This heat might form steam of sufficient tension to burst through the heavier liquid above and do damage by scattering the acid. When the above directions are followed, the heavy acid mixes with the water as it falls through it.

Experiment 285. — Place 30 cu. cm. of water in a beaker of about 250 cu. cm. capacity. Into this, pour 70 cu. cm. of concentrated H_2SO_4 in a fine stream. Stir the mixture with a test-tube containing alcohol or ether, colored with cochineal or other coloring matter. The liquid in the test-tube will boil. Holding the test-tube in a pair of nippers, ignite the escaping vapor. The test-tube may be closed with a cork carrying a delivery-tube, and the jet ignited. It will give a voluminous flame. With a chemical thermometer, take the temperature of the liquids before and after mixture. If the test-tube stirrer contains water instead of the more volatile liquids mentioned, the water will boil.

Experiment 286. — Dip a splinter of wood into H_2SO_4. It will be charred as if by fire.

Experiment 287. — Repeat Experiment 1. The black mass consists partly of carbon, and partly of half-carbonized sugar. The concentrated acid has so great an affinity for water, that it removes the constituents thereof from the carbon with which they are combined to form sugar ($C_{12}H_{22}O_{11}$). It acts similarly with most compounds in which carbon is united with hydrogen and oxygen.

398. Properties. — The sulphuric acid of commerce is largely known as oil of vitriol, because it is of an oily consistency and was originally made by distilling green vitriol (ferrous sulphate). It has a density of about 1.82. It generally contains, as impurities, lead sulphate from the chambers and evaporating pans, and arsenic from the pyrite. For most purposes, however, it answers as well as the "H_2SO_4, C.P.," or chemically pure acid. The pure acid is a colorless, oily, very corrosive liquid with a density of 1.84 at the ordinary temperature. It has a very remarkable attraction for water, the combination being marked by a condensation of volume and the evolution of much heat. It may be mixed with water in all proportions. When exposed to the air at ordinary temperatures, it does not vaporize but absorbs water from the atmosphere, thus increasing both its weight and volume. On account of this hygroscopic action, it should be kept in well-stoppered bottles. It is dibasic.

Sulphuric acid removes water from many organic substances, completely charring some, like sugar and woody fiber, and breaking others, as alcohol and oxalic acid, into new compounds. It is one of the most energetic acids known. Diluted with 1000 times its bulk of water, it still reddens blue litmus. Because of its higher boiling-point, it liberates most of the other acids from their salts. If the concentrated acid comes into contact with the skin, it will (unless washed off at once) produce a wound difficult to heal and likely to leave a scar. Its corrosive action is destructive to clothing with which it comes in contact. Even the dilute acid (unless it is soon neutralized with ammonia) will eventually destroy fabrics with which it comes in contact. Internally, it acts as a corrosive poison, the best antidote for which is a solution of baking-soda, or strong soapy water.

399. Uses. — Sulphuric acid is used as a drying agent for gases, in the preparation of most of the other acids, in the manufacture of soda, phosphorus, and alum, in the preparation of artificial fertilizers, in the refining of petroleum, in the manufacture of glucose, in the processes of bleaching, dyeing, etc. In fact, there is scarcely an art or trade in which, in some form or other, it is not used, it being employed directly or indirectly in nearly all important chemical processes. It is the most important chemical reagent we have and is made in immense quantities.

400. Tests. — The most convenient test for free sulphuric acid is the charring of organic substances. A paper moistened with a natural water containing the free acid and then dried at 100° will be completely charred. The acid or solutions of its salts give a white precipitate with barium chloride. This precipitate is insoluble in hydrochloric acid.

401. Nordhausen Acid. — Nordhausen acid (disulphuric acid, fuming sulphuric acid, pyrosulphuric acid, $H_2S_2O_7$) is prepared by dissolving sulphur trioxide in ordinary sulphuric acid, or by the distillation of dried iron sulphate (green vitriol, $FeSO_4$), in earthen retorts. It is a heavy, oily liquid with a density of 1.89. It fumes strongly in the air and hisses like a hot iron when dropped into water. It is used chiefly for dissolving indigo.

(*a*) The name, Nordhausen acid, is due to the fact that it was formerly prepared in Nordhausen, Saxony. At the present time the acid comes almost wholly from Bohemia. The propriety of the term "disulphuric acid," is shown by the formula, $H_2O, 2SO_3$. It is easily decomposed: $H_2S_2O_7 + \text{heat} = SO_3 + H_2SO_4$.

402. Hyposulphurous Acid. — Hyposulphurous acid (H_2SO_2) is a very unstable, yellow liquid with powerful reducing properties. Its salt, sodium-hydrogen hyposulphite ($NaHSO_2$), is used for the reduction of indigo in dyeing and calico-printing.

403. Thionic Acids. — Besides the foregoing, there is a series of sulphur acids, the corresponding oxides of which are unknown.

Thiosulphuric acid	$H_2S_2O_3$
Dithionic acid	$H_2S_2O_6$
Trithionic acid	$H_2S_3O_6$
Tetrathionic acid	$H_2S_4O_6$
Pentathionic acid	$H_2S_5O_6$

None of these acids is of technical importance, but the sodium salt of the first of the series, commonly called sodium hyposulphite ($Na_2S_2O_3$), is, on account of its solvent action on the halogen salts of silver, largely used in photography and in the extraction of silver from its ores.

(*a*) The thiosulphuric acid is better known by the misnomer of "hyposulphurous" acid, which properly designates the compound symbolized by H_2SO_2. In similar manner the thiosulphates (e.g., sodium thiosulphate, $Na_2S_2O_3$) are commonly, but improperly, spoken of as "hyposulphites." The word "thionic" comes from the Greek name for sulphur.

404. Selenium and Tellurium. — These are rare elements, having properties in general very similar to those of sulphur and forming compounds analogous to those of sulphur. The resistance that selenium offers to an electric current is much diminished by the action of light. This property has been utilized in the construction of the photophone, and the element thus endowed with added interest and importance. (See Appendix, § 1.)

(*a*) The name selenium is from the Greek word meaning the moon, and the name tellurium is from the Greek word meaning the earth.

405. The Sulphur Family. — The resemblances between the members of this family are as well marked as are those of the halogens. As the atomic weight increases, the chemical activity diminishes, selenium being about midway between sulphur and tellurium. Their densities, melting- and boiling-points, show a similar gradation.

(*a*) Some of the chemical resemblances of the members of this group are easily visible in the following table:

H_2S	H_2Se	H_2Te
FeS	$FeSe$	$FeTe$
SO_2	SeO_2	TeO_2
SO_3	SeO_3 (?)	TeO_3
H_2SO_3	H_2SeO_3	H_2TeO_3
H_2SO_4	H_2SeO_4	H_2TeO_4
$(C_2H_5)_2S$	$(C_2H_5)_2Se$	$(C_2H_5)_2Te$
$(C_2H_5)HS$	$(C_2H_5)HSe$	$(C_2H_5)HTe$

EXERCISES.

1. (*a*) What is the molecular weight of SO_2? (*b*) The density of the gas? (*c*) Its percentage composition?

2. H_2S and SO_2 are often found in volcanic gases. When they come into contact, they decompose each other. Write an equation explaining the occurrence of native sulphur in volcanic regions.

3. Why can not H_2SO_4 be used for drying H_2S?

4. (*a*) How much HNO_3 can be formed from 306 grams of KNO_3? (*b*) How much H_2SO_4 will be required? (*c*) What will be the yield of $KHSO_4$?

5. Write the graphic symbol for H_2SO_4: (*a*) representing sulphur as a dyad; (*b*) as a hexad.

6. Write the graphic symbol for $H_2S_2O_7$, introducing SO_2 twice as a bivalent radical. ($H_2S_2O_7$ = anhydrosulphuric acid.)

7. The symbol for potassium sulphate is K_2SO_4; that for lead sulphate is $PbSO_4$. (*a*) What is the valence of potassium? (*b*) Of lead?

8. How would you write the symbol of a binary compound containing a dyad and a triad?

9. How much HNO_3 will just neutralize 1200 grams of ammonium hydroxide?

10. (*a*) How much NH_3 may be formed from 42.8 grams of NH_4Cl? (*b*) How much CaH_2O_2 must be used?

11. (*a*) What volume of chlorine may be obtained from 1 liter of dry HCl? (*b*) What weight?

12. When aëriform water and chlorine are passed through a porcelain tube heated to redness, hydrochloric acid and oxygen are formed. (*a*) Write the reaction in molecular symbols. (*b*) What volume of oxygen may be thus obtained from 2 liters of steam? (*c*) How will the volume of the acid compare with that of the oxygen? (*d*) In what simple way may the oxygen be freed from mixture with the acid?

13. (*a*) From 100 grams of $KClO_3$, how many grams of oxygen may be obtained? (*b*) How many liters?

14. Water and nitrogen are among the products formed when NH_4Cl and $NaNO_2$ are heated together in a flask. Write the reaction.

15. (*a*) I mix hydrogen and chlorine, and expose the mixture to sunlight. What happens? (*b*) I add NH_3 to the product just formed. What is the name of this second product?

16. (*a*) What weight of sulphur would be required to produce a ton of sulphuric acid? (*b*) What weight of steam would be needed? (*c*) What volume of air, if all the oxygen is used?

17. What weight of iron pyrite (FeS_2) would be required to produce a ton of sulphuric acid?

18. Write in tabular form the names, molecular symbols, and molecular weights of 10 ternary compounds that you have studied.

19. When anhydrous magnesium chloride, $MgCl_2$, is burned in air, a white powder and a gas are produced. The powder is magnesium oxide; the gas will color blue a strip of paper wet with a solution of potassium iodide and starch. Write the reaction.

20. When barium oxide, BaO, is gently heated to dark redness in the air it is changed to the dioxide, BaO_2. At a bright red heat this decomposes into barium oxide and oxygen. How may these facts be utilized?

21. Symbolize three molecules of arsenic, two of cadmium, five of oxygen, two of phosphorus, and four of mercury.

22. How many grams of pure cream of tartar ($KHC_4H_4O_6$) are required to make baking-powder with 1000 grams of pure baking-soda ($NaHCO_3$)?

CHAPTER XVII.

THE EIGHTH GROUP.

I. THE IRON FAMILY.

Note. — The five elements of Group 7 were considered in Chapter VII. See § 148, (*e*) and (*f*).

Iron: symbol, Fe; density, 7.8; atomic weight, 56; valence, 2, 3, 6.

406. Occurrence. — Iron, the most important of all the metals, is seldom found native. Metallic iron of meteoric origin has been found. This element is widely distributed, traces of it being found in the blood of animals, in the ashes of plants, in spring, river, and ocean waters, and, in fact, in nearly all natural substances. Its ores are numerous and abundant.

(*a*) The most important iron ores are hematite (Fe_2O_3); limonite or brown hematite (Fe_2O_3, $3H_2O$); magnetite or magnetic iron (Fe_3O_4); siderite ($FeCO_3$), and clay ironstone or black-band ironstone, which is a carbonate ore containing clay or sand with carbonaceous substances and generally found as nodules or bands in the coal measures.

(*b*) The value of an iron ore often depends more upon the nature of its impurities than upon its percentage of iron. When iron is spoken of, a compound of iron and carbon is usually meant. Chemically pure iron is not a commercial product, and has properties quite different from those of commercial iron.

Preparation of Pure Iron.

Experiment 288. — Place about 15 grams of pulverized Fe_2O_3 in the bulb of the tube, *c*. Pass a current of dry hydrogen through the bulb-tube. When the air has been driven from the apparatus, heat the oxide to redness. When it has been reduced to a black powder of metallic iron, remove the lamp and allow the contents of the bulb to cool in a current of hydrogen.

$Fe_2O_3 + 3H_2 = Fe_2 + 3H_2O$.

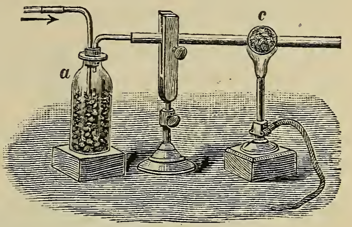


FIG. 96.

407. Pure Iron. — Pure iron may be made by heating iron oxide in a current of hydrogen. The black powder prepared in the preceding experiment may be set on fire by a lighted splinter. It oxidizes so easily that it will take fire if emptied from the bulb-tube into the air while it is still hot. When hammered, pure iron is silver-white, soft, and tenacious. It melts at about 1800°, is permanent in dry air, and rusts rapidly in moist air.

408. Commercial Iron. — All forms of commercial iron contain carbon, and usually manganese, phosphorus, silicon, and sulphur. The proportion of carbon present largely determines the quality of the metal and the use to which it may be applied. When the amount of carbon is so small that the iron can not be hardened by sudden cooling (less than two-tenths per cent), the metal is called wrought iron. When carbon is present in such an amount that the metal can be hardened by sudden cooling and can be tempered (i.e., from about two-tenths per cent to about two per cent), the metal is called steel. The hardness and hardening power of the steel increase with its carbon contents. Soft steel for boiler-plate, sheet steel, and the like, contains about two-tenths per cent;

rail steel and structural steel, from three-tenths to five-tenths per cent; and tool steel, above six-tenths per cent of çarbon. Iron that is too high in carbon contents to be tempered (containing more than about two per cent of carbon) is called cast iron or pig iron.

409. Metallurgy of Iron. — Almost all the iron of commerce is made by smelting and reducing the ores in a blast-furnace. This consists of an upright shaft, *A*, from sixty to a hundred feet high, made of steel plate, and with a lining from three to five feet thick and made of the most refractory fire-brick. The furnace is wider in the middle than at the top or bottom, thus allowing an easy descent of the material. Near the bottom are from six to fourteen apertures (tuyères) for forcing in hot air. At the bottom is the hearth or crucible with an opening near its top for drawing off the slag, and a narrow slit near its bottom for tapping off the molten metal. The top of the blast-furnace is closed by a massive cup-and-cone arrangement that is opened only when a fresh "charge" of materials is to be dropped into the furnace from the hopper above. Trucks containing the materials, mixed in proper quantities, are lifted by large elevators, *E*, to the charging platform, *P*, at the mouth of the furnace. The "burden," as the mixture is called, is dumped from the trucks into the hopper. When the hopper is filled, the cone is lowered, and the charge falls into the furnace. Just below this cone is the opening of a large steel pipe through which the combustible gases that would otherwise escape are led, in part to the boilers used in making steam for the blowing engines, and in part to the cylindrical towers or hot-blast stoves, *B*, *C*, etc. Air is admitted to these stoves and the gases are burned. The stoves are nearly filled with loosely built brickwork which is thus heated red-hot. While several of these stoves are being thus heated, air is forced through another previously

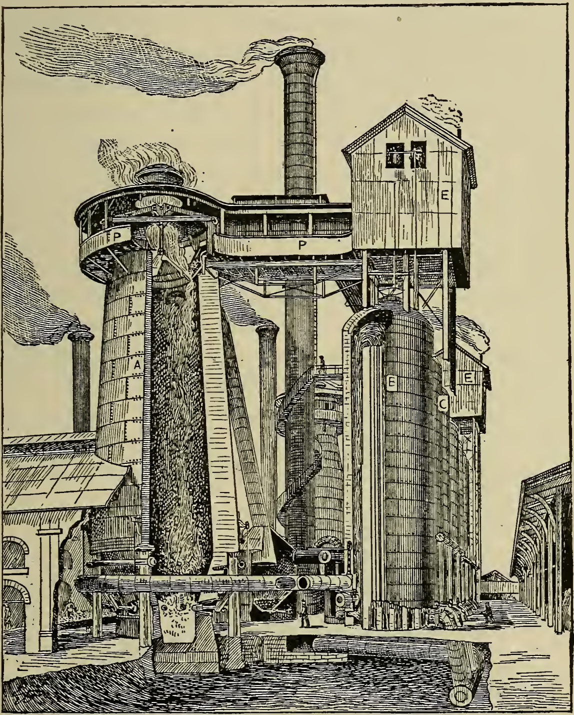


FIG. 97.

heated. The hot brickwork raises this air to a very high temperature, after which the hot air is forced through the circular main blast that surrounds the furnace, and thence through the tuyères into the lower part of *A*. When the brickwork is thus cooled, the air-blast is transferred to another stove, the several stoves being alternately heated by the combustion of the gas from the blast-furnace, and cooled by the air on its way to the blast-furnace. The heat and fuel that would otherwise be lost from the top of *A* are thus utilized in the lower part of *A*.

410. Pig Iron. — The iron ores and the coke necessary for smelting them are charged together almost continuously at the top of the blast-furnace. Most iron ores contain silica. To render this silica fusible, limestone is added to the charge. The limestone acts upon the silica and, with it and the other impurities of the ores, forms silicates that constitute the slag. As the coke falls to the lower part of the furnace and meets the incoming hot air, it is burned.

$$2C + O_2 = 2CO.$$

As the carbon monoxide thus formed rises through the charge, it reduces the downcoming hot iron oxides to the metal.

$$Fe_2O_3 + 3CO = 2Fe + 3CO_2.$$

Only about half of the carbon monoxide is thus used. The other half is led from the top of the blast-furnace to the stoves, where it is burned to furnish heat for the air-blast as already described.

At the high temperature of the lower part of the stack, the reduced iron unites chemically with part of the carbon of the coke to form a compound that contains about four and one-half per cent of carbon and two per cent of silicon. At the hottest part of the furnace this more easily fusible compound melts and settles to the bottom of the furnace ready to be drawn off and run into sand or iron molds. The bars thus formed constitute pig iron. This iron can not be welded or tempered, and is more brittle and less strong than other forms of iron.

(*a*) Pig iron includes *white cast iron*, *gray cast iron*, and several intermediate varieties called *mottled cast iron*. White cast iron contains nearly all its carbon in chemical union. When it is dissolved in hydrochloric or in sulphuric acid, various hydrocarbons are formed that give a disagreeable odor to the hydrogen evolved. In gray cast iron, part of the carbon crystallizes out in cooling, forming graphite, which is left in the form of black scales when the iron is dissolved in an acid. White cast iron contracts on solidifying; gray cast iron expands on solidifying and is, therefore, the better adapted for foundry

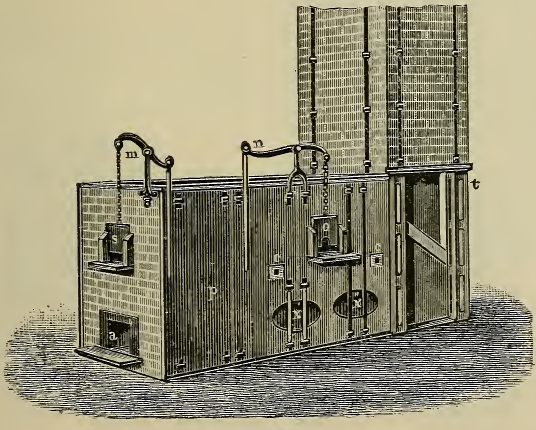


FIG. 98.

use. Spiegeleisen is a variety of white cast iron containing about 30 per cent of manganese. It is very hard and crystalline and is used in various processes of steel manufacture. When it contains 50 to 80 per cent of manganese, it becomes granular and is called ferromanganese.

411. Wrought Iron. — To convert the product of the blast-furnace into soft or wrought iron, the pig iron is melted in a furnace, mixed with oxide of iron, and stirred or puddled, whereby the carbon is burned away and the other impurities are oxidized to a slag; this slag protects the iron from further oxidation. The loss of carbon raises the melting-point of the iron, and the metal becomes less fluid. The pasty mass or "bloom" is then removed from the furnace and freed of its slag, and welded into a solid mass by hammering or squeezing. The iron made in this way is the most nearly pure of the commercial varieties. It is soft and malleable, and may be welded, and rolled or hammered into the shape required.

(*a*) A puddling furnace is shown in elevation in Fig. 98 and in section in Fig. 99. The charge of pig iron and, generally, a quantity of iron-scale or other iron oxide are placed in the bed, *h*, separated from the fire-grate by the fire-bridge, *b*, and from the chimney by the flue-bridge, *d*.

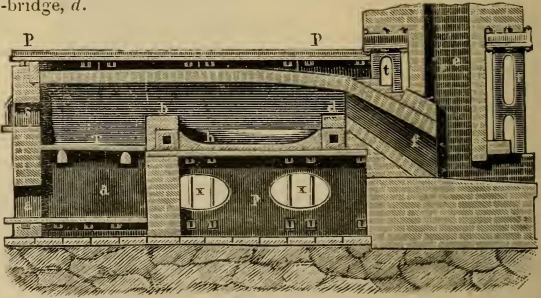


FIG. 99.

412. Steel. — Steel is intermediate between cast iron and wrought iron in respect to properties and chemical composition. It contains from two-tenths to two per cent of carbon. Its most characteristic property is that of acquiring remarkable hardness by heating and quickly cooling as by plunging into water. Steel thus hardened can not be worked with a file and is very brittle and elastic. The hardness and brittleness are lessened by tempering, which process consists in heating the steel to a temperature between 200° and 400° and then cooling it quickly.

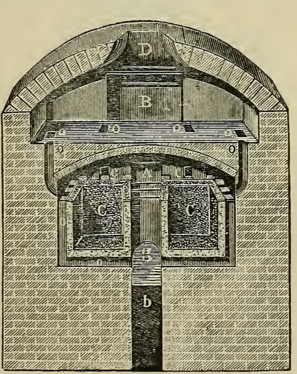


Fig. 100.

413. The Cementation Process. — Fifty years ago the only method of making steel was to decarbonize cast iron in the puddling furnace and then to recarbonize the wrought iron in the cementation furnace. This furnace contains two boxes, *cc*, made of fire-clay. In these boxes, bars of wrought iron are packed in soot or powdered charcoal. Six or seven tons of iron are put into each box. A fire is built on the hearth, *g*, and the boxes are kept at a red heat for from seven to ten days. At the end of the process, it is found that the metal has become finer grained, more brittle, more fusible, that its surface has a blistered appearance, whence the name, "blister steel," and that carbon has penetrated the metal, *although the iron has not been melted or the carbon vaporized.* The bars are then taken out and welded, or melted and cast into shape.

414. The Bessemer Process. — In this process, so named for its inventor, steel is made by decarbonizing cast iron by a current of air forced through the melted metal in a vessel called the converter. The converter is made of iron plates lined with infusible material. The bottom is a shallow wind-box, *e*, from which numerous small openings lead into the converter. The vessel is supported upon trunnions, one of which, *i*, is hollow and connected with the wind- or tuyère-box. When the converter has been turned upon its trunnions until the line, *ac*, is horizontal, melted cast iron is run through the mouth into the belly, *abc*. The air-blast is then turned on and the converter raised into an upright position, the compressed air bubbling through the molten metal, burning out the carbon and silicon, and combining with part of the iron. This combustion in the converter causes an intense heat that keeps the iron melted despite its approach to the less easily fusible condition of wrought iron. During this time, the flame that rushes from the mouth of the converter is accompanied by a magnificent display of sparks due to the combustion of iron particles. After six or eight minutes, the exact moment being indi-

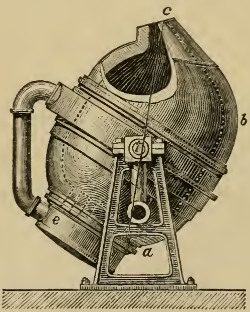


Fig. 101.

cated by the appearance of the flame, the converter is turned until the melted iron leaves the tuyère openings uncovered and the air-blast is stopped. The decarbonized iron is now recarbonized by the addition of a carefully determined quantity of spiegeleisen. The molten mass is poured into molds, and the cast steel worked up under the hammer or in the rolling mill. In about twenty minutes, from ten to twenty tons of cast iron have been converted into steel.

(*a*) All the movements of the converter, ladle, cranes, etc., are produced by hydraulic power, and controlled by a workman at "the piano," as the assemblage of wheels and levers is called.

(*b*) Steel might be produced by stopping the oxidation before all of the carbon of the cast iron had been burned out. But the difficulties arising from too nearly complete oxidation and the practical impossibility of making successive "blows" yield the same quality of steel led to the adoption of the present plan. Bessemer steel is largely used in the construction of railway tracks, bridges, etc.

415. The Siemens-Martin or Open-hearth Steel Process. — In this process, iron high in carbon (pig iron) and iron low in carbon (soft scrap iron and steel) are fused together in the proportions proper to produce such a carbon contents in the resulting metal as will yield the desired kind of steel. In practice, part of the carbon of the pig iron is removed in a gas-fired furnace by the oxidizing flame, or by its reaction with the iron rust (oxide) on the surface of the scrap iron or of added iron ore.

$$Fe_2O + 3C = 2Fe + 3CO.$$

Because of the very high temperature necessary to melt soft iron, this method did not become a commercial possibility until, about 1860, Siemens invented a process for

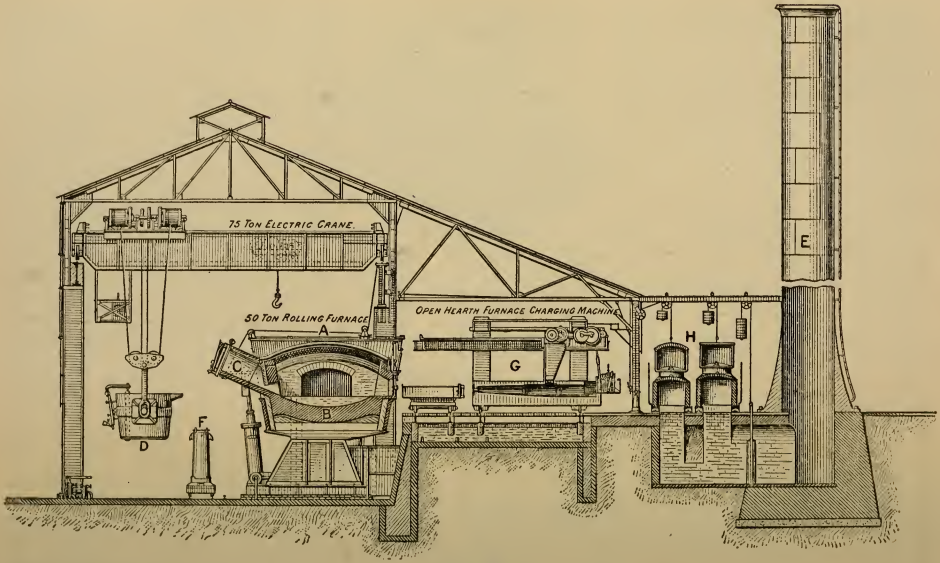

75 Ton Electric Crane.
50 Ton Rolling Furnace
Open Hearth Furnace Charging Machine
A
B
C
D
E
F
G
H

Fig. 102.

returning to the furnace a large part of the heat of the exit furnace gases, i.e., a heat regenerative process.

The open-hearth steel furnace consists of a rectangular chamber, *A*, lined with highly refractory fire-brick and having a concave sand bottom, *B*, upon which the metals are melted. The Wellman machine for mechanically charging the metals and fluxes into the furnace is shown at *G*, and the valves for reversing the direction of the fuel gases are shown at *H*.

The regenerative chambers for heating the fuel gas and air before their admission to the chamber, *A*, are usually built below the level of the working platform and at the back of the furnace. They are not represented in Fig. 102, but their construction is shown in Fig. 103. These chambers, *M*, *N*, *O*, *P*, are built in pairs and filled with loosely set brick that are alternately heated by the hot gaseous products of combustion on their way from the furnace to the chimney-stack, *E*, and cooled by the fuel gas and air on their way to *A*.

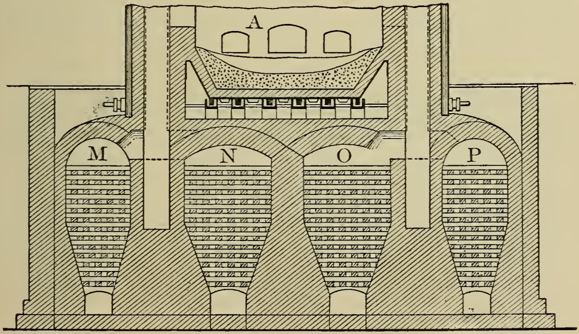


FIG. 103.

Fuel gas being admitted by a duct to the bottom of *M*, and air being similarly admitted to the bottom of *N*, both are heated by contact with the hot brick-work, pass thence through separate flues to the chamber, *A*, and there develop a much higher temperature than they would if they had been supplied cold. The hot exit products pass out through similar flues at the other end of *A*, heating the brick work in *O* and *P* as they pass on to *E*. As the brick work in *M* and *N* are thus soon cooled, the direction of the gases is reversed by the valves at *H*, admitting fuel gas through *P* and air through *O*, while the exit gases escape to *E* by way of *M* and *N*. In practice, this reversal is made about every fifteen minutes.

If the sand bottom, *B*, is made of silica sand, the method is called the acid open-hearth process. This process does not remove the phosphorus and sulphur that are often present as injurious impurities in the ores or metals used. If the sand bottom is made of calcium and magnesium oxides, and lime is added to the molten charge, the method is called the basic open-hearth process. This process does remove the phosphorus and sulphur if such impurities are present.

When the metal has been melted and refined to its desired purity, and brought to the desired carbon contents, it is tapped or poured, with the accompanying slag, through the spout, *C*, into the ladle, *D*, from the bottom of which the pure, slag-free, white-hot metal is tapped into an ingot mold, *F*. When the ingots are cooled to a full red heat, they are rolled into billets or other desired shapes. The process affords a convenient method of utilizing scrap and, with or without modification, is largely used.

416. Crucible Steel. — A very fine quality of steel is made for edge-tools by fusing, in graphite crucibles, a fine quality of wrought iron with powdered charcoal. The crucibles are closely covered and heated in a coke fire. The steel is cast into ingots, and worked into bars under the hammer. For very hard metal-cutting tools, the steel is alloyed with a small quantity of tungsten, molybdenum, or vanadium.

417. Malleable Iron Castings. — Intermediate between cast iron and wrought iron is an article known in commerce as malleable iron. Small castings are made of white cast iron for a great variety of purposes, such as for harness, wagons, agricultural implements, etc. These castings are packed with iron-scale or oxide in "annealing boxes" and then heated to a high temperature. The carbon of the cast iron is thus removed in great part and the material changed from white, hard, and brittle cast iron to black, soft, and tough malleable iron. Articles thus made are nearly as tough as they would be if made of wrought iron and much less expensive.

418. Oxides of Iron. — Iron forms three well-known oxides: ferrous oxide (iron monoxide, FeO), ferric oxide (iron sesquioxide, Fe_2O_3), and ferrosoferric oxide (magnetic oxide of iron, Fe_3O_4). The ferric and magnetic oxides are found native as iron ores.

(*a*) Ferrous oxide may be prepared by heating ferrous oxalate in a closed vessel or by passing hydrogen over Fe_2O_3 heated to 300°. If exposed to the air within a few hours after its preparation, it oxidizes so rapidly as to take fire.

(*b*) Ferric oxide is one of the most important iron ores. This oxide is prepared artificially for use as a paint. A fine variety is known as jeweler's rouge, and is used for polishing glass and metals. Another artificial variety is called crocus, and is also used for polishing metals.

(*c*) Ferrosoferric oxide is found in large quantities as the richest of iron ores. Many specimens attract iron and are called lodestones. Scale oxide is chiefly Fe_3O_4. We may consider Fe_3O_4 as a mixture or compound of FeO and Fe_2O_3.

Ferric Hydroxide.

Experiment 289. — Cover a teaspoonful of fine iron filings with 3 or 4 times its volume of dilute sulphuric acid. When the evolution of hydrogen ceases, pour off the clear liquor, add a few drops of strong nitric acid, and boil the liquid. The yellowish red color is due to the presence of ferric sulphate. Add NH_4OH to the solution and shake the liquids together. A red precipitate of ferric hydroxide will be formed; it may be collected upon a filter.

419. Iron Hydroxides. — Ferrous hydroxide [$Fe(OH)_2$] is obtained by treating a solution of a pure ferrous salt with potassium or sodium hydroxide in absence of air. The precipitate thus formed is an unstable, white powder, which rapidly oxidizes with change of color, evolution of heat and, sometimes, incandescence when exposed to the air. Ferric hydroxide [$Fe(OH)_3$] is prepared by precipitating a moderately dilute solution of a ferric salt (e.g., $FeCl_3$) with an excess of ammonia-water. When freshly prepared, it is one of the best antidotes for arsenic.

420. Iron Sulphides. — Iron and sulphur form two well-known compounds, iron monosulphide (ferrous sulphide, FeS) and iron disulphide (FeS_2). Iron monosulphide is formed by direct union of its constituents. It is generally prepared by gradually throwing a mixture of three parts of iron filings and two parts of sulphur into a red-hot crucible. It is the cheapest source of hydrogen sulphide and, hence, very important. Iron disulphide occurs widely distributed in nature as pyrite (or iron pyrites). It is largely used in the manufacture of sulphuric acid.

Mordants.

Experiment 290. — Dip a piece of cotton cloth into a solution of nut-galls and allow it to dry; dip it into a solution of green vitriol and hang it up in a moist atmosphere. It will be permanently colored by the precipitation of an insoluble iron tannate.

421. Iron Salts. — Iron forms two well-defined series of salts. In the ferrous series, the iron atom acts as a dyad as it does in ferrous oxide. In the ferric series, the iron atom acts as a triad as it does in ferric oxide. These relations clearly appear in the following table :

	Chlorides.	*Nitrates.*	*Sulphates.*
Ferrous	$FeCl_2$	$Fe(NO_3)_2$	$FeSO_4$
Ferric	$FeCl_3$	$Fe(NO_3)_3$	$Fe_2(SO_4)_3$.

(*a*) Solutions of ferrous salts readily absorb oxygen; unless an excess of acid is present, they are thereby oxidized to ferric salts which are precipitated. They, therefore, act as powerful reducing agents, and are largely used as such in the laboratory and the arts. The ferric salts are readily reduced to the corresponding ferrous compounds.

(*b*) Ferrous sulphate (green vitriol, $FeSO_4, 7H_2O$) is made in immense quantities by exposing pyrite to the action of the atmosphere, as an incidental product in the manufacture of copper sulphate, or by dissolving iron in dilute sulphuric acid. It is largely used in the arts. Ferric nitrate is prepared by dissolving iron in nitric acid. It is largely used as a mordant in dyeing and calico-printing. Ferrous carbonate ($FeCO_3$) is found as an iron ore.

Iron Cyanides.

Experiment 291. — Half fill each of two test-glasses with a very dilute solution of ferrous sulphate, and each of two other glasses with a similar solution of ferric sulphate. Prepare a dilute solution of potassium ferrocyanide ($K_4C_6N_6Fe$) and one of potassium ferricyanide ($K_3C_6N_6Fe$). Add a drop of the ferrocyanide to one of the solutions of ferric sulphate; a deep blue precipitate will be formed and color the liquid. In similar manner, add potassium ferrocyanide to a solution of ferrous sulphate; no such deep blue color will appear. In similar manner, add potassium ferricyanide to ferrous sulphate; the deep blue color will appear. In similar manner, add potassium ferricyanide to ferric sulphate; no such color will appear. In the names of these cyanides the pupil will notice contractions for ferrous and for ferric. When, in this experiment, an *-ous* and an *-ic* compound were brought together, a characteristic blue color was formed. When two *-ous* and two *-ic* compounds were brought together, no such color was produced. These potassium-iron cyanides act thus with all ferrous and ferric salts and may, consequently, be used as tests to detect the presence of these salts in any solution or to distinguish between them.

Experiment 292. — Soak a piece of cotton cloth in a solution of ferric sulphate, and then dip it into an acidulated solution of potassium ferrocyanide. Prussian blue will be precipitated upon the cloth and will color it.

422. Iron Cyanides. — Iron unites with cyanogen to form ferrous and ferric cyanides. The most important iron cyanides, however, are double compounds. When crude potash (K_2CO_3) is fused with nitrogenous organic matter, such as horn, feathers, dried blood, leather clippings, etc., in the presence of iron filings, and the fused mass is leached with water, and the liquid is evaporated, large yellow crystals are formed. These crystals are potassium ferrocyanide (K_4Cy_6Fe) better known as yellow prussiate of potash. This compound is important as it serves as the point of departure for the preparation of nearly all the cyanogen compounds. It may also be formed by the addition of a ferrous salt to an aqueous solution of potassium cyanide. The tendency to form this salt is so great that metallic iron is rapidly dissolved when heated in such a solution of potassium cyanide. When a current of chlorine is passed into a solution of potassium ferrocyanide, the reaction yields potassium ferricyanide (K_3Cy_6Fe) or red prussiate of potash. The class of compounds known as Prussian blues are chiefly compounds of ferrous and ferric cyanides, generally united with potassium.

423. Ferric Acid. — Acting with a valence higher than that manifested in any of the compounds so far mentioned, iron enters into composition to form ferric acid, H_2FeO_4. Potassium ferrate (K_2FeO_4) is a salt of this acid.

EXERCISES.

1. Name the compounds symbolized as follows: $FeBr_2$, $FeBr_3$, $K_4(CN)_6Fe$, $Fe_2(SO_4)_3$.

2. A certain iron oxide has a molecular weight of 232 and contains 27.6 per cent of oxygen. What is its formula?

3. How many tons of pure iron may be made from a thousand tons of iron ore containing 90 per cent of pure hematite (Fe_2O_3)?

4. (*a*) What weight of iron sulphide will be needed to yield 1 liter of hydrogen sulphide? (*b*) How much air will be required to burn the H_2S?

5. What weight of marble is needed to convert a ton of soda crystals into bicarbonate of soda?

6. How many liters of air will be necessary to burn a liter each of marsh-gas, olefiant gas, and acetylene?

7. The vapor density of NH_4Cl is one-fourth its molecular weight. Why is it said to be abnormal? Can you suggest an explanation of the variation?

8. Give the names and atomic weights of the elements represented by the following symbols: Fe, Mg, Hg, Zn, Ca, C, Cl, I, P, K, N, Na, S, Br, Fl, H, Pb, O, Al, Sb, Si.

EQUATION.	H_2 +	Cl_2 =	2 HCl.
Name of molecules	Hydrogen	Chlorine	Hydrochloric acid
No. of molecules	1	1	2
Molecular weights	2	71	36.5
Total weights	2	71	73
Gaseous volumes	2 unit volumes	2 unit volumes	4 unit volumes
Laboratory exp.	500 cu. cm.	500 cu. cm.	1 liter

9. According to the above or a similar schedule, write out the following equations:

(*a*) $2H_2O + 2Cl_2 = 4HCl + O_2$.

(*b*) $2CO + O_2 = 2CO_2$.

(*c*) $CO_2 + C(\text{solid}) = 2CO$.

(*d*) $2NH_3 = N_2 + 3H_2$.

(*e*) $2NH_3 + 3Cl_2 = N_2 + 6HCl$.

(*f*) $NH_4NO_3(\text{solid}) = N_2O + 2H_2O$.

(*g*) $MnO_2 + 4HCl = MnCl_2 + Cl_2 + 2H_2O$.

(*h*) $SO_2 + 2H_2O + Cl_2 = H_2SO_4 + 2HCl$.

(*i*) $2MnO_2 + 2H_2SO_4 = 2MnSO_4 + 2H_2O + O_2$.

10. Write the formula for uranyl sulphate.
11. Write the graphic formula for ferric acid.
12. Complete the following equations:

$$SO_3 + H_2O =$$
$$H_2SO_4 + NaOH = Na_2SO_4 +$$
$$H_2SO_4 + NaOH = NaHSO_4 +$$

13. Sulphur trioxide may be obtained by heating concentrated sulphuric acid with phosphoric anhydride. Write the reaction.
14. Complete the following equations:

$$Na_2SO_3 + O =$$
$$SO_2 + O =$$

15. Tell clearly how you would separate the nitrogen from the oxygen of the air, and make a sketch of the apparatus that you would use.

NICKEL: symbol, Ni; density, 8.9; atomic weight, 58.6; valence, 2, 3.

424. Nickel.— Nickel is almost always associated with cobalt in either terrestrial or extra-terrestrial matter. It is a lustrous, white metal, ductile, malleable, magnetic, very hard, and susceptible of a high polish. It can be welded. It is largely used for electroplating articles of iron and steel to protect them from rusting. It is also used in making alloys. The United States five-cent coin is made of an alloy composed of twenty-five per cent nickel and seventy-five per cent copper. German silver is an alloy of nickel, copper, and zinc. A small proportion of nickel combined with steel forms an alloy of so great strength that it is used in armor-plate for war-ships. There are two important sources of nickel,—a sulphide and a silicate. The sulphide occurs in large quantities near Sudbury, Ontario. A silicate of nickel and magnesium, called garnierite, occurs in New Zealand. These two deposits at present furnish practically all the nickel of commerce.

(*a*) The oxides of nickel are the monoxide (nickel oxide, NiO) and the sesquioxide (nickelic oxide, Ni_2O_3). Nickel salts are derived from the monoxide.

Cobalt.

Experiment 293. — Into a small loop of platinum wire fuse some borax until it forms a clear glass. Into this fuse a minute portion of some cobalt compound. The glass will be colored blue. This forms a very delicate test for cobalt.

Experiment 294. — Partly fill a test-tube with a concentrated solution of bleaching-powder. Add a small quantity of cobalt sesquioxide and heat gently. A brisk effervescence takes place. Test the gas evolved with a glowing splinter. The calcium hypochlorite contained in the bleaching-powder is, under the catalytic influence of the Co_2O_3, decomposed. Write the reaction.

Experiment 295. — Prepare an aqueous solution of cobaltous chloride ($CoCl_2$) by dissolving CoO or Co_2O_3 in hydrochloric acid. Make a drawing with this nearly colorless solution. Heat the sketch to about 150° C.; it will appear blue. Breathe upon it; the blue color will disappear.

Experiment 296. — To 2 cu. cm. of the pink solution of $CoCl_2$ in a test-glass, add an equal quantity of sodium silicate or "water glass," well diluted so as to be thin. A blue precipitate appears.

$$CoCl_2 + Na_2SiO_3 = 2NaCl + CoSiO_3, \text{ or}$$
$$2CoCl_2 + Na_4Si_5O_{12} = 4NaCl + Co_2Si_5O_{12}.$$

COBALT: symbol, Co; density, 8.6; atomic weight, 58.6; valence, 2, 3.

425. Cobalt. — Cobalt is not found free, except in meteoric matter. Its ores are not widely distributed. The metal may be obtained from an artificially prepared oxide by reduction with hydrogen, or from a chloride by ignition. It is harder than iron and melts more easily. It is magnetic, malleable, and very tough. When pure, it is silvery-white.

(*a*) Cobalt has three oxides, — the monoxide (cobaltous oxide, CoO), the sesquioxide (cobaltic oxide, Co_2O_3), and an intermediate compound, cobaltous-cobaltic oxide (Co_3O_4) which corresponds to the magnetic oxide of iron. There are also two series of salts, — the cobaltous and the cobaltic. Their peculiar property of appearing pink in combination with water and changing to a more easily perceptible blue when dried leads to their use in the preparation of "sympathetic inks." Cobalt is principally used as an oxide for coloring glass and as a blue color in porcelain-painting.

EXERCISES.

1. What is the difference between hard water and soft water?

2. Read the following, naming each symbolized substance by its full systematic name: $FeSO_4, 7H_2O$ is pale green; $MnSO_4, 7H_2O$ is pale pink; $CoSO_4, 7H_2O$ is bright red; $NiSO_4, 7H_2O$ is bright green; and $CrSO_4, 7H_2O$ is pale blue.

3. (*a*) How is hydrogen sulphide made, and what are its properties? (*b*) What is meant by oxidizing agents, and what by reducing agents?

4. Manganese dioxide and hydrochloric acid are heated together. Give the properties of the gas evolved.

5. In § 129 (*d*) it is stated that when a solution of manganous chloride is treated with lime we have the reaction:

$$MnCl_2 + Ca(OH)_2 = Mn(OH)_2 + CaCl_2.$$

Whence comes the calcium hydroxide that appears as a factor in the equation?

6. When a thin stream of sulphuric acid flows into a retort filled with broken bricks heated to redness, the following reaction takes place:

$$H_2SO_4 = SO_2 + H_2O + O.$$

(*a*) What weight and (*b*) what volume of oxygen can be thus prepared from 50 grams of H_2SO_4, C.P.? (C.P. = chemically pure.)

7. Which is the correct symbol for nickel hydroxide, $NiOH$ or $Ni(OH)_2$?

8. (*a*) Write the symbol for cobaltous hydroxide. (*b*) For cobaltic hydroxide.

9. Write the equation for the preparation of sulphurous acid from its anhydride and water.

10. Write the formula for the potassium salt of the hydroxide of manganese heptoxide. What is the name of the salt?

11. How many grams of nickel may be made from a kilogram of nickel sulphide (NiS)?

12. Name the substances symbolized as follows: K_2SO_3, $C_{12}H_{22}O_{11}$, SiO_2, $C_2H_4O_2$, K_2SO_4, $NaHSO_3$, CH_4, $KHSO_4$, H_4SiO_4.

13. Complete the following equations:

$$S + O + \text{heat} =$$

$$H_2SO_3 + O =$$

14. Describe the electrolysis of water, and tell how you would determine which of the products is oxygen.

15. Compute the percentage composition of ferric acid.

COPPER: symbol, Cu; density, 8.95; atomic weight, 63.1; valence, 1, 2, 4.

426. Source. — Copper was probably the first metal used by man, as it is often found native and then requires no metallurgical treatment. Native copper is found in quantities of commercial importance only in the Lake Superior mines (Keweenaw Point, northern Michigan).

(*a*) Among the more important of the copper ores are cuprite or red copper ore (Cu_2O), malachite ($CuCO_3 + CuO_2H_2$), azurite ($2CuCO_3 + CuO_2H_2$), chalcocite or copper glance (Cu_2S), and chalcopyrite or copper pyrites ($CuFeS_2$), the last being the most important. About nine-tenths of the world's supply of copper comes from sulphide ores.

427. Preparation. — The reduction of copper oxides and carbonates is easily effected by smelting with carbon. The sulphides are roasted to volatilize some of the constituents and to oxidize others. The roasted ore is then fused with a silicate, whereby a slag containing most of the iron is formed, and nearly pure copper and iron sulphide are obtained. This sulphide is then treated by forcing a blast of air through it while in a molten state and in a vessel called a Bessemer converter such as is used in the manufacture of steel. The sulphur and iron are burned, leaving an impure copper. This is purified by partly oxidizing it in a reverberatory furnace or by electrolysis.

428. Properties. — Copper is a reddish metal, hard, very tenacious, and highly malleable and ductile. Excepting silver, it is the best-known conductor of heat and electricity. It is not much affected by air or by most of the acids at the ordinary temperature. It is readily soluble in dilute nitric acid, and is dissolved in hot sulphuric acid. It melts at about 1200°.

(*a*) Copper forms two distinct series of compounds, the cuprous and the cupric; e.g.: —

Monad copper.	*Dyad copper.*
$\text{Cuprous}\begin{cases} CuCl \\ CuBr \\ Cu_2O \end{cases}$	$\text{Cupric}\begin{cases} CuCl_2 \\ CuBr_2 \\ CuO \end{cases}$

429. Uses. — Copper is largely used for many familiar purposes. On account of its toughness, it is used in the manufacture of small tubular boilers, for coating the bottoms of ships, etc.; on account of its conductivity, it is employed in ocean cables and for other electric uses. Brass, bronze, bell-metal, and other copper alloys are of great technical importance and are, perhaps, used more than copper itself.

(*a*) Brass, an alloy of zinc and copper, is of especial value because it does not contract when solidifying and, therefore, takes the mold perfectly, and because it takes a high polish. Bronze, an alloy of tin and copper, has much more strength than most other copper alloys.

Copper Oxides.

Experiment 297. — Hold a *bright* copper coin obliquely in the small flame of a gas- or an alcohol-lamp. Move it to and fro and notice the beautiful play of iridescent colors. Cool the coin in water and notice its coating of red oxide. Heat the coin again, holding it in the hot, oxidizing part of the flame, just above the luminous cone, and notice that it becomes coated with a black oxide. Quickly cool the coin in water and notice that the black coat scales off and reveals the red coat beneath.

Experiment 298. — Place a small quantity of dry copper nitrate upon a piece of porcelain and heat it until red fumes are no longer given off. A black copper oxide will be left upon the porcelain.

430. Copper Oxides and Hydroxides. — Cuprous oxide (copper suboxide, red oxide of copper, ruby copper, Cu_2O) is found native and is prepared artificially. It is used in coloring glass. Cupric oxide (copper monoxide, black oxide of copper, CuO) may be prepared by heating the metal in a current of air, or by igniting the hydroxide, carbonate, or nitrate. It is used in coloring glass green. Two other oxides, tetra-cupric monoxide (Cu_4O) and copper dioxide (cupric peroxide, CuO_2), are also known. There are two hydroxides, the cuprous ($CuOH$) and the cupric [$Cu(OH)_2$].

Copper Salts.

Experiment 299. — Powder some blue vitriol and heat it upon a piece of porcelain; as it loses its water, the light blue powder will turn white. A drop of water upon the anhydrous powder will restore the color.

431. Some Copper Salts. — Copper nitrate [$Cu(NO_3)_2$] is prepared by treating copper with nitric acid and evaporating the solution. On crystallizing from its solution, it absorbs three molecules of water ($CuN_2O_6, 3H_2O$). It is easily decomposable and, therefore, has strong oxidizing properties. Copper sulphate ($CuSO_4$) is formed by dissolving copper in hot sulphuric acid or the oxide in dilute sulphuric acid. It is also prepared from the ores and, as a secondary product, in silver refining. It is generally found as hydrated crystals ($CuSO_4, 5H_2O$) known as blue vitriol, which is largely used in the arts. The color of blue vitriol depends upon the presence of its water of crystallization. Two native carbonates, malachite and azurite, have been mentioned. Some varieties of malachite are susceptible of a high polish and are highly prized for jewels and other ornamental articles. Copper acetate is called verdigris, although the term is sometimes used to designate the green carbonate that forms on the exposure of copper to moist air. Paris green is a copper arsenite. It is used in green paints and as an insecticide.

Note. — The soluble copper salts are active poisons. Such salts are formed in copper cooking utensils that are not kept bright. Acid solutions (e.g., vinegar) form poisonous compounds with brass or copper utensils even when they are kept perfectly clean. Some persons prefer to pickle cucumbers in brass or copper kettles because they take a more brilliant color. This added color is due to the formation of a *poisonous* copper compound with the green chlorophyll of the pickle.

EXERCISES.

1. Read the following equation by unit volumes:

$$CH_4 + 2O_2 = CO_2 + 2H_2O.$$

2. Write the equations for the following reactions: (*a*) Copper and nitric acid yield copper nitrate, nitric oxide, and water. (*b*) Mercury and sulphuric acid yield mercuric sulphate, sulphurous anhydride, and water.

3. The combustion of 1 liter of marsh-gas requires what volume of oxygen?

4. What volume of CH_4 is needed to yield 1 cu. m. of steam in its combustion?

5. How many cubic centimeters of SO_2 (at 20° and 740 mm.) can be obtained by the action of copper upon 20 grams of H_2SO_4?

6. Give the symbol and the name of a substance the vapor-density of which is 30, and the percentage composition of which is as follows: C, 40; H, 6.67; O, 53.33.

7. Compare the cost of making HNO_3 from KNO_3 and from $NaNO_3$ when the cost of KNO_3 is 44 cents per kilogram, that of $NaNO_3$ is 33 cents per kilogram, and that of H_2SO_4 is 11 cents per kilogram.

8. Required the volume of gases in an eudiometer after the explosion of 50 cu. cm. of hydrogen with 75 cu. cm. of oxygen at 150° and 760 mm.

9. Red oxide of copper contains 88.8 parts of copper and 11.2 parts of oxygen by weight. Black oxide of copper contains 79.87 of copper and 20.13 of oxygen. The formula for the black oxide is CuO; what is the formula for the red oxide?

10. How many pounds of copper can be manufactured from a ton of pure chalcopyrite ($CuFeS_2$)?

11. When a current of H_2S is passed through a solution of a certain salt, copper sulphide ($Cu''S$) is precipitated with the formation of H_2SO_4. Write the reaction.

12. You are given NaCl and H_2SO_4 and required to fill a jar with HCl. Describe the process and sketch the apparatus you would use.

13. What is the difference between liquid ammonia and ammonia-water?

14. What is the weight of the oxygen contained in 10 grams of pure potassium chlorate?

15. Compute the percentage composition of common alcohol.

16. What is the percentage composition of lampblack?

II. THE SILVER FAMILY.

SILVER: symbol, Ag; density, 10.5; atomic weight, 107.6; valence, 1.

432. Source. — Silver is a widely diffused and somewhat abundant element and has been known from the earliest times. It is found native, sometimes in masses weighing several hundred pounds and often alloyed with copper, mercury, and gold. It more commonly is found as a sulphide, mixed with other metallic sulphides. Its most abundant source is argentiferous galena, although the carbonates have been found in richly paying quantities, especially in the Leadville (Colorado) mining region.

433. Preparation. — The processes of preparing metallic silver from its ores are numerous and widely different, depending largely, in any given case, upon the nature of the ore, the position of the mine, the price of labor and fuel, etc. It is most commonly obtained by smelting the silver ore with lead or copper ore and subsequently separating the silver from the lead or copper.

434. Properties. — Silver is a beautiful, brilliant white metal, harder than gold, softer than copper, exceedingly malleable and ductile, and the best-known conductor of heat and electricity. It melts at 1040°. The metal is unaltered in the air and resists the action of hydrochloric acid and cold sulphuric acid, but dissolves readily in nitric acid.

(*a*) Silver is so malleable that it may be formed into leaves so thin that 4000 measure only 1 mm. in thickness; so ductile that 1 gram of it may make 1800 meters of wire; and so tenacious that a wire 2 mm. thick will sustain a weight of more than 80 kilograms.

(*b*) Silver unites slowly with the halogen elements and more readily with sulphur and phosphorus. The tarnishing of silver is generally due to the formation of a silver sulphide by the action of hydrogen sulphide present in the atmosphere.

435. Uses. — Owing to its susceptibility of high polish, its permanency and other properties, silver is much used for jewelry, plate, and coin. Owing to its softness, it is generally hardened with copper. American and French coin contain ten per cent and English coin seven and a half per cent of copper. This latter alloy is known as "sterling silver," and is most commonly used for silver utensils. In some of the states, the mark is protected by law. The alloy is also used for chemical utensils as it is not acted upon by the fused hydroxides of the alkali metals as glass and platinum are.

436. Oxides. — There are three oxides of silver: silver tetrant-oxide (Ag_4O), silver oxide (Ag_2O), and silver peroxide or dioxide (Ag_2O_2). When silver oxide (Ag_2O) is digested with ammonia, it forms a very explosive black powder, known as fulminating silver.

Silver Haloids.

Experiment 300. — Fill three test-tubes one-third full of water and pour into each a few drops of a strong solution of $AgNO_3$. Add 2 or 3 cu. cm. of a solution of common salt to the contents of the first tube and shake it vigorously. Silver chloride will be precipitated as a dense, white curdy mass. Add 2 or 3 cu. cm. of a solution of potassium bromide to the contents of the second tube and shake as before; a yellowish precipitate of silver bromide will be thrown down. Add 1 or 2 cu. cm. of a solution of potassium iodide to the contents of the third tube and shake as before; yellowish, flocculent silver iodide will be formed.

Experiment 301. — Try to dissolve one-third of each of these precipitates separately in nitric acid. They will not thus dissolve.

Experiment 302. — Treat a second third of each precipitate with ammonia-water. Determine which dissolves most easily and which least easily.

Experiment 303. — Treat the remainder of each precipitate with a strong solution of sodium thiosulphate (§ 403, *a*). Each of the halogen salts is quickly dissolved.

Experiment 304. — Precipitate more silver chloride from a solution of silver nitrate by hydrochloric acid or a solution of sodium chloride. Filter the solution and wash the precipitate retained upon the filter thoroughly with water. Open the filter, spread the curdy silver chloride evenly over it, and expose it to the direct rays of the sun. The white precipitate quickly changes to violet, the color deepening with continued exposure.

NOTE. — The last five experiments illustrate the principal processes of photography.

437. The Silver Haloid Compounds. — Silver chloride ($AgCl$) is found native in semitransparent masses, called horn silver. It may be prepared by precipitation from a solution of any silver salt by a solution of hydrochloric acid or of any other chloride. It is insoluble in water and acids but easily soluble in ammonia-water. Silver iodide or bromide is precipitated from a similar solution by a solution of an iodide or bromide. These compounds are much used in photography.

438. Photography. — When silver chloride, bromide, or iodide has been exposed to the light, it is more easily reduced to the metal than before such exposure. This fact, discovered by Niepce and Daguerre, is the foundation of all photographic processes using silver salts. The process of Daguerre consisted in converting the surface of a polished silver plate into silver iodide by exposing it to iodine vapor. This surface, after exposure to light in the camera, was developed and fixed by exposure to mercury vapor which converted into the metal so much of the silver iodide as had been acted upon by the light.

In a later process the silver salts were dissolved in collodion or gelatin and then coated on glass or on a celluloid film. When such plates are exposed to light in the camera, and then immersed in a reducing bath or "developer," an image of black, finely divided silver appears where the light had touched the plate. In order that the remaining silver salt may not become black by exposure to light, it is dissolved out and washed away by a solution of sodium hyposulphite, which readily dissolves the chloride or iodide of silver, but is without effect upon the image of metallic silver. This is the function of the "fixing" bath. By this series of operations, the photographic negative is produced, with dark areas where the light in the camera touched the plate. The photographic positive (i.e., the photograph) is made by placing a similarly prepared paper below the negative, exposing it to light transmitted by the negative, and developing it as above described. The silver of the image thus formed on the paper is replaced by gold or platinum in the "toning" bath, because the resulting picture is more permanent and of a more pleasing color.

439. Silver Sulphide and Cyanide. — Silver sulphide (Ag_2S) is an important silver ore and is formed artificially by the action of sulphur or hydrogen sulphide upon the metal. Silver cyanide ($AgCN$) is a white curdy precipitate, insoluble in dilute nitric acid but soluble in ammonia-water or in solutions of the cyanides of the alkali or alkaline earth metals. It is used in electroplating.

(*a*) When a silver spoon is left for a time in an egg or in mustard, it becomes blackened by the formation of silver sulphide. Hence silver egg-spoons are often gilded.

Silver Nitrate.

Experiment 305. — Dissolve a small silver coin in a mixture of about 20 cu. cm. of concentrated nitric acid and 20 cu. cm. of water.

$$3Ag + 4HNO_3 = 3AgNO_3 + NO + H_2O.$$

The silver nitrate thus formed is dissolved in the blue solution, from which disagreeable reddish fumes seem to escape into the air.

Experiment 306. — To separate the silver nitrate formed in the last experiment from the copper salt that was formed at the same time, dilute the solution to about 300 cu. cm. Add a solution of sodium chloride, a little at a time, until no further precipitate is produced after the settling of the solution and the addition of more salt.

$$AgNO_3 + NaCl = AgCl + NaNO_3.$$

If too much NaCl is added, part of the precipitated silver chloride will be redissolved and lost. Filter out the silver chloride, and wash it with hot water until it is free from a soluble chloride. Dry the precipitate, separate it from the paper, and gently heat it in a porcelain crucible with a flame until it fuses. Cover the fused silver chloride with a piece of sheet zinc, so that the two come into as close contact as possible. Add about 10 cu. cm. of dilute sulphuric acid, and let the materials stand for a day or two. The zinc will replace the silver, forming a solution of zinc chloride.

$$2AgCl + Zn = 2Ag + ZnCl_2.$$

Separate the silver from the residual zinc, wash it with dilute sulphuric acid, and then with water until it is clean. Heat a small portion of the silver on a piece of charcoal and in a blowpipe flame until it fuses to a bead. Dissolve this pure silver in dilute nitric acid and evaporate the solution to dryness on a water-bath. Dissolve in distilled water as much of this pure silver nitrate as is needed, making a solution of about 1 part of the nitrate to 20 parts of water.

440. Silver Nitrate. — Silver nitrate ($AgNO_3$) is prepared on a large scale by dissolving silver in dilute nitric acid and evaporating to crystallization. It is found in commerce in crystals. When fused and cast into sticks, it is called lunar caustic. In this form it is used in surgery, acting as a powerful cautery. Pure silver nitrate is not altered by exposure to sunlight, but when in contact with organic substances it blackens, forming insoluble compounds of great stability. It is consequently used in making indelible inks and hair dyes. It is also used in medicine and in photography. Like all of the other soluble silver salts, it is poisonous.

441. Other Silver Salts. — Silver sulphate (Ag_2SO_4), silver phosphate (Ag_3PO_4), and silver carbonate (Ag_2CO_3) are among the many important silver salts.

442. Other Members of this Family. — Ruthenium, palladium, and rhodium are rare metals that closely resemble each other. They occur in platinum ores and palladium is found native. The melting-point of palladium is about that of wrought iron; rhodium is melted with more difficulty than is platinum; ruthenium is still less easily fusible. Palladium possesses the power of absorbing hydrogen in a greater degree than any other metal, one volume of the former taking up 600 volumes of the latter and forming an alloy with the composition Pd_2H, one of the foundations of the theory that hydrogen is a metallic element.

EXERCISES.

1. Why do silver coins become blackened when carried in the pocket with common sulphur matches?
2. How much lead may be obtained from 564 kilograms of lead sulphide?
3. At a very high temperature, Ag_2O may be decomposed much as the HgO was in Experiment 29. Write the reaction in molecular symbols.
4. What action have the alkalis upon silver?

5. If recently precipitated and moist AgCl is placed upon a sheet of zinc, a dark color will soon appear at the edge of the salt. The chloride will soon be converted into a dark gray powder of finely divided silver. Explain.

6. The change mentioned in Exercise 5 will be much more rapid if the AgCl is moistened with HCl. Why?

7. When silver chloride is fused with an alkaline hydroxide, the chloride is reduced to a metal, a non-combustible gas is set free, and an alkaline chloride is formed. What is the gas?

8. If a silver dime is dissolved in HNO_3, the solution will be blue. A solution of $AgNO_3$ is colorless. Whence the blue color?

9. I want $\frac{10}{.0896 \times 16}$ liters of oxygen. What weight of $KClO_3$ must I use?

10. (*a*) How many cubic centimeters of hydrogen may be obtained from 1 liter of ammonia? (*b*) Of nitrogen? (*c*) How may the elementary gases be obtained from the compound? (*d*) How may the eudiometer be used to free the nitrogen from the hydrogen?

11. If HCl is used instead of cream of tartar with $HNaCO_3$, what residue will remain in the biscuit?

12. (*a*) Read the equation: $2Ag'_3PO_4+3H_2S=2H_3PO_4+3Ag_2S$.
(*b*) Read the equation: $Ag_4P_2O_7+2H_2S=H_4P_2O_7+2Ag_2S$.
(*c*) Read the equation: $2AgPO_3+H_2S=2HPO_3+Ag_2S$.

13. Considering the silver salts symbolized in Exercise 12 to be in aqueous solution, summarize the teaching of these three reactions with reference to the formation of phosphoric acids.

14. Write in complete molecules the equation representing the reaction to which is due the red fumes noticed in Experiment 73.

15. How many grams of silver may be prepared from 1000 grams of silver chloride?

III. THE PLATINUM FAMILY.

PLATINUM: symbol, Pt; density, 21.5; atomic weight, 193.3; valence, 2, 4.

443. Occurrence, etc. — Platinum is found only in the native state, but very seldom pure. The so-called "platinum ore" is an alloy with ruthenium, palladium, rhodium, osmium, iridium, iron, copper, etc. It is found in the Ural Mountains, in Brazil, Borneo, California, Alaska, and a few other places. It is treated with strong aqua regia, and the platinum chloride thus obtained is precipitated by means of ammonium chloride. The ammonium-platinum chloride is then decomposed by intense heat, metallic platinum remaining as a residue. The preparation of pure platinum is a matter of great difficulty. For fusing the metal on the large scale, a crucible made of two pieces of lime is used with a compound blowpipe. The lime of the crucible successfully resists the high temperature produced, and absorbs the slags formed during the operation.

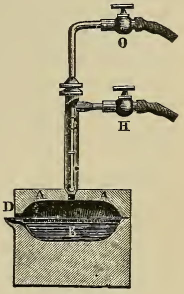


FIG. 104.

Properties of Platinum.

Experiment 307. — Boil 0.5 of a gram of platinum in small fragments in 10 cu. cm. of aqua regia as long as the metal seems to be acted upon. Pour the liquid into an evaporating dish, add aqua regia to the remaining platinum and proceed as before, continuing thus until all of the platinum has been dissolved. Evaporate the solution to dryness upon the water-bath. Dissolve this residue ($PtCl_4$) in water.

Experiment 308. — Heat a few drops of the solution of $PtCl_4$ in a test-tube. Notice the odor of the gas evolved. Hold a strip of moistened litmus-paper at the mouth of the test-tube. It will be bleached.

$$2PtCl_4 = Pt_2 + 4Cl_2.$$

Experiment 309. — Pour a teaspoonful of a solution of ammonium chloride into a test-tube, acidulate it with hydrochloric acid, and to it add a drop of the solution of the $PtCl_4$ just prepared. A yellow powder ($2NH_4Cl,PtCl_4$) will soon be precipitated. Repeat the experiment, taking enough of the solutions to make half a teaspoonful of the yellow precipitate, being careful that at last there shall be a slight excess of free NH_4Cl rather than of $PtCl_4$ in the overlying liquid. Allow the precipitate to settle, separate it from the clear liquor by decantation, and partly dry it at a gentle heat. When the precipitate has acquired the consistence of slightly moistened earth, transfer it to a cup-shaped piece of platinum foil and heat it to redness in the gas-flame until fumes of NH_4Cl are no longer driven off. A gray, loosely coherent, sponge-like mass of metallic platinum will remain in the cup; it is platinum sponge.

Experiment 310. — Make a support for a piece of platinum sponge the size of a pea by winding a fine wire spirally into the form of a little cup. Heat the sponge to redness in the lamp, and when cold hold it 2 or 3 cm. above a small jet of dry hydrogen. The cold gas will soon heat the cold sponge to redness; the sponge will in turn ignite the gas. In repeating the experiment, the preliminary heating of the sponge, probably, will not be necessary.

NOTE. — The heating of the sponge drives off traces of certain absorbable gases, such as ammonia, which interfere with the inflaming power of the platinum. This property of platinum has been explained by saying that the metal condenses or even liquefies a film of hydrogen and one of oxygen on its surface, and that the two elements, when brought together under circumstances of such intimate contact, chemically unite at the ordinary temperature.

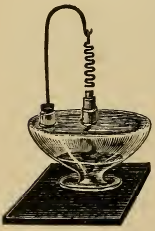


FIG. 105.

Experiment 311. — Fill a spirit-lamp with a mixture of alcohol and ether. Suspend a spiral of platinum wire over the wick and light the lamp. When the wire is red-hot, blow out the flame. The mixed vapors rising from the wick are oxidized by the heated platinum; the spiral is thus kept brightly incandescent. This is Davy's glow-lamp.

444. Properties. — Platinum is a heavy, soft metal of tin-white color. It is infusible at the highest temperature of the blast-furnace, but yields before the oxyhydrogen flame. Its melting-point has been estimated at 2000°. It is very malleable, and so ductile that it may be drawn into a wire less than 0.001 of a millimeter in diameter. Like gold, it has little affinity for the other elements. It is not oxidized by oxygen, water, nitric or sulphuric acid at any temperature. It dissolves in aqua regia more slowly than gold does. It also dissolves in chlorine water. Like iron, it may be welded at a white heat. It has two oxides, the monoxide (PtO), and the dioxide (PtO_2); it has two chlorides, the dichloride ($PtCl_2$), and the tetrachloride ($PtCl_4$).

(*a*) Red-hot platinum absorbs 3.8 volumes of hydrogen, which it gives off when heated in a vacuum, the surface of the platinum becoming then covered with bubbles. Similarly, hydrogen is absorbed by platinum, at the negative electrode in the electrolysis of water, the occluded hydrogen being given off when the current is reversed. Oxygen is not absorbed by platinum, but it is condensed on a clean surface of the metal.

(*b*) Platinum-black is a form of metallic platinum, even more finely divided than platinum sponge. It is a soft, dull, black powder. It can absorb more than 800 times its volume of oxygen. When boiled in water and dried in a vacuum over sulphuric acid, it absorbs oxygen from the air so rapidly that the mass becomes red-hot. If upon the powder, when cooled after such absorption of oxygen, some alcohol or ether is dropped, the oxidation of the liquids will heat the metal red-hot.

445. Uses. — On account of its infusibility and its chemical inertness, platinum is invaluable to the chemist. In the laboratory it is used for crucibles, evaporating dishes, stills, tubes, spatulas, forceps, wire, blowpipe tips, etc. In sulphuric acid manufacture, large platinum stills and siphons are used for concentrating the acid. As its rate of expansion is nearly equal to that of glass, it is used in the manufacture of eudiometers, Geissler tubes, incandescent electric lamps, etc.

(*a*) On account of platinum forming easily fusible alloys, care should be had not to heat platinum utensils with an easily fusible metal, e.g., lead, bismuth, tin, or antimony, or any easily reducible compound of a metal. They should not be used for fusion with niter, the alkalis, or the alkaline cyanides. They should not be heated in contact with phosphorus or arsenic nor brought into direct contact with burning charcoal.

(*b*) "Without platinum it would be impossible, in many cases, to make the analysis of a mineral. The mineral must be dissolved. Vessels of glass and all non-metallic substances are destroyed by the means we used for that purpose. Crucibles of gold and silver would melt at high temperatures. But platinum is cheaper than gold, harder and more durable than silver, infusible at all temperatures of our furnaces and is left intact by acids and alkaline carbonates. Platinum unites all the valuable properties of gold and of porcelain, resisting the action of heat and of almost all chemical agents. Without platinum the composition of most minerals would have yet remained unknown."—*Liebig.*

446. Osmium and Iridium.—These rare metals are found in "platinum ore," as already stated. They are of extreme infusibility. Osmium is the heaviest known substance, it having a density of about 22.48. Its alloy with iridium (osmiridium) is used for tipping gold pens as it is not attacked by acids, and for the bearings of the mariner's compass as it does not oxidize and is non-magnetic. Iridium has a density of about 22.38. It has a white luster resembling that of polished steel. An alloy of one part of iridium and nine parts of platinum is extremely hard, as elastic as steel, more difficultly fusible than platinum, unalterable in air, and susceptible of a beautiful polish. This alloy was adopted by an international commission for the standard metric measures.

EXERCISES.

1. Sulphuric acid is poured upon niter; name the two substances that you obtain. Write the reaction.

2. Why is moist calico more easily bleached with chlorine than is dry calico?

3. From 8 kilograms of potassium nitrate, how much nitric acid can be liberated? How much sulphuric acid will be required?

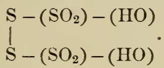
4. Write the formulas for selenic acid and for tellurious acid.

5. Complete the following equations:

$$NaCl + H_2SO_4 = HCl +$$

$$NaCl + H_2SO_4 = 2HCl + Na_2SO_4$$

6. Write the name and full graphic formula for



$$\begin{array}{l} S-(SO_2)-(HO) \\ | \\ S-(SO_2)-(HO) \end{array}.$$

7. If sulphuryl chloride is poured into water, we have the following reaction: $SO_2Cl_2 + 2H_2O = H_2SO_4 + 2HCl$. How much dry HCl may be thus prepared from 135 grams of SO_2Cl_2?

8. If a factory uses daily 100 tons of coal that contains 2 per cent of sulphur, assuming that all the sulphur is converted to sulphuric acid, what weight of sulphuric acid will the products of combustion contain during 300 days' run?

9. Write the reactions expressing the preparation of at least $5H_2SO_4$, using not more than two molecules of nitric acid.

10. Which is the more easily fusible, platinum or calcium oxide?

11. What is the difference between ammonia and ammonium?

12. How many grams of silver chloride may be prepared from 1000 grams of American coin silver?

13. Write the names and formulas for the salts formed by the union of potassium hydroxide with each of the following acids: sulphurous, sulphuric, nitrous, nitric, chlorous, and chloric.

14. Write the names and the formulas for the salts formed by the union of calcium hydroxide and each of the acids mentioned in the preceding exercise.

GOLD: symbol, Au; density, 19.265; atomic weight, 195.7; valence, 1, 3.

447. Occurrence.—Gold is widely distributed in nature, but in only a few places is it found in quantities sufficient to repay the cost of obtaining it. It is generally found in the native state alloyed with silver. Native gold is found in the quartz veins that intersect metamorphic rocks and in the alluvial deposits, called placers, formed by the disintegration of gold-bearing rocks.

(*a*) The richest deposits of gold are in California, Colorado, Nevada, Alaska, Siberia, South Africa, and Australia. Native gold is found in crystals, nuggets, grains, and scales. While the particles are sometimes so small as to be invisible in even "paying" quartz, a single nugget, weighing 184 pounds and valued at £8376, 10*s.* 6*d.*, was found in Australia. Gold compounds are also found in nature.

448. Preparation.—In quartz-mining the ore is first pulverized. The gold is then extracted from the powdered mineral by means of mercury. The gold amalgam thus formed is subjected to distillation. In "placer digging" the lighter constituents of the alluvial deposit are washed away, the heavier gold remaining in the "wash-pan" or "cradle." In "hydraulic mining" immense streams of water are directed, under great pressure, against the surface of the auriferous deposit. In this way great quantities of sand, clay, and gravel are disintegrated and hurried forward in a turbid torrent, from which the heavy gold particles settle into interstices previously prepared in the sluices through which the muddy mass is caused to flow. Much of the gold now mined is contained in sulphide ores which must be roasted before the gold can be recovered. The gold of such roasted ores is commonly made soluble by treatment with potassium cyanide or by chlorine. The solution is then washed out with water. The gold is precipitated from the potassium cyanide solution by zinc, and from the chloride by ferrous sulphate.

Properties of Gold.

Experiment 312. — Add a few drops of a strong solution of auric chloride ($AuCl_3$) to a liter of water. Into this dilute solution drop one or two pieces of phosphorus the size of a mustard seed, and place the whole in the sunlight. In the course of a few hours the water will have a distinct purplish tint. This will deepen in color until finally, if the solution has the proper strength, a beautiful ruby-red liquid will be obtained. The color of this liquid is due to finely divided metallic gold.

449. Properties.— Gold is a brilliant, beautiful, orange-yellow metal. It is the most malleable and ductile of the metals. It may be beaten into leaves not more than 0.0001 of a millimeter thick; one gram of it may be drawn into 3240 meters of wire. It is softer than silver and nearly as soft as lead. It fuses at 1063.5° and volatilizes at very high temperatures. It is not attacked by oxygen or water at any temperature. It does not dissolve in any simple acid except selenic, but dissolves readily in aqua regia or in any other acid liquid that evolves chlorine.

(*a*) One ounce of gold-leaf may be made to cover 189 square feet, while 280,000 leaves placed one upon another measure only one inch in thickness. One grain of gold will gild two miles of fine silver wire. Ordinary gold-leaf transmits green light. Gold may be precipitated in so fine a state that it remains suspended in the liquid, causing it to appear ruby-red by reflected light or blue by transmitted light. The red color of ruby glass is due to the presence of gold in a finely divided state. Gold is sometimes called the "king of metals."

450. Uses.—Gold is used for coinage, jewels, gilding, and other purposes, for which it is well adapted by its beautiful color and luster, its unalterability and comparative rarity. Pure gold is so soft that coins and jewels made of it would soon wear out. It is, therefore, hardened by alloying with copper. American and French gold coins contain one-tenth copper; British gold coins, one-twelfth.

(*a*) The purity of gold in jewels is estimated in carats, pure gold being "24 carats fine." An alloy containing two-thirds gold is "16 carats fine."

(*b*) The compounds of gold are of little chemical interest. There are two oxides, the monoxide (aurous oxide, Au_2O) and the trioxide (auric oxide, gold sesquioxide (Au_2O_3). There are two chlorides, $AuCl$ and $AuCl_3$. Aurous cyanide ($AuCN$) dissolved in a solution of potassium cyanide is used in electrogilding.

EXERCISES.

1. What takes place when sodium is thrown into water?

2. Describe an experiment showing the difference between a mixture and a compound.

3. State the effect of heat upon MnO_2, $KClO_3$, NH_4Cl, NH_4NO_3, phosphorus, and sulphur respectively.

4. You are given Zn, H_2SO_4, KHO, and H_2O, and required to prepare hydrogen from them by two distinct processes. Describe the processes and write the reaction for each.

5. I have two cylindrical jars of hydrogen, one of which I hold mouth upward, the other mouth downward. At the end of 30 seconds, I plunge a lighted taper into each jar. Tell what you would expect to take place in each case.

6. What are the products of the combustion of hydrogen sulphide in the air?

7. How can you make H_2SO_4 from sulphur, water, and nitric acid?

8. What elements can be obtained from HCl, NH_3, and H_2O? How would you obtain them in each case?

9. (*a*) When hydrogen is burned in air, what is the product? (*b*) When it is burned in chlorine?

10. An electric spark is produced in a mixture of 120 cu. cm. of hydrogen and 60 cu. cm. of oxygen. How would you conduct the experiment so as to show the gaseous condensation?

11. You are required to prepare oxygen from chlorine and water. How would you do it?

12. You are given some mercury in a glass flask, a lamp, and some glass tubing, and required to make pure oxygen. How will you do it under ordinary barometric conditions?

13. When nitric acid is poured on copper, how does the action differ from a simple solution?

14. You are given ammonium carbonate and nitric acid and required to prepare laughing-gas from the materials. How will you do it?

15. What is the fineness of British gold coin in carats?

16. (*a*) Where is sulphur found? (*b*) How is hydrogen sulphide made, and what are its properties? (*c*) What is meant by oxidizing agents and what by reducing agents?

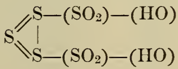
17. When a thin stream of sulphuric acid flows into a retort filled with broken bricks heated to redness, the following reaction takes place:

$$H_2SO_4 = SO_2 + H_2O + O.$$

(*a*) What weight and (*b*) what volume of oxygen can be thus prepared from 50 grams of H_2SO_4, C.P.?

18. Write the formulas for potassium sulphite, potassium-hydrogen sulphite, calcium sulphite, and calcium-hydrogen sulphite.

19. Write the name and a full graphic formula for



20. Write the graphic formula for phosphorus tetriodide (P_2I_4) indicating trivalent phosphorus.

21. Write the graphic formula for pyrophosphoric chloride ($Cl_4P_2O_3$).

22. (*a*) Write the graphic formula for H_3PO_3. (*b*) Does this formula indicate a dibasic or a tribasic acid?

23. Explain the fact that when new flannel is first washed in an alkaline soap, it becomes yellow.

24. (*a*) How would you distinguish between platinum and silver? (*b*) Between platinum and tin? (*c*) Between silver and tin? (*d*) Between gold and "fool's gold"?

APPENDIX.

1. The Chemical Elements. — An alphabetical list of the elements with their symbols and atomic weights is given below. In the body of the book, some of the atomic weights were given in approximate numbers, for greater ease in memorizing and computation. In the table below, the atomic weights are given according to the latest report of the American committee on atomic weights. (See third page of cover.)

Name.	Symbol.	Atomic Weight.
Actinium		
Aluminum	Al	26.9
Antimony	Sb	119.5
Argon	Ar	40.?
Arsenic	As	74.45
Barium	Ba	136.4
Beryllium	Be	9.0
Bismuth	Bi	206.5
Boron	B	10.9
Bromine	Br	79.34
Cadmium	Cd	111.55
Cæsium	Cs	131.9
Calcium	Ca	39.8
Carbon	C	11.9
Cerium	Ce	138.0
Chlorine	Cl	35.18
Chromium	Cr	51.7
Cobalt	Co	58.55
Columbium	Cb	93.0
Copper	Cu	63.1
Crypton	*See Krypton*	
Erbium	E	164.7
Ethereon ?		
Fluorine	F	18.9
Gadolinium	Gd	155.8
Gallium	Ga	69.5
Germanium	Ge	71.9
Glucinum	*See Beryllium*	
Gold	Au	195.7
Helium	He	4.?
Hydrogen	H	1.0
Indium	In	113.1
Iodine	I	125.89
Iridium	Ir	191.7
Iron	Fe	55.5
Krypton	Kr	59.?
Lanthanum	La	137.6
Lead	Pb	205.36
Lithium	Li	6.97
Magnesium	Mg	24.1
Manganese	Mn	54.6
Mercury	Hg	198.5
Molybdenum	Mo	95.3
Neodymium	Nd	142.5
Neon	Ne	20.?
Nickel	Ni	58.25
Niobium	*See Columbium*	
Nitrogen	N	13.93
Osmium	Os	189.6
Oxygen	O	15.88
Palladium	Pd	106.2
Phosphorus	P	30.75
Platinum	Pt	193.4
Polonium		
Potassium	K	38.82
Praseodymium	Pr	139.4
Radium	Ra	225.?
Rhodium	Rh	102.2
Rubidium	Rb	84.75
Ruthenium	Ru	100.9
Samarium	Sm	149.2
Scandium	Sc	43.8

NAME.	SYMBOL.	ATOMIC WEIGHT.	NAME.	SYMBOL.	ATOMIC WEIGHT.
Selenium	Se	78.6	Thulium	Tm	169.4
Silicon	Si	28.2	Tin	Sn	118.1
Silver	Ag	107.11	Titanium	Ti	47.8
Sodium	Na	22.88	Tungsten	W	182.6
Strontium	Sr	86.95	Uranium	U	237.8
Sulphur	S	31.83	Vanadium	V	51.0
Tantalum	Ta	181.5	Xenon	X	128.?
Tellurium	Te	126.5	Ytterbium	Yb	171.9
Terbium	Tr	158.8	Yttrium	Y	88.3
Thallium	Tl	202.61	Zinc	Zn	64.9
Thorium	Th	230.8	Zirconium	Zr	89.7

2. Weighing. — The laboratory should be provided with at least two balances, one of the platform type for the heavier weighings, and one of the scale-pan type sensitive to 0.01 of a gram. A really good balance is a delicate piece of apparatus and requires careful use and preservation. Substances that corrode metal (iodine for example) should not be allowed to come into contact with the scale-pans, and all metallic parts of the balance should be protected from corrosion by acid fumes, etc. With the object to be weighed on one side of the balance and an exact counterpoise on the other, count up the total weight from the vacant places in the box of weights (Fig. 108) and then verify the result by another count as the weights are returned to

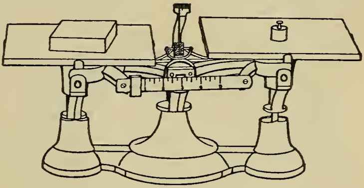


FIG. 106.

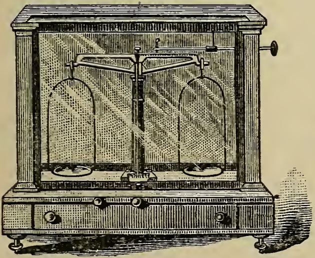


FIG. 107.

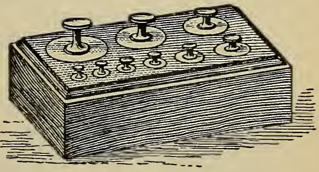


FIG. 108.

their proper places in the box. The process looks simple, but accurate weighing requires technical skill.

3. Metric Measures. — Chemists of all countries use the international or metric units almost exclusively. The decimeter rule is shown as being divided into 10 centimeters, each of which is divided into 10 millimeters. The cubic decimeter measures a volume called a liter (pronounced *leeter*). The cubic centimeter (cu. cm.) is 0.001 of a liter (l.). The weight of 1 cu. cm. of water at the temperature 4° is a gram (g.). These three units, the liter, the cubic centimeter, and the gram, are the ones of most frequent occurrence in chemical works. The actual weights and measures should be habitually used in every school laboratory.

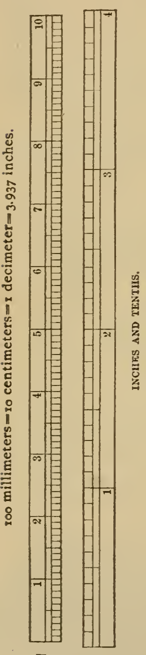


FIG. 109.

4. Thermometers. — Chemists use the centigrade thermometer almost exclusively. One or more centigrade thermometers (chemical), having the scale marked on the glass tube, and having no frame like that of the ordinary house thermometer, should be in every school laboratory. Straight glass tubes, of uniform diameter, with cylindrical instead of spherical bulbs, are preferable; such instruments can be passed tightly through a cork, and are free from many liabilities to error to which thermometers with paper or metal scales are always exposed. A cheaper kind of thermometer, having a paper scale inclosed in a glass envelope, will answer for many experiments.

FIG. 110.

5. Glass-working. — Much of the chemist's apparatus is made of glass which softens and becomes plastic when heated. Skillful workers in wood or metal may be found in almost any town, but glass-working will generally devolve upon the teacher and pupil. It is, therefore, discussed at some length in this place.

(*a*) *Glass Tubing.* — Glass tubes bent into various shapes are constantly needed. The pupil should acquire dexterity in preparing these for himself. Glass tubing is of two qualities, hard and soft. The former softens with difficulty and is desirable only for ignition- or combustion-tubes. But little of it will be needed. It is generally better to buy the ignition-tubes required. Soft glass tubing will be needed in larger quantities. In purchasing, it is recommended that the greater part be of a single size. Figure 111 shows desirable sizes and the proper thickness of the glass for each size. By using, habitually, one size of tubing, the various articles made therefrom are more easily interchangeable than they would otherwise be.

FIG. 111.

(*b*) *Cutting and Bending Tubes.* — Glass tubing and rods must generally be cut the desired length. For this purpose, lay the tube or rod upon the table and make a scratch at the required distance from one end with a three-cornered file. Hold the tubing in both hands, as shown in Fig. 112, with the scratch away from you and the two thumbs opposite the mark. With a sharp motion, push out the thumbs and pull back the fingers. The glass will snap squarely off at the desired place. The best flame for bending ordinary tubes is that of a fish-tail gas-burner, but that of a spirit-lamp will do. Be sure that the tube is dry; do not breathe into it before heating it. Bring the part of the tube where the bend is desired into the hot air above the flame; when it is thoroughly warm, bring it into the flame itself. Heat about an inch of the tube, holding it with both hands and turning it constantly that it may be heated uniformly on all sides. The tube should be held between the thumb and first two fingers of each hand, the hands being below the tube, palms upward and the lamp between the hands. The desired yielding condition of the glass will be detected by feeling better than by seeing, i.e., the fingers will detect the yielding of the glass before the eye notices any change of color or form. When the glass yields easily, remove it from the flame and gently bend the ends from you. If the concave side of the glass is too hot, it will "buckle"; if the convex side is too hot, the curve will be flattened and its channel contracted. Practice, and practice only, will enable you to bend a

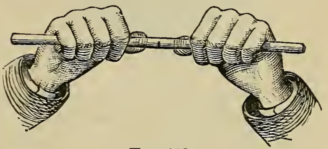


FIG. 112.

tube neatly. When a tube or rod is to be bent or drawn near its end, a temporary handle may be attached to it by softening the end of the tube or rod, and pressing against the soft glass a fragment of glass tube which will adhere strongly to the softened end. This handle may subsequently be removed by a slight blow or by the aid of a file. If a considerable bend is to be made, so that the angle between the arms will be very small or nothing, as in a siphon, the curvature can not be well produced at one place in the tube, but should be made by heating, progressively, several centimeters of the tube, and bending continuously from one end of the heated portion to the other (Fig. 114). The several parts of such a bent tube should all lie in the same plane so that the finished tube may lie flat on a level surface. It is difficult to bend tubing large enough for U-tubes which would better be bought. When the end of a tube or rod is to be heated, it is best to begin heating the glass about 2 cm. from the end, as cracks start easily from an edge. Smooth the sharp edges at the ends of the tube by slight fusion in a flame. Anneal the bent tube by withdrawing it very gradually from the flame so as not to let it cool suddenly. Never lay a hot tube on the bench, but put it on some poor conductor of heat until it is cool. Asbestos board or paper is convenient for this purpose. Gradual heating and gradual cooling are alike necessary. Glass tubing may be advantageously united by rubber tubing when the substance to be conducted will not corrode the latter, or when the temperature employed is not too high. Short pieces of rubber tubing are much used as connectors to make flexible joints in apparatus. Gas delivery-tubes, etc., are generally made in several pieces joined by rubber tubing connectors, which, by their flexibility, add much to the durability of the apparatus. Long glass tubes bent several times and connecting heavier pieces of apparatus

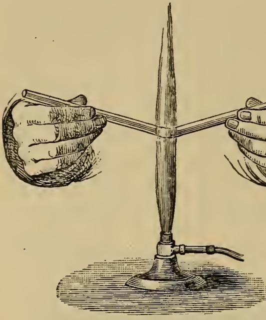


Fig. 113.

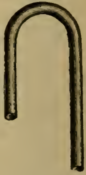


Fig. 114.

are almost sure to break, even with careful use. The internal diameter of the connector should be a little less than the external diameter of the glass tubing. The connection may be made more easily by wetting the glass.

(*c*) *Drawing Tubes.* — In order to draw a glass tube down to a finer bore, thoroughly soften it on all sides uniformly for 1 or 2 cm. of its length and then, taking the glass from the flame, pull the parts asunder by a cautious movement of the hands. The length and fineness of the drawn-out tube will depend upon the length of tube heated and the rapidity of motion of the hands. If the drawn-out part of the tube is to have thicker walls in proportion to its bore than the original tube, keep the heated portion soft for two or three minutes before drawing out the tube, pressing the parts slightly together the while. By this process the glass will be thickened at the hot ring. By cutting the neck at *a*, with a file, jets are formed.

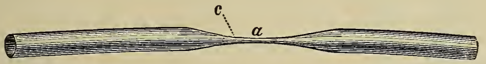


Fig. 115.

(*d*) *Closing Tubes.* — Take a piece of tubing long enough to make two closed tubes of the desired length. Heat a narrow ring at the middle of the tube and draw it out slightly. Direct the point of the flame upon the point *c* (Fig. 115) which is to become the bottom of one tube, draw out the heated part and melt it off. Each half of the original tube is now closed at one end, but they are of different forms. You can not close both ends satisfactorily at the same time. A superfluous knob of glass generally remains upon the end. If small, it may be removed by heating the whole end of the tube, and blowing moderately into the open end. The knob being hotter than any other part, yields to the pressure from within and disappears. If the knob is large, it may be drawn off by sticking to it a fragment of tube, and then softening the glass above the junction. The same process may be applied to the too-pointed end of the right-hand half of the original tube, or to any bit of tube that is too short to make two closed tubes. When the closed end of a tube is too thin, it may be strengthened by keeping the whole end at a red heat for two or three minutes, turning the tube constantly between the fingers. In all of these processes keep the tube in constant rotation

Fig. 116.

that it may be heated on all sides alike. It will be difficult for the pupil satisfactorily to work tubing large enough for test-tubes. They would better be bought. They come in nests of assorted sizes.

(*e*) *Blowing Bulbs.* — This is a more delicate operation than any yet described. It requires considerable practice to secure even moderate success. It is better, as a general thing, to buy funnel-tubes and bulb-tubes than to make them.

(*f*) *Welding Glass Tubes.* — The well-fitted ends of two pieces of glass tubing may be joined by heating them to redness and pressing them together while in a plastic condition. Practice is necessary to good results, but the skill should be acquired as funnel-tubes and other pieces of apparatus often need mending. If necessary, the end of one tube may be enlarged by rapidly turning the glass in the flame until it is highly heated, and then, while it is still in the flame, flaring it outward with an iron rod. Hold the ends together and heat them well with a pointed flame, until they are united all around. Force air in at one end to swell out the joint a little, heat it again until the swelling sinks in, blow it out again, and repeat the process until the joint is smooth and the pieces well fused into each other. Without this repeated heating and blowing, the joint is likely to crack open when cooled.

(*g*) *Piercing Tubes.* — A hole may be made in the side of a tube or other thin glass apparatus by directing a pointed blowpipe flame upon the glass until a spot is red-hot, closing the other end, if open, with the finger and blowing *forcibly* into the open end. The glass is blown out at the heated spot. The edge may be strengthened by laying on a thread of glass around it, and fusing the thread to the tube in the blowpipe flame.

(*h*) *Glass-cutting and Cracking, etc.* — For cutting glass plates a glazier's diamond is desirable, but efficient and cheap "glass-cutters," made of hardened steel, may be bought. For shaping broken flasks, retorts, and other pieces of thin glassware, cracking is more satisfactory. A scratch is made with a file, preferably at the edge of the glass. Apply a pointed piece of glowing charcoal, a fine-pointed flame or a heated glass or metal rod to this scratch. The sudden expansion by heat will generally produce a crack. If the heat does not make one, touch the hot spot with a wet stick. A crack thus started may be led in any desired direction by keeping the heated rod or fine flame moving slowly a few millimeters in front of it as it advances.

A flask or retort neck may sometimes be cracked round by tying a string soaked in alcohol or turpentine round the place, setting fire to the string and keeping the flask turning. When the string has burned out, invert the flask and plunge it into water up to the heated circle. It will generally crack as desired.

The lower ends of glass funnels and the ends of gas delivery-tubes that enter the generating bottle or flask should be ground off obliquely on a wet grindstone, or shaped thus with a file wet with a solution of camphor in turpentine, to facilitate the dropping of liquids from such extremities. With a little care and patience, a hole may be drilled through glass by using a file kept wet with the solution mentioned. Such a hole may easily be enlarged or given any desired shape with a file thus wet.

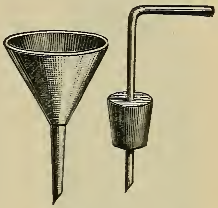


FIG. 117.

The lips of bottles may be ground flat by rubbing them on a flat surface sprinkled with emery-powder kept wet. The bottle should be grasped by the neck and rubbed around with a gyratory motion, pains being taken to prevent a rocking motion whereby first one side of the lip is ground and then another, thus leaving the bottle in as bad a condition at the end of the work as at the beginning. The work may be finished by rubbing with fine emery-powder on a piece of plate or window-glass until all parts of the ground surface lie in the same plane.

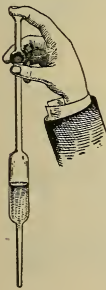


FIG. 118.

6. Pipettes and Graduates. — Tubes drawn out to a small opening at one end and used to remove a small quantity of a liquid from a vessel without disturbing the bulk of its contents, are called pipettes. They often carry a bulb or cylindrical enlargement. The manner of using them is shown in Fig. 118. They are often graduated. A cylindrical measuring-glass, graduated to cubic centimeters (Fig. 119), is almost indispensable in the laboratory.

FIG. 119.

7. Wouliffe Bottles. — A very convenient substitute for Woulffe bottles may be made by perforating the glass cover of a fruit jar, as already described. The holes carry cork or rubber stoppers through which the several tubes pass, as shown in Fig. 120.

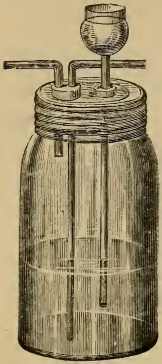


FIG. 120.

8. Thin-bottomed Glassware. — Glass vessels are largely used for heating liquids in the laboratory. Such vessels should have uniformly thin bottoms that they may not be broken by unequal expansion when heated. If moisture from the atmosphere or other source accumulates on the outer surface, it should be carefully wiped off before or during the heating.

Retorts are often used. Those that have tubulures (Fig. 35, *s*) are preferable to those that have not.

Florence flasks are much used instead of retorts, as they cost much less. They may be bought in any size desired and with their bottoms rounded or flattened. Heated retorts and flasks should not be placed on the table, as the sudden cooling may break them. They may better be placed on rings covered with listing or made of straw or other poor conductor of heat.

Beakers are thin, flat-bottomed glasses with slightly flaring rims. They are convenient for heating liquids when it is desirable to reach every part of the vessel, as with a stirring-rod. They are generally sold in nests of different sizes. Beakers of more than a liter's capacity are too fragile to be desirable.

Test-tubes are thin glass cylinders, closed at one end and having lips slightly flared. The mouth should be of such a size that it may be closed by the ball of the thumb. A test-tube rack should be made or bought, to hold the tubes upright when in use and to hold them inverted when not in use.

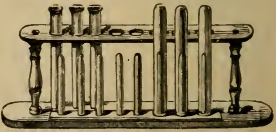


FIG. 121.

Test-tubes may be held in an inverted position, as at the pneumatic trough or water-pan, by weighting them with lead rings cut with a saw from lead pipe. The ring should be of such a size that it will easily slip over the tube, but not over the lip of the tube. Test-tubes may be easily cleaned with little cylindrical brushes made of bristles held between twisted wires. They cost but a few cents each. The chief danger in cleaning a test-tube is that the bottom may be broken out. The brush should therefore have a tuft of bristles at its end. When the upper end of a tube is held in the fingers during the heating, the tube should be rolled or turned in the flame so that all sides may be equally heated.

9. Filtering. — Funnels that have an angle of exactly 60° should be chosen. The circular piece of filter-paper should be folded first on its diameter, then again at right angles to the first fold, and then opened out so as to leave three folds on one side and one on the other. It is then to be placed in a funnel, the funnel placed in proper position, and the liquid to be filtered carefully poured upon the paper. If the first filtration does not clear the liquid, the filtrate should be poured back upon the same filter for refiltration. Observation and experiment will show other good ways of folding the filter-paper for the funnel.

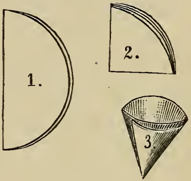


FIG. 122.

For coarse and rapid filtering, the neck of the funnel may be plugged with tow or cotton. For filtering solutions that would destroy the texture of the filter-paper, a plug of asbestos or of gun-cotton is placed in the neck of the funnel.

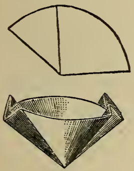


FIG. 123.

The funnel may be supported in any convenient way. Sometimes it may be placed in the neck of the bottle, care being had that it does not fit air-tight (see Fig. 57). It may often be supported from the retort-stand or other independent support. When convenient, the lower end of the funnel should touch the side of the vessel that receives the filtrate, so that the latter may fall quietly rather than in splashing drops. The end of the funnel neck should be ground off obliquely, as shown in Fig. 117.

When a precipitate has been collected upon a filter, it may be washed by filling the filter two or three times with distilled water and allowing it to run through. A washing-bottle is of great convenience, the stream of water being driven out at *c* by air from the lungs forced in at *a*. The stream of water is

FIG. 124.

directed so as to wash the precipitate from the sides of the filter toward its apex. The jet may be carried by a piece of flexible tubing attached to *c*, so that it may be turned in any direction without moving the bottle. When a precipitate is very heavy, it may be washed by shaking it up with successive quantities of water in a test-tube, and pouring off the water when the precipitate has settled down. A wet glass rod held against the lip of the test-tube greatly assists in pouring off the liquid without disturbing the precipitate.

10. Corks, etc. — It is not always easy to obtain corks of good quality and considerable size. Many experiments have failed through defects in the corks used. Use bottles with small mouths when you can. Choose corks cut across the grain rather than those cut with the grain, as the latter often provide continuous channels for the escape of gases. Select those that are as fine grained as you can get. They will generally need to be softened before use. This may be done by rolling on the floor with the foot, on the table with a board, or with a cork-squeezer made for that purpose. Corks may be made less porous by holding them for a few minutes under the surface of melted paraffin wax.

In boring holes through corks, a small knife-blade or rat-tail file may be used, but a set of brass cylinders made for the purpose is more convenient. Such a set of cork borers and the way of using them are shown in Fig. 125. Use a borer with a diameter a little less than that of the glass tubing to be used. When the borer becomes dull, grind or file the outer beveled edge and, with a sharp knife-blade, pare off the rough metal on the inside of the edge.

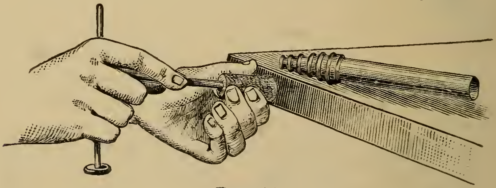


FIG. 125.

Rubber stoppers are more durable than cork and much to be preferred. They may be bored as above described. If they harden, they may be softened by being kept for a time in a closed flask containing a few drops of turpentine. If the glass tube enters the bored stopper with much difficulty, wet the outside of the tube with turpentine.

In passing glass tubes through stoppers of cork or rubber, see that the end of the tube is smooth, hold the tube as near as possible to the stopper, and force it in with a slow, steady, rotary, onward motion. Do not hold a funnel-tube by the funnel, or a bent tube at the bend, if you can avoid doing so. If the glass tube enters the bored cork with much difficulty, smear the outside of the tube with soap and water. Test all joints made in the manner described in § 22.

The sticking of glass stoppers is a frequent source of trouble in the laboratory. Many methods of loosening them have been suggested. When one fails, another must be tried. Under such circumstances, patience and persistence are recommended. It is hardly ever necessary to break the bottle. Generally, the stopper may be started by tapping it lightly on opposite sides alternately with a block of soft wood. The expansion of the bottle neck by heat will often loosen the stopper. The heat may be applied by friction with the fingers or a piece of tape, by a flame, or by hot water. If the application of heat is continued too long, the stopper as well as the neck will expand, and the trial end in failure. As a last resort, fit two pieces of soft wood between the lip of the bottle and the lower side of the projecting part of the stopper. Tie them firmly in place and soak in water for several hours. If the wood does not swell enough to start the stopper, pour hot water over the wooden pieces, and the trouble will generally be at an end.

When you pour a liquid from a bottle, as into a test-tube, hold the bottle in the right hand with the label toward the palm. Remove the stopper with the little finger or with the third and fourth fingers of the left hand, the thumb and forefinger of which may hold the test-tube. Remove the liquid drop that adheres to the lip of the bottle by touching it with the stopper, replace the stopper, and return the bottle to its proper place. It is seldom necessary to place either stopper or bottle on the table. In a little while you will acquire the habit of doing these things in this way and thus avoid much annoyance.

11. Stands, Supports, Baths, etc. — Flasks, etc., are often supported over the lamp by a retort-stand, as shown in Figs. 32 and 35. This stand has a heavy base and several movable iron rings of graduated sizes secured to the vertical rod by binding screws. Glass vessels thus supported are well protected from the direct flame of the lamp by a piece of wire-gauze, as shown in Fig. 32. Occasionally a very gradual and even heating is desired. Under such circumstances, the wire-gauze may be replaced by a sand-bath, which consists of a shallow pan, beaten out of sheet-iron and filled with sand. Sometimes it is desirable to heat a vessel moderately, keeping it continuously below a certain temperature. This may be accomplished by placing the vessel in another vessel, partly filled with water, and heating the water, as shown in Fig. 71. Copper cups with tops made of concentric rings that may be adapted to the size of the vessel are offered for sale. A good enough water-bath may be made of an old tinned fruit-can. Care should be had that the water of the bath is not allowed to boil away. Figure 126 shows various clamps and fittings for a retort-stand, by means of which tubes, flasks, retorts, etc., are easily held in any desired position. Many convenient supports may be made with corks and glass rods stuck on inverted funnels. A convenient support for a small vessel may be made in the form of an equilateral triangle by twisting together three pieces of soft-iron wire at the corners, as shown in Fig. 127. Each of the wires may be run through the stem of an ordinary clay pipe. The support may be placed upon the ring of a retort-stand, or held by a cork into which the twisted wires at one corner have been thrust. A convenient support for test-tubes, etc., may be made by binding the middle part of a copper wire, 1 or 2 millimeters in diameter, about a stout cork. The free ends of the easily flexible wire may be wound spirally around the test-tube. The cork serves as a handle; if perforated, it may be placed upon the rod of the retort-stand. The wire may be bent so as to place the tube in any desired position.

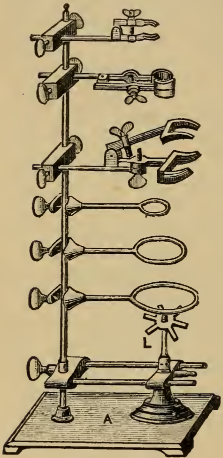


FIG. 126.

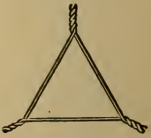


FIG. 127.

12. Mortars. — A mortar is a vessel, *m*, in which solid substances may be powdered with a pestle, *i*. They are made of iron, porcelain, agate, etc. Porcelain mortars of the best quality are made of "Wedgwood"; they are unglazed, should not be suddenly heated, and may be cleaned by rubbing them with sand wet with nitric acid, or sulphuric acid, or caustic potash, or soda, according to the nature of the substance to be removed. Agate mortars are very small and expensive. In many cases a stout bowl will answer as a mortar, while a pestle may be made of *hard* wood. Many substances may be powdered on a hard surface by the use of a rolling-pin, like that used by a pastry cook, or by rolling a stout bottle over them. If a solid is to be broken by blows preparatory to powdering, an iron mortar and pestle are desirable. The pestle may be worked through a hole in a pasteboard cover, which will prevent fragments of the solid from flying out of the mortar. Often it is better to wrap the solid in a paper or a cloth, and then to break it with blows of a hammer. In using a mortar for pulverizing, it is better to put only a small quantity of the substance into the mortar at once, sifting it frequently, and returning the coarser particles to the mortar for further trituration. The sifting may be done by rubbing the powder lightly with the finger upon a piece of muslin tightly stretched over the mouth of a beaker.

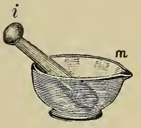


FIG. 128.

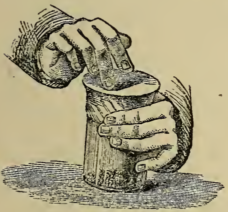


FIG. 129.

13. The Pneumatic Trough. — For collecting gases over water, the pneumatic trough, in some form, is indispensable. A convenient trough is shown in Fig. 7, and described in § 21. The pan, *f*, may be of earthenware, while a flower-pot saucer will answer for *e*. Two flat blocks of any material heavier than water may be used, instead of the saucer, for the support of the inverted gas receiver, *g*. With this apparatus the receiver must be filled outside of the trough. The mouth being closed with the hand, a flat piece of wood, glass, or cardboard, the bottle may be quickly inverted and placed in position so that its mouth is closed by the water in *f*. If any air gets into *g* during this operation, the work must be done again. While one bottle is filling with gas, another is to be made ready. When filled with gas, the first bottle may be removed from the trough by slipping a shallow plate or saucer beneath its mouth and removing plate and bottle together. Enough water will be retained in the plate to seal the mouth of the bottle. If the lip of the bottle has been ground flat, a piece of window-glass will answer instead of the plate. As successive bottles are filled, the trough may become inconveniently full of water, some of which may be dipped out or removed with a rubber-tube siphon.

Any bucket or tub with a hanging shelf having holes bored in it, will make an efficient pneumatic trough.

When it can be secured, a pneumatic trough similar to that shown in Fig. 130 is desirable. It may be made of boards carefully joined and painted, but is preferably lined with sheet-lead. It should be sunk in a table and provided with a water-cock and a drain-pipe. Gas receivers are easily filled with water in the well, *mn*, and placed upon the shelf, *b*, which is to be below the water level. The dimensions of *mn* are to be determined by the size of the largest vessels that are to be sunk in it, and the size of *b* by the size and number of gas receivers that are likely to be in use at any one time. Grooves may be provided in the shelf, *b*, running parallel to the side, *ac*. These grooves allow the rubber delivery-tube to pass under the edges of the receivers without compression. In lifting large receivers from the well of a small trough, the water level may be brought below the shelf, *b*. Under such circumstances, more water may be introduced from a pail or by the water-cock, or a jug of water previously placed within convenient reach may be placed in the well and subsequently removed when the filling of the receiver with gas raises the level of the water too high.

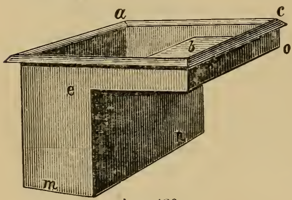


FIG. 130.

Porcelain pneumatic troughs for use with mercury may be bought for a little money of any dealer in chemical wares, but a cheap substitute may be made by cutting, or by burning with a blowpipe flame or with a red-hot iron, a depression in a block of hard wood. The principal dimension of the trough thus made should be horizontal, the bottom being rounded so that it will conform to the outline of a test-tube or of a cylinder placed in it. Its depth should be a little more than the diameter of the test-tube or cylinder used.

In collecting gases over water, two difficulties must be guarded against. First, if from any cause the tension of the gas within the apparatus becomes less than the atmospheric pressure, water from the pneumatic trough may be forced back through the delivery-tube into the generating-flask. Cold water being thus suddenly admitted to a hot flask, the latter is broken and sometimes a more serious explosion takes place. This danger is especially present in thus collecting a gas somewhat soluble in water. In stopping the evolution of a gas, remove the delivery-tube from the trough, and remove the adhering water-drops before removing the lamp. Whenever the delivery of a gas begins to slacken, watch the delivery-tube; if water begins to "suck back" toward the flask, quickly remove the delivery-tube from the water, or, still better, break a rubber connection or loosen the stopper of the generating-flask. When a liquid is used in the flask, this danger of "sucking back" may be avoided by the use of a safety-tube, as shown at *s*, Fig. 29. In case a partial vacuum should be formed in the flask, *b*, atmospheric pressure would force down the liquid in the lower part of the tube, *s*, and thus admit air instead of raising the liquid in *c* to the greater height necessary to allow it to enter *b*.

The second difficulty to be guarded against is the production of too great a pressure within the apparatus by allowing any part of the delivery-tube to dip too far beneath the surface of the water in the trough. Owing to the high density of the liquid used, this difficulty is especially present in the collection of gases over mercury. The pressure thus produced may develop leaks in the apparatus or, in certain cases, force the liquid of a flask out through the funnel- or safety-tube.

14. Gas-holders. — It is often convenient to have a supply of oxygen, hydrogen, and other gases on hand. Gas-holders are convenient for storing such gases for use. One form of easy construction is shown in Fig. 131. It consists of an outer vessel, *a*, open at the top, and an inner vessel, *b*, open at the bottom. Both may well be made of galvanized iron; *a* may be a barrel, cask, or earthen crock. The upper end of *b* is hammered into saucer-shape so that its highest point shall be at the middle. At this highest point is inserted a gas-cock, having its free end smooth and slightly tapering, for the reception of rubber tubing. Three hooks or eyes are attached to the edge of the upper end of *b*, from which extend cords that are knotted together at the lower end of the supporting cord, *c*. The cord, *c*, may pass over pulleys in a frame, as shown in the figure, or over pulleys supported from the ceiling, the frame being omitted. Fill *a* with water. Open the stop-cock, remove the weights from *c*, and allow *b* to sink into *a*. Be sure that there is enough water in *a* to cover the highest point of *b*. Connect the stop-cock, by rubber tubing, with the gas generator, but not until all air has been expelled from the tubing. Open the stop-cock and place weights at the free end of *c*. By making these weights heavier than *b* the pressure in the generating apparatus may be reduced as far as desired. As gas is delivered, *b* will rise. The apparatus is shown on a larger scale at *G*, Fig. 69. When the generation of gas has ceased, or when *b* is full, close the stop-cock, remove the tubing, and leave suspended from *c* only enough weights to counterbalance *b*. For most schools, a 6- or 8-gallon crock (preferably tall and narrow) will be large enough for the outer vessel. The stop-cock may be had of any plumber or gas fitter; any tinsmith can make the vessel, *b*.

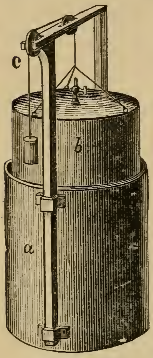


FIG. 131.

When gas is wanted from the holder, connect the gas-cock of *b* with the apparatus to be used, open the cock, remove weights from *c* and, if necessary to produce the desired pressure, place them upon *b*. It is customary to paint the oxygen holder red and the hydrogen holder black for purposes of ready distinction.

A convenient gas-holder may be made from a large glass bottle or a jug by passing two glass tubes through the cork, providing one with a piece of rubber tubing and the other with a stop- or pinch-cock. The bottle being filled with water, the gas-generator is connected with the stop-cock which is then quickly opened. As the gas enters

FIG. 132.

g through *a*, water escapes through the siphon, *c*. The pressure on the generator at starting may be relieved by sucking at *c* to start the action of the siphon. Gas is delivered from *g* through *a*, by connecting *c* with a supply of water elevated on a shelf (siphon delivery, if desired) or with any other supply of water under moderate pressure.

When a gas is to be kept for only a short time, a rubber gas-bag is a convenient substitute for a gas-holder. It is easily portable and has other advantages. One may be bought for two or three dollars.

15. Lamps. — In laboratories, where illuminating-gas is provided, the most convenient form of lamp for heating purposes is the Bunsen burner, which gives a very hot and smokeless flame. A fair substitute for a Bunsen burner may be made by inverting a wide-necked glass funnel over any ordinary gas-burner, supporting it in any convenient way so that air may have free passage between the sides of the burner and the glass as shown in Fig. 133. The funnel is to be put into position before the gas is lighted. The gas supply is to be controlled so as to produce a smokeless flame.

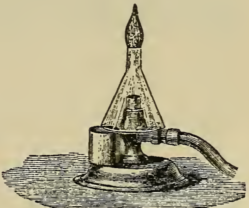


Fig. 133.

When a very small flame is used with the Bunsen burner, the flame may drop down into the tube. This may be prevented by laying a small piece of wire-gauze over the top of the tube and pressing its edges down against the sides of the tube before lighting the gas.

If the laboratory is not supplied with gas, an alcohol-lamp may be used. The Berzelius or Argand lamp burns alcohol, and is convenient for many purposes where much heat is necessary, e.g., the preparation of oxygen in considerable quantity. Lamps made especially for burning gasoline vapor, and provided with a variety of burners, may be bought. The vertical pipe that supports the gasoline supply may be utilized for retort-stand purposes. Gasoline is cheaper than alcohol. Special heating apparatus is made in great variety.

16. Blowpipes. — Bunsen blast-lamps, hot-blast blowpipes, etc., are provided in great variety for use with a blower (Fig. 134). Mouth blowpipes, one form of which is shown in Fig. 135, may be bought in a great variety of forms. In using the mouth blowpipe, air should be forced through it by the action of the cheeks rather than by the action of the lungs. A little practice will enable teacher or pupil to maintain a continuous current of air from the nozzle of the blowpipe, breathing naturally in the meantime. When this air current is directed against a lamp- or a gas-flame, the appearance of the flame varies according to the strength of the blast and the position of the jet relative to the flame. When the tip of the blowpipe is held in the flame and a strong blast is forced through it, we have a well-defined cone of blue flame beyond or outside of which is an outer and more luminous cone. This is the oxidizing flame. Oxidation takes place most rapidly at the point of the outer cone or just beyond it.

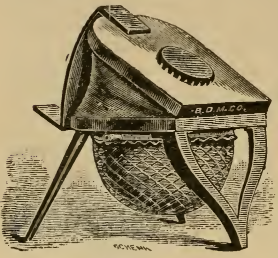


FIG. 134.

But if the tip of the blowpipe is held just outside the flame and the blast is gentle, the flame is less changed in its general character, the greater part of it consisting of intensely heated carbonaceous vapors ready to take up oxygen. This is the reducing flame. The substance to be reduced is held in the large, luminous cone and thus out of contact with the air. Charcoal makes a good support for the substance to be reduced.

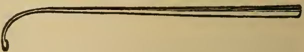


FIG. 135.

17. Soldering. — It is often very convenient to be able to solder together two pieces of metal. A bit of soft solder, the size of a hazelnut, may be had gratis of any good-natured tinsmith or plumber. Cut this into bits the size of a grain of wheat. Dissolve a teaspoonful of zinc chloride in water and bottle it. It may be labeled "soldering fluid." Having bought or made an alcohol-lamp, you are ready for work. For example, suppose you are to solder a bit of wire to a piece of tinned ware. If the wire is rusty, scrape or file it clean at the place of joining. By pincers or in any convenient way hold the wire and tin together. Put a few drops of "soldering fluid" on the joint, hold the tin in the flame so that the wire shall be on the upper side, place a bit of solder on the joint and hold in position until the solder melts. Remove the joint from the flame, holding the tin and wire together until the solder has cooled. The work is done. The mouth or blast blowpipe, previously mentioned, will be a convenient substitute in many cases for the alcohol-lamp. If you have a "soldering iron" — strange misnomer, for it is made of copper — you can do a wider range of work, as many pieces of work can not be held in the lamp-flame.

18. Deflagration-spoon. — A deflagration-spoon for burning phosphorus, sulphur, etc., in oxygen may be bought for a few cents of any apparatus dealer. One may be made by soldering the bowl of any ordinary metal spoon or any other metal cup to a long wire handle and bending the wire upward at a right angle near the cup. A cup may be hollowed in the side of a piece of chalk or lime and then fastened to a wire handle. If a metal cup is used for combustions in oxygen, it is well to line it with some infusible material like clay, powdered chalk, lime, or plaster of Paris. A coated cork capsule, smaller than the one mentioned in Experiment 53, may be provided with a wire handle and used as a deflagration-spoon. In any case, the upper part of the wire handle should be straight so that it may be thrust through the cover of the jar.

19. Evaporating Dishes, Crucibles, and Furnaces. — Evaporating dishes are generally made of porcelain and provided with a projecting lip and glazed on both sides, or only on the inside. The latter are the cheaper, but the former are the more desirable. Sizes from 8 to 15 cm. in diameter are best adapted to the needs of most classes. They should be supported upon wire gauze, the sand- or the water-bath, and never exposed to the naked flame. For granulating zinc or fusing salt, Hessian and clay crucibles and capsules are cheap, and largely used. They will endure a very high temperature, but should be heated somewhat gradually. They may be heated in a coal or coke fire in any ordinary stove. Heated crucibles may be handled conveniently with crucible tongs, two common forms of which are shown in Fig. 137.

Fig. 136.

Fig. 137.

20. Metal Retorts. — Many gases may be prepared by carefully heating the materials in a Florence flask or a glass retort, but an iron or a copper retort is very desirable. Such retorts may be had in a variety of forms, made of iron, sheet-iron, or copper, of dealers in chemical or physical apparatus, at prices ranging from one dollar upward. The author has made a very cheap and wholly efficient retort as follows: Cut a thread on each end of a piece of inch gas-pipe, *a*, 6 or 8 inches long. Screw an iron cap, *K*, over one end. For the other end, provide an iron "reducer," *t*, carrying a piece of $\frac{3}{8}$-inch gas-pipe, *e*, about 15 or 18 inches long. The materials being placed in the capped tube, the reducer with its pipe is screwed on the open end of the tube. The closed retort may then be thrust into the coals of any ordinary stove. A piece of glass tubing may be sealed with plaster of Paris into the end of the small iron tube. This affords a good means for connecting the retort with rubber tubing, and protects the latter from burning. If desirable, the inner surface of *K* may be smeared with wet plaster of Paris before screwing it upon *a*. If, at the end of the experiment, *t* is not easily removed from *a*, a few blows will generally start it. The parts of this retort may be had of any gas- or steam-fitter.

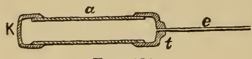


FIG. 138.

21. Ventilating Chamber, etc. — A chamber, 50 cm. by 75 cm., or larger, with glass sides and provided with a ventilating flue *that has a good draught* is important for experiments with chlorine, hydrogen sulphide, etc. The ventilating flue may, in some cases, be advantageously connected with the chimney. The chamber may be built against the chimney and provided with two or three narrow slits through the brickwork from top to bottom of the closet. At least one side of the chamber should be made so that it may be opened, but when shut it should fit closely. Openings that may be closed should be made in the bottom of the chamber for the admission of air so that a current may be obtained. A lamp burning in the chamber will aid in keeping up the current and carrying off the offensive gases.

22. Test Papers, etc. — Litmus-paper, both blue and red, should be kept on hand for the detection of acids and alkalis. Litmus is a blue coloring matter prepared from certain lichens and found in commerce in small cubical masses somewhat soluble in water. White, unsized paper is stained with an infusion of 30 grams of litmus in 250 cu. cm. of boiling water. Such a paper is reddened by an acid. The blue litmus-paper may be faintly reddened by immersion in vinegar or any other dilute acid. This reddened paper is colored blue by the action of an alkali.

A purple liquid may be prepared by steeping red-cabbage leaves in water, and filtering. Such a cabbage solution will be colored red by an acid or green by an alkali.

A ruby-red tincture of cochineal may be prepared by digesting 3 grams of cochineal in a mixture of 50 cu. cm. of alcohol and 200 cu. cm. of water at the ordinary temperature for several days. Acids will change the color of such a tincture to orange; alkalis will change it to violet carmine.

Turmeric-paper, prepared by staining unsized paper with a tincture (alcoholic solution) of turmeric root (curcuma), is sometimes used as a test for alkalis which turn it from yellow to brown.

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