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Title Romance of Chemistry

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THE ROMANCE OF CHEMISTRY

THE ROMANCE OF CHEMISTRY

CHAPTER I

ALCHEMY AND THE RISE AND DEVELOPMENT OF CHEMISTRY

Alchemy may be compared to the man who told his sons that he had left them gold buried somewhere in his vineyard; where they by digging found no gold, but by turning up the mold about the roots of the vines, procured a plentiful vintage.—BACON.

. . . 'Tis delightful to transfuse yourself
Into the spirit of the ages past;
To see how wise men thought in oldentime.
—ERNST MACH.

1 THE ORIGIN AND MEANING OF ALCHEMY AND CHEMISTRY

WHEN we attempt to find the meaning of the word "chemistry," we are carried back to the most ancient peoples—to the very beginning of civilization. Scholars are not in agreement as to its meaning. Some hold that the word refers to the land of Chêmi (Egypt), which was the cradle of chemistry, while others believe it to have been derived from a Greek word meaning a mingling or an infusion, for chemistry was at first the art of extracting the juices from plants for medicinal purposes. It is said therefore, that chemistry originated

in the temples where priests experimented in making medicines.

Egypt was overrun by the Arabians about the middle of the seventh century. The invaders learned something about chemistry from the Egyptians, and they prefixed the Arabic article *al* to the word *chemia;* hence the word "alchemy." The aim of this imaginary art was to transmute the baser metals into silver and gold, and to find the panacea, or universal remedy for disease. Alchemy led the way to modern chemistry.

The Egyptians, the Phœnicians, the Jews, and other ancient peoples possessed some knowledge of chemical processes, which were developed, no doubt, largely by accident and were applied for their practical results alone. Indeed, a practical knowledge of certain chemical operations must have antedated the dawn of history. Ancient records and the result of excavations show that the Egyptians were acquainted with the working of gold, silver, copper, and iron; that they understood the art of manufacturing vessels of glass, and pottery from clay; knew how to produce enamels, alloys, and artificial gems; greatly developed the arts of dyeing and of embalming their dead, and prepared many medicines, paints, and other products. Inscriptions representing glass-makers plying their art have been unearthed in Egyptian monuments of the eleventh dynasty, showing that considerable skill in glass-making was developed at least two thousand years before the Christian era. Glass beads have been found in mummy cases at least three thousand years old, and glass articles have been discovered in the excavations of Nineveh.

The ancients used indigo, in dyeing, hundreds of years before our era; and they were also familiar with vinegar, salt, wine, and other products. Certain chemical substances are mentioned in the Bible. For instance, we read in Job: "Can that which is unsavoury be eaten without salt? or is there any taste in the white of an egg?" Noah's experience with wine makes it clear that the art of producing alcoholic beverages was known before Genesis was written. We also know that Noah coated his boat with pitch.

There is evidence that the Egyptians employed paints for the decoration of their tombs as early as 2500 B.C. The Assyrians, the Greeks, and the Romans also practised the decorative art. The color pigments discovered at Pompeii and Herculaneum are of much interest; for they were liberally applied in the decoration of buildings and other structures. The colors used were largely earth colors, such as yellow ochers, the red oxide of iron, lapis lazuli, naturally occurring vermilion, and copper-bearing minerals. Pompeian red, for example, is famous. Chemicals have been employed as cosmetics for thousands of years; the women in the East have long used antimony trisulphide for painting the eyebrows, Jezebel having so decorated herself. (See 2 Kings IX. 30, and Ezekiel XXIII. 40.)

While the ancient world possessed certain facts in the field of chemistry, experimental investigation was almost unknown. At that time the leading scholars were fond of speculation, and thought it beneath their dignity to experiment with gross matter. There was a vast amount of speculation on the part of philosophers as to the nature of things, but the hypotheses

advanced to explain occurrences or phenomena were often fanciful and extravagant. Beyond or above the material world there were certain philosophical principles such as the divine spirit or essence which pervaded all matter.

In the narrow sense of the term, alchemy is the pretended art of transmuting the base metals into the noble metals—silver and gold. From early records it appears that the idea of transmutation arose in the Greek colony of Alexandria, Egypt, the "Queen City of the Mediterranean," the "modern Athens," where Christianity became a world-religion and where astronomy and mathematics were greatly developed. In this ancient city, where alchemy had its beginning, the Greek philosophy—the teachings of Plato and of Aristotle—was predominant. The so-called doctrine of Empedocles (about 450 B.C.) and Aristotle of the four elements—earth, water, air, and fire—signified that matter had certain characteristics and fundamental properties. Thus, "earth" implied the properties of cold and dryness; "water," cold and moisture; "air," heat and moisture; and "fire," heat and dryness. Presumably all matter was of one kind, and the wide variety of matter was thought to be due to the greater or less abundance of these four elements or principles.

The ancients believed that there was a fundamental form of matter which entered into the composition of all forms of matter; this they termed *hyle* (Greek: matter). "Matter is one," was a basic proposition of Plato's. The early philosophers also held that all nature is striving toward improvement. From such ideas one would conclude that all metals are alike in

substance; that there is no essential difference between copper and gold. It was believed that material things were capable of infinite change; and it was known that metals, on exposure to the agencies of heat, air, and moisture, underwent certain changes, such as rusting. These changes naturally suggested the idea of transmutation. Metals were supposed to possess different degrees of purity, and it was believed that, by subjecting them to fire and other agencies, it was possible to pass step by step from the base metals to the noble metals—silver and gold—the only perfect ones. The alchemists obtained lead from galena, or lead sulphide, and silver from the lead; but they did not realize that silver is often associated with lead. It is not so strange that they thought they should be able to make gold.

According to Gibbon, the persecution by Diocletian is the first authentic event in the history of alchemy. About A.D. 290 he caused an inquiry to be made "for all the ancient books which treated of the admirable art of making gold and silver, and without pity committed them to the flames, apprehensive, as we are assured, lest the opulence of the Egytians should inspire them with confidence against the empire." In commenting upon this act of Diocletian, Gibbon says:

> But if Diocletian had been convinced of the reality of that valuable art, far from extinguishing the memory, he would have converted the operation of it to the benefit of the public revenue. It is much more likely that his good sense discovered to him the folly of such magnificent pretensions, and that he was desirous of preserving the reason and fortunes of his subjects from the mischievous pursuit.

It may be remarked that these ancient books, so liberally ascribed to Pythagoras, to Solomon, or to Hermes, were the pious frauds of more recent adepts. The Greeks were inattentive either to the use or to the abuse of chemistry.

In the Leyden museum there are several papyri which were discovered in Thebes, and were perhaps written in the third century of our era. One of these gives a number of recipes, written in Greek, for the treatment of base metals to form products resembling gold, which were to be used in the manufacture of imitation jewelry. The oldest works of a strictly chemical character date, therefore, from the third century.

It appears that there were two types of alchemists —the knavish, or alchemistic charlatans, and the alchemists proper. The latter were honest men, and sincerely believed that it was possible to make gold. No doubt many of these early workers were men animated by lofty ideals. They were overworked individuals who were sooty and black like smiths and colliers.

As so well expressed by Gibbon:

> The conquest of Egypt by the Arabs diffused that vain science over the globe. Congenial to the avarice of the human heart, it was studied in China and in Europe, with equal eagerness, and with equal success. The darkness of the Middle Ages insured a favorable reception to every tale of wonder, and the revival of learning gave new vigor to hope, and suggested more specious arts of deception.

We are told that "the germs of chemical knowledge which had lain hidden in the brains of a few philosophers, attained to a marvelous growth among the Arabians." Geber, as he became known to the Western

nations, was the most celebrated alchemist among them.

The Arabians carried alchemy into Spain, from which country it spread over western Europe. In the fourteenth century the study of alchemy extended throughout the civilized world. While transmutation was the leading idea of alchemists for a thousand years, alchemy was more than a vain thirst for silver and gold; in its broader meaning it stands for the chemistry of the Middle Ages. According to Liebig, alchemy was "never at any time anything different from chemistry." Alchemy as practised during the Middle Ages was the logical outgrowth of the philosophical thinking of the ancient Greeks.

It should be added that the ancients thought the transmutation of the metals could be brought about with the philosopher's stone, which was mentioned in their writings as a red powder with a peculiar odor. It was called the grand elixir, or the magisterium (masterpiece); and it was believed by such eminent men as Roger Bacon, who lived in the thirteenth century, to possess the power of prolonging life and of healing disease. Bacon was a man of remarkable ability and intellectual curiosity. He may be regarded as the originator of experimental research, for he carefully planned experiments to test various theories. According to Bacon, "gold is the most perfect of metals because in it Nature has finished her work."

The alchemists graded metals according to color; the base metals possessed little color and were readily tarnished. They placed the yellow color of gold above the pale white of silver; indeed, gold was

supposed to reflect the yellow or red firelight of the sun, the color of which never changed, while silver reflected the soft white light of the moon; but as the light of silver was paler, the metal was capable of taking on a bronze color.

Even before the Christian era, an industry which may be termed imitation had arisen throughout the Mediterranean countries. Thus, imitation pearls were produced from secretions found in bamboo; and an excellent imitation of royal or Tyrian purple (which was obtained from a snail-like shell-fish of the Mediterranean, and was very expensive) was secured from plants. Certain alloys which resembled silver and gold were also produced. The alchemists "made the discovery that certain colors, some very beautiful, were produced upon the surface of the alloys thus prepared and that these colors could be varied by the use of different fluxes, just as the colors of fabrics depended on the mordants used." According to Professor Hopkins of Amherst College, the medieval alchemist was primarily interested in color-effect and decoration. He holds that real alchemy did not last more than a few centuries after the persecution by Diocletian, and terms the writers and adepts in alchemy, about the thirteenth century, *pseudo-alchemists.*

2 The Medical Chemists

In the sixteenth century, chemistry strove to free itself from the domination of the alchemistic idea, and the era of medical chemistry, or the iatrochemical period, began. Chemistry was regarded as the hand-

maid of medicine, and many valuable medicines were discovered. The great precursor of the medical chemists was the renowned Paracelsus, who was born in Switzerland in 1493, and was the son of a physician. He gave a new direction to alchemy by declaring that "the object of chemistry is not to make gold but to prepare medicines"; and this union of chemistry with medicine was a dominant characteristic of the iatrochemical school.

Paracelsus declared that the human body consisted of sulphur, mercury, and common salt, and that the health of the body depended upon the presence of the proper amount of these substances; when any of these ingredients changed, illness resulted, and it could be cured only by the administration of chemical medicines. He was familiar with the works of magicians and alchemists, and traveled long distances on foot, collecting a variety of information regarding the art of healing, from wise men and women, barbers, blacksmiths, and others. He also spent much time in the mines of the Tyrol. After many strange experiences and vicissitudes this remarkable man again resumed his wanderings, and was finally thrown from a window and killed, by the servants of a physician in Salzburg, in 1541.

Paracelsus contributed to medicine many valuable preparations, such as tincture of opium, or laudanum—the name by which it is still known. He was a close observer, and his practice of medicine was based upon careful observation now universally recognized. He used to say all the accumulations of the medical lore before him were not worth the sole of his boot. His

motto was: "Let him not belong to another who may be his own"; and among the remarkable sayings attributed to him is the following: "The air is not so full of flies in summer as it is at all times of invisible devils." Other renowned men of the iatrochemical period were Georg Agricola, Van Helmont, and Glauber. Agricola was born in Germany in 1490, and became a noted physician. He was therefore a contemporary of Paracelsus, but, unlike the latter, he was not much interested in the storms which raged in the field of medicine at that time. Agricola did pioneer work in metallurgy, or the art of extracting metals from their ores. He was led to devote himself to mineralogy and metallurgy by the flourishing mining and smelting industry of Saxony. His great work on winning metals from their ores, "De Re Metallica," served as a useful textbook until comparatively recent times.

The era of medical chemistry continued up to the end of the seventeenth century, when certain views entertained by Paracelsus and others were overthrown by Robert Boyle, a far-seeing philosopher, who was the first real chemist in the scientific sense of the term.

3 Ancient Theory of Combustion

About this time Becher and Stahl of Germany advanced the phlogiston theory of combustion. The nature of fire or combustion was a riddle until after the discovery of oxygen by Joseph Priestley in 1774.

Plato assumed that all combustible bodies or substances contained a common element—inflammable principle—which enabled them to burn. This explana-

tion of combustion was quite generally accepted until the eighteenth century. Some scholars thought that the inflammable principle was sulphur; hence the saying, "Where there are fire and heat, there is sulphur."

Johann Becher, in 1669, pointed out that there are many combustible materials which do not contain sulphur; and he postulated a principle termed by him *terra pinguis,* fatty, or inflammable earth. Subsequently Georg Ernst Stahl, who was a professor at Halle and a good chemist and successful teacher, developed Becher's hypothesis and gave the name phlogiston (Greek: set on fire) to his *terra pinguis.* It is well known to all chemists that Stahl and his followers held that when bodies burned or when metals were calcined a sort of fire-stuff (phlogiston) escaped. Nobody seemed to have a very definite notion as to the real nature of phlogiston. Some thought that sulphur and soot were nearly pure phlogiston; others, that phlogiston was immaterial, or light, or hydrogen. The principle was supposed to be united with combustible bodies and to be separated from incombustible bodies.

The phlogistic theory became thoroughly entrenched in the eighteenth century, being advocated by all the leading chemists.

4 The Development and Uses of Chemistry

The discovery and investigation of gases, such as oxygen, nitrogen, hydrogen, and carbon dioxide, played a great part in shaping chemistry. Many gases were

discovered by Joseph Priestley and by K. W. Scheele, and their properties excited the chemical world. Improved methods for collecting, handling, and studying gases were devised, Priestley being the first to describe their collection over mercury. After the discovery of oxygen, a new era dawned in the history of chemistry; for the brilliant and versatile Frenchman Lavoisier proved that combustion is the rapid chemical union of a substance with oxygen, the change being accompanied by the evolution of heat and light. Joseph Black showed the precise difference between carbon dioxide and air, and Henry Cavendish established the elementary nature of hydrogen and proved that it burns in air or oxygen to form water.

The chemical balance became an important instrument in the hands of the chemist in the latter part of the eighteenth century, and Lavoisier demonstrated the supreme importance of the proportions by weight in chemical change.

About the beginning of the nineteenth century, John Dalton propounded his atomic hypothesis, which assumed that chemical elements consisted of ultimate particles not further divisible—of atoms. The atomic hypothesis has had a supreme influence in the development of chemistry.

Since the introduction of the experimental method in the study of the science, progress has been steady and rapid. The advance which has been made in the domain of chemistry since the discovery of oxygen has been truly remarkable. It is almost startling to know that chemists have already prepared over 230,-

000 carbon compounds, such as the alcohols, ethers, chloroform, and sugars. The field is an inviting one, and many marvelous discoveries will be made in the years to come, and many of these discoveries will not only bring renown and joy to the discoverer, but confer a blessing upon mankind. Scheele, the great Swedish chemist, characterized his own efforts in the following words: "It is the truth alone we desire to know, and what joy there is in discovering it."

The utility of chemistry is vast. According to Pasteur, the propounder of the germ theory of disease, one of the most important theories ever enunciated: "In our century science is the soul of the prosperity of nations and the living source of all progress. What really leads us forward are a few scientific discoveries and their application."

Chemistry has a direct and very important bearing upon the material interests of life. It is the science which deals primarily with all material things and the changes which they undergo. It treats of the rocks, the soil, fertilizers, metals, foods, gasoline, and innumerable other things. The importance of chemistry is well expressed by Professor L. W. McCay of Princeton University, in the following words:

There is scarcely an article in common use which does not owe its existence, directly or indirectly, to the application of some chemical principle. Close your eyes, enter any room and touch at random any object, and ninety-nine times out of one hundred the object will be related somehow to one or more of the chemical industries. The pen with which I write, my ink, my ink bottle, my paper, the green

baize on which my arm is resting, the varnish on my desk, the bronze figures supporting my books, my lamp, my ash tray, the box of matches—indeed, almost all the articles on which my eye falls bear witness to the activities of the chemist.

Chemistry has provided us with glass for our windows, medicines to heal our diseases, chemicals to destroy disease-producing germs, kerosene for our lamps, and gasoline for our automobiles, gas to heat and light our houses, and fertilizers for feeding the plants. Chemistry shows us how gas, ammonia, tar, and coke are produced from coal, as well as the lovely colors called aniline dyes from black coal-tar. It also shows that rubber is obtained from a milky liquid furnished by trees, and how it is transformed into material for coats and shoes. Again, it shows how paper and artificial silk are produced from cotton or wood, and how soap is made from fats and lye. Chemistry has provided modern explosives and made possible painless surgery by supplying nitrous oxide (laughing-gas), ether, chloroform, ethylene, and novocain. The science has enabled us to find remedies for such diseases as goiter and leprosy, and to lessen the terrors of diphtheria and of scarlet fever. It has also provided us with better foods, with fireproof buildings and clothing.

Chemistry not only is of cultural value but is necessary for those who intend to enter certain of the professions. It is required in the study of medicine, pharmacy, and biology. It is of fundamental importance in mineralogy, geology, and chemical engineering, and finds wide application in agriculture and in forestry. The possibilities of chemistry are boundless. These

applications of the science are sufficient to show us that chemistry is most intimately connected with everyday life, that our bodily comfort and, to a certain extent, our happiness are dependent upon it. The science is of the greatest utility in both peace and war.

CHAPTER II

THINGS SEEN AND UNSEEN: THE TANGIBLE AND THE INTANGIBLE

> Force, Force, everywhere Force; we ourselves a mysterious Force in the centre of that. There is not a leaf rotting on the highway but has Force in it: how else could it rot?—CARLYLE.

1 MATTER AND ITS BEHAVIOR

THE natural philosopher tells us that the universe consists of matter and energy. By the term matter we mean anything which possesses weight or mass and occupies space. Matter may be perceived ordinarily by the sense of touch and is recognized by its properties or qualities. Energy, the capability of doing work, is always associated with matter, so the latter is often called the vehicle of energy. There are immense quantities of potential energy in our coal-deposits, invisible and in the quiescent state. When the coal is burned the potential energy is transformed largely into heat, a form of kinetic energy by means of which most of the work of the world is carried on.

Now, the chemist is concerned primarily with matter and its transformations, while the physicist is more concerned with energy and the transformation of one kind of energy into other kinds. Since energy is always associated with matter and energy changes accompany

chemical changes or transformations, the chemist also is concerned with energy.

Chemistry deals with all kinds of matter; it treats of the composition of the earth's crust; of the transformations which are carried out in test-tube, retort, crucible, and furnace; of the preparation and digestion of foods; of change and decay, and of many other things.

Matter exists in three states—the solid, the liquid, and the gaseous states. We have the best of reasons for believing that it is composed of exceedingly small invisible particles which are termed atoms and molecules. The states of matter depend upon temperature and pressure. Thus, water exists as ice, liquid, and vapor (gas). Ice and liquid water are visible; but water vapor, or steam, is invisible, as may be seen by observing water boiling in a tea-kettle; near the spout nothing is visible, but farther away there is a cloud which consists of droplets of liquid formed by the condensation of water vapor. Invisible water vapor is a normal component of the air we breathe, which is never "dry."

It is believed by scientists that the small particles of matter are perpetually in motion; hence the kinetic theory (Greek: move). In the case of gases the tiny particles or molecules are quite separate and distinct and have great freedom of movement. The particles of a gas appear to be perfectly elastic, and as a consequence their motion is not slowed up when they collide with one another or when they bombard the sides of the inclosing vessel. The pressure of a gas upon the vessel is due to the hail-storm of molecules upon its walls. A definite portion of a gas left in an open vessel is capable of indefinite expansion. A gas is sometimes

likened to a swarm of gnats. Gases are therefore very compressible. To illustrate: When a quart of water is evaporated it yields about seventeen hundred quarts of steam, measured under normal atmospheric pressure and at the boiling-point of water. This shows us why a strong vessel is required to confine steam at high pressure.

A liquid is more compact than a gas; that is, its particles are closer to one another, and therefore have less freedom of movement. Possibly the particles glide over one another in curved courses. Matter in the liquid state assumes the shape of the containing vessel. When a liquid evaporates, some of the particles pass off in the gaseous state. Since the speed of a particle depends upon its temperature, the warmer particles of a liquid are lost first, which results in a fall in temperature when a liquid evaporates. It is well known that water is cooled in certain countries by placing it in porous vessels in order to promote evaporation.

In 1827, Robert Brown, a botanist, first observed that when a little lycopodium, or the spores of the club-moss, is suspended in water and examined under the microscope, the small particles move about in zigzag paths, vibrating with a slow, trembling motion. This phenomenon is most interesting, and may be observed by suspending other insoluble substances in water, provided that the particles are exceedingly small. The phenomenon is known as the Brownian movement, and is believed to be due to bombardment of the suspended particles by the molecules of water, which appear to be in perpetual motion.

A solid body retains or tends to retain any form imposed upon it by nature or by art. Solids, like liquids, are much more compact than gases. The particles of solids are much restricted in their movements, and appear to vibrate or rotate about centers of rest. All true solids tend to assume crystalline forms, and ordinarily show definite cleavage, which is very marked in the case of mica. Many solids give off particles of vapor just as do volatile liquids. For instance, camphor, iodine, ice, and snow evaporate spontaneously. Snow and ice in the Arctic regions are slowly transformed into water vapor even during the coldest weather.

The different kinds of matter have qualities known as properties, and these are employed in the recognition of matter, since they make either direct or indirect impressions upon our organs of sense. Gold, for example, is a yellow metal possessing a characteristic luster, great malleability and ductility, a melting-point of 1063° C.,* and a specific gravity of 19.3 (*i.e.*, it is 19.3 times as heavy as an equal volume of water). It is termed one of the noble metals. Iron, copper, salt, and sugar have properties very different from those of gold.

2 Changes in Matter

It is a familiar fact that things are ever changing; hence the poet has written, "Change and decay in all around I see." In certain cases the changes are so

*C. is the abbreviation for the centigrade thermometer scale. On this scale the melting-point of ice is 0° and the boiling-point of water 100°.

slow as to be quite imperceptible day by day, as in the corrosion of metals. This change alone, however, costs us hundreds of millions of dollars annually. Other changes, such as the combustion of fuel, are rapid and are often accompanied by the evolution of heat and light.

There are many changes which are more or less temporary and do not involve the transformation of the body or material into a new one having essentially different properties. Changes of this kind are called physical changes. Familiar illustrations are the magnetization and heating of iron, the crushing of stone, and the formation of dew and frost. We have just seen that water may exist as ice, liquid, and vapor. The inhabitant of the Arctic regions is more familiar with ice and snow, while to the inhabitant of the tropical regions this state of water is virtually unknown. Water vapor, which is always present in the atmosphere, frequently condenses to form clouds, rain, fog, and dew. The three familiar forms of water may be transformed into one another without gain or loss in weight and, from the point of view of the chemist, without any essential change in their nature.

Many changes which occur involve the transformation of various forms of matter into other forms or substances possessing radically different properties. We are all familiar with the souring of milk, the combustion of fuel, the decay of animal and vegetable matter, the transformation of cider into vinegar, the breaking down of explosives, and the corrosion or rusting of metals. Transformations of this sort are called chemical changes, for the chemical compositions of the vari-

ous materials are altered. Iron, for example, is changed into iron rust, or oxide of iron; and when fuel burns, water and carbon dioxide are common products. The corrosion of metals, the production of animal heat, and change and decay in general are largely dependent upon the oxygen of the air. Large quantities of paints and varnishes are applied to metals and wood to protect them from slow but sure destruction by the agency of the atmosphere. When a big gun is fired, a chemical change on a large scale occurs, enormous quantities of nitrogen and other gases being liberated; hence Slosson says: "In the eyes of the chemist the Great War was essentially a series of explosive reactions resulting in the liberation of nitrogen."

There are several varieties of chemical change. Thus, when iron rusts to form an oxide, the change is known as combination or synthesis, and may be represented in a condensed form as follows:

$$\text{Iron} + \text{Oxygen} = \text{Iron oxide (Rust)}$$

Stated in words, this simple chemical equation reads: iron unites with oxygen to form iron oxide.

When the electric current is passed through water to which a little sulphuric acid has been added to make it a conductor, the invisible gases hydrogen and oxygen are formed. The decomposition of water into its constituent elements by means of the electric current is known as electrolysis, and can be readily demonstrated by means of the simple apparatus shown in Figure 1.

The tubes are filled with water and then inverted in a vessel about half full of water to which a small amount of sulphuric acid has been added. Platinum

electrodes attached to wires are introduced into the mouths of the tubes, and the wires are then connected with a source of current. Bubbles of gas arise in the tubes—hydrogen at the cathode (negative pole) and oxygen at the anode (positive pole). The volume of the former gas is double that of the latter.

Decomposition is the converse of combination.

A third variety of chemical change may be termed

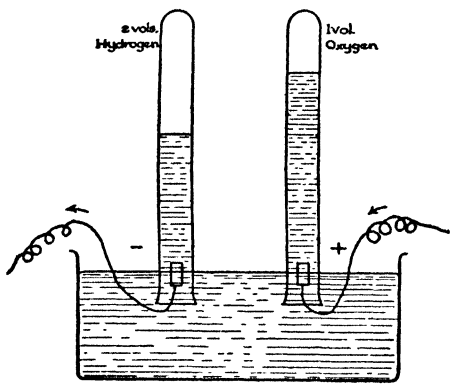


FIGURE 1
The Electrolysis of Water

displacement. This variety of change may be readily illustrated by dipping a bright steel knife-blade into a water solution of copper sulphate. The blade is soon coated with the red metal, copper, some of the iron going into solution to displace the copper:

Iron + Copper sulphate = Copper + Iron sulphate

When a piece of copper is immersed in a solution of a mercury salt for a short while, a coating of mercury (quicksilver) appears on the copper. When the coat is rubbed with a piece of cloth, it has the appearance of

silver. Displacement may also be very strikingly illustrated by suspending in a water solution of silver nitrate a small bag containing mercury. The mercury displaces the silver to form exquisite crystals of the latter.

The alchemists carried out similar experiments, and were erroneously led to believe that the cheaper metals could be transmuted into the more precious metals; but it is now clear that these apparent transmutations were cases of displacement, the more active metals taking the place of the less active ones, which are the metals that do not corrode appreciably when exposed to the air.

Any chemical change in matter which involves the transformation of the matter into a new substance or substances is called a chemical reaction. It is of interest to note that a chemical change is always accompanied by the production or consumption of some form of energy, such as heat, light, or electricity.

A most interesting and fundamental fact in connection with the study of matter is that the chemist is unable either to create or to destroy it. We have, therefore, a law known as the law of the indestructibility of matter, or the law of the conservation of mass, which runs as follows:

In every chemical change the weight of the materials taking part in the change is exactly equal to the weight of the substances produced by the change.

3 Can Matter and Energy Be Destroyed?

During the latter part of the eighteenth century the brilliant Lavoisier, a French chemist, laid great stress

upon the use of the chemical balance in chemical work. He heated tin and air in a closed vessel and observed that there was no change in the weight of the system notwithstanding the fact that the metal combined with oxygen to form the white powder tin oxide. This experiment is a good illustration of the above law.

When a paraffin candle is allowed to burn in air and the products of combustion—water and carbon dioxide—are absorbed in a mixture of lime and caustic soda, there is an apparent gain in weight; but it has been demonstrated that this is due to the component oxygen, which is drawn in from the surrounding air. The oxygen which combines with the hydrogen and carbon of the candle was not weighed in the first weighing. When this factor is taken into account, it is found that *the sum of the weights of the factors equals the sum of the weights of the products.*

In one of his famous lectures to workingmen John Tyndall said:

> The entire play of the scientific intellect is confined to the combination and resolution of the ideas of Matter and Force. Newton, it is said, saw an apple fall. To the common mind this presented no difficulty and excited no question. Not so with Newton. He observed the fact; but one side of his great intellectual nature was left unsatisfied by the mere act of observation. He sought after the principle which ruled the fact. . . . To the conception of the matter of the apple, Newton added that of the force that moved it. The falling of the apple was due to an attraction exerted mutually between it and the earth. He applied the idea of this force to suns, and planets, and moons, and showed that all their motions were necessary consequences of this attraction.

Now, the layman often uses the terms force and energy interchangeably; so in a popular sense "physical force," or "brute force," means energy. The scientist, however, makes a slight distinction between the two terms. Force is usually defined as that which changes or tends to change the motion of a body by altering either its direction or its magnitude, as the force of gravity. Energy, on the other hand, may be defined as work and all else that can arise from work and be converted into work; and the work performed is equal to the energy expended.

4 Forms of Energy

Energy, the capacity for doing work, may be divided into potential energy, or stored-up energy, and kinetic energy, or energy of motion. Our coal- and oil-deposits represent, at present, our greatest stores of energy, or potential work. There is a vast amount of potential energy in high explosives, ready for transformation into the kinetic form. Furthermore, a stone raised above the surface of the earth possesses potential energy, for in falling it can do work; and it is well known that a brick in motion can do some things which a brick at rest cannot do.

Kinetic energy is therefore the energy a body possesses by virtue of its motion. It is well represented by a moving projectile, water in motion, the wind, and the combustion of fuel.

It is of fundamental importance to know that there are many forms of energy, such as heat, light, electricity, and mechanical energy, and that they are mutu-

ally convertible. To illustrate, the potential energy of coal, which is the stored-up energy of very long geologic ages, is transformed into heat by burning the fuel in the furnace of a steam-boiler. Heat generates steam, which possesses great kinetic energy, due to the motion of the water molecules. As the steam accumulates in the boiler the pressure increases, and the kinetic energy of the moving machinery may be transformed into electricity, light, motion, and finally into heat again.

The sun is the great source of energy, which is radiated, appearing as heat, visible light, and ultraviolet light. In a sense we are all "souls of fire and children of the sun." Lucretius wrote:

> Perhaps too the sun as he shines aloft with rosy lamp has round about him much fire with heats that are not visible, and thus the fire may be masked by no radiance, so that fraught with heat it increases to such a degree the stroke of the ray.

When solar energy reaches the earth in the form of heat, water is lifted by evaporation, some of it appearing in the form of clouds, followed by precipitation as rain, a portion of which finds its way into the rivers. When the water appears at the brink of a mighty precipice such as Niagara, it possesses a vast amount of potential energy; in falling, the potential energy is transformed into kinetic energy, which may set a wheel in motion, producing mechanical energy, which is capable of operating a dynamo, thus generating electricity, which may in turn be transformed into light, heat, mechanical energy, and work.

During the transformation of energy, there is neither

gain nor loss. This transformation is sometimes likened to Proteus, a sea-god in the service of Neptune, who could assume different forms at will, such as that of a fish, a man, or a sea-monster, but remained always Proteus. Energy may be called the modern Proteus. No body or system of bodies can acquire energy save at the expense of the energy possessed by another system. Man has never been able to create energy, neither has he been able to destroy it. It is utterly impossible to get something for nothing, which should make it clear that perpetual motion is an impossibility. The science of physics is built upon a law called the law of the conservation of energy, which may be stated thus:

Energy may be changed from one form to another, but it can be neither created nor destroyed.

Throughout its various transformations, it may be observed that potential energy cannot be apprehended until converted into kinetic energy; or, "so long as energy changes in neither amount nor position, in space, it belongs to the unseen and eternal."

It is interesting to note that very little was known about energy a century ago. The great modern development of civilization is due very largely to the utilization of energy. Our age may be truly called the Age of Energy, or the Age of Steam and Electricity. Man has acquired gradually a mastery over matter, or the material world. The Stone Age was followed by the Bronze Age, which was followed by the Age of Iron and Steel. As expressed by Frederick Soddy of Oxford University, "materials are employed merely as weapons, tools, or instruments for the utilization of power or energy." He also says: "Think of the ages that elapsed after

man kindled his first fire before the world hummed to the tune of the steam engine. . . . Primitive man froze on the site of what are now coal mines, and starved within the sound of waterfalls that now are working to provide our food."

The intelligent application of energy has done much to differentiate human beings from beasts of burden.

It may be that we are on the eve of a new era in energy; for it has been discovered in recent years that the energy locked up in atoms of matter is vastly greater than that obtained when a chemical process is carried out, such as the combustion of coal. According to Lord Kelvin (William Thomson, a British physicist), the combustion of a mass of coal the size of the sun would suffice for only five thousand years at the present rate of output of solar energy. Now, astronomers tell us that the sun has been giving out this vast amount of heat for millions of years and may do so for many millions more. The source of so much heat has been a great riddle; but since the discovery of radium and radioactivity, new knowledge has been gained. It appears that the metal radium breaks down spontaneously, yielding other elements, accompanied by the evolution of a vast amount of energy. A radium compound is always a few degrees warmer than the surrounding atmosphere. Sir William Ramsay, a British chemist, estimated that if the energy of a ton of radium could be evenly liberated during a period of thirty years, it would be sufficient to propel a ship of 15,000 tons displacement, driven by engines of 15,000 horse-power at the rate of 15 knots for the entire thirty years. It is therefore suggested by astron-

omers that the subatomic energies of chemical elements of the sun and stars may be the source of the radiant energy of these bodies.

It should be clearly kept before us that the application of energy is closely connected with the wealth and prosperity of a nation; and it is fortunate that one nation after another has taken intelligent steps for the conservation of natural resources. The necessity of conservation was brought home to us particularly during the recent war.

We may conclude with the Apostle Paul that "the things which are seen are temporal; but the things which are not seen are eternal." His words reveal the essential nature of energy, or of the great invisible world around us.

CHAPTER III

ELECTRONS, ATOMS, AND MOLECULES: THE ULTRA-MICROSCOPIC WORLD

> The quantity of electricity which courses every second through a common sixteen-candle-power electric-lamp filament, and for which we pay 1/100,000 of 1 cent, is so large that if all the two and one-half million inhabitants of Chicago were to begin to count out these electrons and were to keep on counting them out each at the rate of two a second, and if no one of them were ever to stop to eat, sleep, or die, it would take them just 20,000 years to finish the task.—R. A. MILLIKAN.

1 ATOMS AND MOLECULES

THE structure of matter engaged the attention of philosophers of the East long before the days of Grecian philosophy. Kanada, the founder of a system of Hindu philosophy, taught that matter was made up of exceedingly small, indivisible, eternal particles called atoms (Greek: uncut, indivisible), which were supposed to be in perpetual motion and separated from one another by void space.

The ancient Greek philosophers were divided into two schools. On the one hand there was the school of Aristotle, called the Peripatetic, because the pupils received instruction while walking in the Lyceum at Athens, who taught that matter is infinitely divisible. On the other hand, the school of Atomistic philosophers, led by Democritus, held that matter is finitely

divisible—*i.e.*, composed of atoms. Democritus taught that atoms of different sizes and forms, floating about in the void, impinge on one another, the atoms of similar form tending to group themselves together. The theory of the Atomistic philosophers contained the germ of the modern theory of the structure of matter. The speculation of ancient philosophers was virtually all that was known about the structure of matter until the beginning of the nineteenth century, when John Dalton, an English schoolmaster, quickened the dead dogma of the philosophers into a living hypothesis. Dalton assumed that every chemical element, such as oxygen, iron, or gold, is made up of small indivisible particles called atoms; that the atoms of different chemical elements possess different weights, but those of a particular element are alike and constant in weight; and that chemical compounds, such as common salt and water, are formed by the chemical union of different elements in the simplest numerical proportions. Thus, an atom of sodium unites with an atom of chlorine to form the smallest particle (molecule) of table salt, while two atoms of hydrogen combine with one atom of oxygen to form the smallest particle of water.

A few years after Dalton outlined his atomic theory, Avogadro, an Italian scientist, introduced the term molecule (Latin: a little mass). A molecule is a cluster formed by the chemical union of atoms, or it is the smallest particle of matter capable of existing in the free state. For instance, a molecule of the gas carbon dioxide consists of one atom of carbon and two atoms of oxygen. A molecule of a substance has the same

properties as has the mass as a whole; for a particular mass is an aggregation of many molecules, each of which in turn is composed of atoms. The atomic-molecular theory suggested that matter has a "grained" structure. Ordinary matter appears to be continuous. The behavior of gases, liquids, and solids cannot be satisfactorily explained, as was pointed out in Chapter II, unless we assume that matter is discontinuous—*i.e.*, made up of exceedingly small, distinct particles. Hence the kinetic theory.

The idea of the discontinuity of matter is well expressed by Bertrand Russell in the following words:

> To the eye or to the touch, ordinary matter appears to be continuous; our dinner-tables, or the chairs on which we sit, seem to present an unbroken surface. We think that if there were too many holes the chairs would not be safe to sit on. Science, however, compels us to accept a quite different conception of what we are pleased to call "solid" matter; it is, in fact, something much more like the Irishman's net, "a number of holes tied together with pieces of string." Only it would be necessary to imagine the strings cut away until only the knots were left.

2 Electrons and Protons

In the study of the properties of matter scientists have been forced to assume the existence of particles still more minute than atoms; so Dalton's conception of the atom has been somewhat modified. The atom is no longer regarded as being indivisible, unchangeable, and eternal; but it is believed to be composed of tiny granules of negative and positive electricity, re-

spectively known as electrons and protons, which means that Nature employs only two kinds of bricks in element-building. According to the modern theory, an atom of an element consists of one or more protons and the same number of electrons; so the atom as a whole is electrically neutral. The hydrogen atom, which may be represented by the symbol H, is the lightest and simplest atom, consisting of, it is generally accepted, one proton and one electron, as shown in Figure 2. It is believed that the electron revolves around

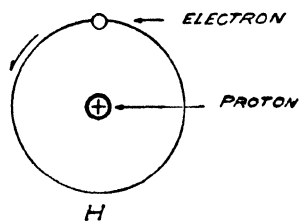


FIGURE 2
The Hydrogen Atom

the proton, or the nucleus, very much as the earth revolves around the sun. All other atoms contain more electrons and protons, the number increasing with the increase in the weight of the atom. It is now customary to speak of an atomic system, which consists of a nucleus and associated planetary electrons.

It is interesting to know that it takes 1845 electrons to weigh as much as one hydrogen atom; so the mass of an atom depends almost entirely upon the proton.

The information concerning the structure of atoms has been secured largely by the marvelous instrument known as the spectroscope, by X-rays, and by radioactivity.

3 The Size and Motion of Invisible Particles

Molecules, atoms, and electrons belong to the world of the almost infinitely little. The kinetic theory has made it possible for scientists to compute approximately magnitudes of the molecular world. It has been determined that it would take about forty million molecules, touching one another, to make a row one inch long. It has also been computed that one cubic centimeter (less than a small thimbleful) of a gas, say oxygen, at standard temperature and pressure, contains approximately twenty-seven billion billion molecules. Professor R. A. Millikan says we can now count this number with probably greater precision than we can attain in determining the number of people living in New York city.

A hydrogen molecule has a mean velocity of over a mile a second and collides with its neighbors, at room temperature and pressure, about ten billion times per second! It would take one individual counting at the rate of three per second twenty-four hours per day over a century to count this number!

That molecules of water are exceedingly minute, is strikingly shown by W. R. Whitney of the General Electric Company, who has calculated that if the molecules in a glass of water could each be changed into a grain of sea-sand, the sand thus produced would be sufficient to cover the whole of the United States to the depth of one hundred feet.

If we poured a quart of water into the sea and, after complete mixing with the entire body of water, dipped

out from any part of the sea another quart of the liquid, the second quart would contain many thousands of the original molecules which were poured into the sea.

Small as molecules are, atoms and electrons are still more minute. Not all atoms are of the same size. Under normal conditions the diameter of a hydrogen atom is estimated to be about a hundred millionth of a centimeter (2.54 centimeters equal 1 inch), which appears to be about twice the usual distance of its electron from its nucleus. While the size of an electron is not known with accuracy, it is only a tiny fraction of the size of the whole atom, and the nucleus, or central sun, appears to be still smaller. An atom is therefore largely a vacuum. It has been computed that if the nucleus of a helium atom were represented by a pea, its two planetary electrons could be represented by two peas a quarter of a mile away. Imagine that a tiny demon possessing vision infinitely keen is standing, gun in hand, an inch from an atom. Now if the little demon fired a ball the size of an electron at the nucleus of the atom, there is hardly a chance in a billion that he could hit the almost infinitely small bull's-eye.

As stated by Bertrand Russell, the electron of the hydrogen atom goes round its tiny orbit very rapidly, covering, under normal conditions, about fourteen hundred miles per second, which means that it has to revolve seven billion times in one millionth of a second! In other words, the electron completes seven billion of its years in a millionth of a second! These facts show that electrons, atoms, and molecules are far too little

for our comprehension; they truly belong to the ultra-microscopic world, to the world of the almost infinitely little.

It is a startling and marvelous fact that these tiny particles of matter, like the celestial bodies, are never at rest. What makes them move? We do not know. Perhaps the following lines of Vergil, as is suggested by J. W. Mellor, are as good a guess as any concerning the birth-history of motions:

> Know first, the heaven, the earth, the main,
> The moon's pale orb, the starry train,
> Are nourished by a soul,
> A bright intelligence, whose flame
> Glows in each member of the frame,
> And stirs the mighty whole.

It truly seems, as expressed in the following lines of an anonymous writer, as if

> Full many a secret in her sacred veil
> Hath Nature folded. She vouchsafes to knowledge
> Not every mystery, reserving much
> For human veneration, not research.

4 Chemical Shorthand. How Elements and Compounds Are Named

Let us now learn something about the language of chemistry. Facts, which form the subject-matter of the science, are represented by ideas, and these ideas may be expressed in words or, in certain cases, by means of symbols.

In the first place, a great many of the chemical elements have been given names derived from the Greek:

e.g., hydrogen (water-producing); chlorine (yellowish-green); iodine (like a violet—from its violet vapor); helium (the sun—from its occurrence in the sun); phosphorus (the light-bringer). Some elements are named after particular localities: *e.g.*, strontium, from Strontian in Scotland. Platinum owes its name to the Spanish *plata*, silver.

The names of metals usually end in *um* or *ium*. Thus, aurum (gold), ferrum (iron), sodium.

The names of non-metals end, as a rule, in *gen*, *ine*, or *on*. For example, oxygen, chlorine, carbon.

The constant use of the full names of the elements would be burdensome; therefore, it is the universal custom of chemists to use an abbreviation or symbol.

The alchemists employed crude symbols to represent different substances. For instance, the names of the metals were generally represented by the astronomical symbols of the planets. Thus, in the language of the alchemist, ☉ represents gold (Sol), ☽ silver (Luna), ♁ copper (Venus), ♂ iron (Mars), and ☿ quicksilver (Mercury). Gold typified the bright yellow glow of the sun; silver, the soft white of the moon; copper, the looking-glass of Venus; iron, the weapons of Mars, the God of War; and quicksilver, the fleet-footed messenger of the gods, Mercury. Many other and more obscure symbols were employed by the alchemists.

Dalton represented the atoms of elements by symbols, and combined these to represent the elements in a particular compound. For example, ☉ stood for hydrogen; ○ for oxygen. Water was represented by ☉○. These symbols were too cumbrous, so they have been abandoned.

In 1811, J. J. Berzelius, a famous Swedish chemist, introduced a set of symbols for the elements, which are still in use. The universal practice is to use the first letter (or the first along with another letter) of the name of the element—usually from the Latin or Greek names. Thus, Au indicates the element gold (aurum), while Fe represents iron (ferrum). Such abbreviations are called symbols. Au and Fe are the symbols for gold and iron, respectively. The chemical symbols are, therefore, a sort of chemical shorthand, with which the student of chemistry gradually becomes familiar. Also, most of them are international, whereas their names are not.

It should be known that the symbols have a definite and exact meaning. For instance, O stands for 16 parts by weight, or one atom, of oxygen. S stands for 32 parts by weight, or one atom, of sulphur, which is twice as heavy as the oxygen atom. Likewise, Pt represents 195 parts by weight, or one atom, of the metal platinum, which is now more valuable than gold. When carbon or charcoal burns, the element unites with oxygen of the air to form the chemical compound carbon dioxide, or carbonic acid gas. This compound is also a product of respiration, as may be shown by forcing one's breath through a little lime-water by means of a tube. Lime-water becomes turbid in the presence of carbon dioxide. Now, as we have learned, particles formed by the union of atoms are called molecules. We may therefore regard molecules as clusters, or aggregates, of which the atoms are the units. Chemists rep-

*A full list of the chemical elements, with their symbols and relative weights (atomic weights), is to be found in the Appendix.

resent a molecule of a substance by a combination of symbols, which is known as a chemical formula. Thus, CO_2 stands for one molecule of carbon dioxide, whilst H_2O represents one molecule of water, which consists of two atoms of hydrogen and one atom of oxygen.

Furthermore, when a mixture of iron filings and sulphur is heated in a test-tube, the elements unite chemically to form the compound iron sulphide, FeS. The chemist represents such a change as follows:

$$\begin{array}{lllll} \text{Iron} & + \text{ Sulphur} & = & \text{Iron sulphide} \\ \text{Fe} & + \quad \text{S} & = & \quad \text{FeS} \end{array}$$

It is known that oxygen gas consists of molecules composed of two atoms in chemical union: O—O, or O_2. The hydrogen, nitrogen, and chlorine molecules are also known to be diatomic: H_2, N_2, Cl_2.

The sum of the weights of the atoms of a molecule gives what is known as a molecular weight. Thus, the molecular weight of carbon dioxide, CO_2, is equal to $12 + (16 \times 2)$, or 44. This means that 44 parts by weight of carbon dioxide contain 12 parts by weight of carbon and 32 parts by weight of oxygen. If we burned 12 tons of pure carbon, 32 tons of oxygen would be required, and 44 tons of carbon dioxide would be formed.

As a result of thousands of experiments, chemists have reached the conclusion that *a particular compound always contains the same elements, chemically united in the same proportion by weight.* This is known as the law of constant proportions, and is one of the fundamental laws of chemistry. The compound carbon dioxide, to illustrate, always contains 27.3 per cent. of

carbon and 72.7 per cent. of oxygen. Likewise, pure water, table salt, sugar, and alcohol have constant compositions the world over.

In the naming of compounds certain general rules are to be followed. Let us illustrate this in the case of a few simple substances. When there are only two elements in a compound, the name of the second element is modified so as to end in *ide:*

CuO, copper oxide
NaCl, sodium chloride
$MgBr_2$, magnesium bromide
AgI, silver iodide
ZnS, zinc sulphide
SiC, silicon carbide (carborundum)

The names of compounds are so chosen that they shall as far as possible indicate their composition. Thus, to distinguish one oxide from another or others prefixes are used:

CO, carbon *mon*oxide; CO_2, carbon *di*oxide
BaO, barium *mon*oxide; BaO_2, barium *di*oxide (*per*oxide)
P_2O_3, phosphorus *tri*oxide; P_2O_5, phosphorus *pent*oxide

It is easy to see that if the molecule of any particular compound is made up of definite numbers of stable atoms, its composition is necessarily constant.

Let us suppose that the smallest particle of copper oxide imaginable (a molecule) consists of one atom of copper and one of oxygen in chemical union. If we assume that copper atoms are indivisible, homogeneous, and of constant mass or weight, and that atoms of oxygen are the same, except that the weight of this atom is different from that of the copper atom, it is

clear that copper oxide has a constant composition; for any particular mass of the compound, say one gram, is made up of a very large number of particles of copper oxide each of which contains one atom of copper and one of oxygen. The molecular formula of copper oxide is CuO.

CHAPTER IV

CHEMICAL ELEMENTS AND COMPOUNDS

I must not look upon any body as a true principle or element, which is not perfectly homogeneous, but is further resolvable into any number of distinct substances.—ROBERT BOYLE.

1 THE CHEMICAL ELEMENTS AND THEIR RELATIVE ABUNDANCE

IN decomposing certain materials by means of such agencies as heat and electricity, one always comes to substances which resist all efforts further to decompose them. These simple and fundamental forms of matter are termed elements, about ninety of which have been discovered.

When the red oxide of mercury is heated it decomposes into the elements mercury (quicksilver) and oxygen, the latter being a colorless gas in which a glowing splinter bursts into flame. Water, under certain conditions, yields the gases hydrogen and oxygen, and common salt yields the metal sodium and the greenish-yellow gas chlorine. Other simple or elementary forms of matter are iodine, iron, carbon, nitrogen, silver, and gold.

Robert Boyle, in 1661, was the first chemist clearly to define an element. According to him, "the elements are the practical limits of chemical analysis, or are substances incapable of decomposition by any means with which we are at present acquainted."

A chemical element is usually defined as a substance which the chemist cannot form from, or decompose into, other substances, while a chemical compound is a substance composed of two or more elements in chemical union and having a constant composition.

While the definition of an element as given above answers for practical purposes, it is very interesting to know that certain substances which were once regarded as elements have been decomposed into simpler substances. Early in the nineteenth century, for example, Sir Humphry Davy succeeded in the isolation of such metals as calcium, sodium, and potassium from hitherto undecomposed substances which were regarded as elements. Ordinary lime, or quicklime, was thought to be an element until Davy showed that it is an oxide of calcium.

In recent years scientists have discovered that certain substances, known as radioactive elements, decompose spontaneously into other elements; the chemist has no control over these transformations. This fact is well illustrated in the metal radium, which spontaneously splits up, yielding a number of other elements, such as helium, radon, and lead.

It is a remarkable fact that when elements unite to form compounds, they lose completely their identity. We have an excellent example of this in common salt, which contains sodium (a soft, silvery metal that liberates hydrogen from water) and chlorine (a greenish-yellow, poisonous gas). In chemical union, however, these elements form salt, a white compound which is agreeable to the taste.

As compared with the thousands of known com-

pounds, the number of elements is not large. In the time of the immortal Lavoisier only twenty-three substances were listed as elements.

There is in the library of Princeton University a note-book on chemistry which belonged to John Eager Howard, Jr., of Baltimore, Maryland. Howard was a member of the class of 1806 and was a son of General Howard, who served throughout the Revolutionary War and received a medal from Congress for his valor at Cowpens, January 17, 1781. The younger Howard, like his distinguished father, was at one time a member of Congress.

This chemistry note-book is beautifully written and is evidently a transcript of the systematic lectures on chemistry delivered in Nassau Hall by Dr. John Maclean, who came from Glasgow University to Princeton in 1795, and taught chemistry until 1812. The following extract is taken from this most interesting note-book:

Matter may be divided into dead and living. Of dead substances some are simple and others compound. The simple are those whose composition is unknown, and the compound are such as have been analyzed into simpler parts. The substances which, according to the above definitions, may be considered as simple are:

caloric	silex	fluoric acid	antimony
light	alumine	boracic acid	mercury
electricity	magnesia	arsenic	zinc
oxygene	lime	tungstein	tin
azote	barytes	cobalt	lead
hydrogene	strontites	molybdena	copper
sulphur	potash	bismuth	silver
phosphorus	soda	nickel	gold
carbone	muriatic acid	manganese	platina

There are thirty-seven of these "simple substances," which constitute the titles of so many chapters in the note-book. Seventeen of these were regarded as metals, which were divided into semi-metals (brittle) and metals.

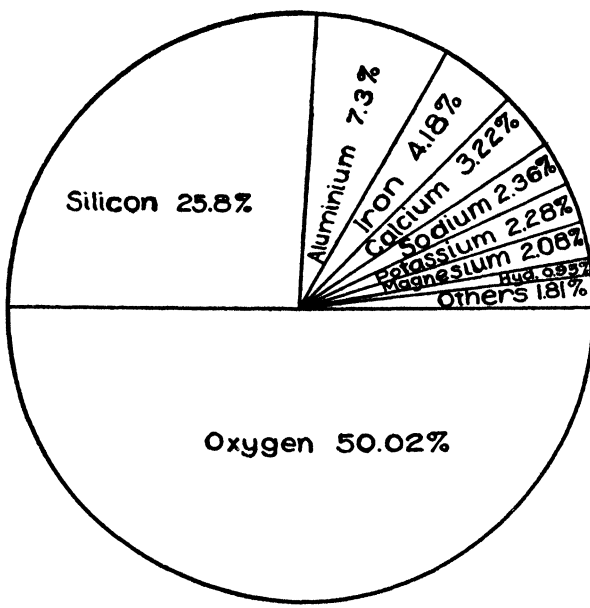


FIGURE 3
Relative Abundance of the Elements

As previously stated, there are about ninety elements known at the present time, but many of the terms in the above table do not stand for chemical elements. Among these are: caloric, light, electricity, silex (silica), lime, soda, and potash. Lime was called a simple substance, for Davy did not isolate the alkali and alkaline earth metals until 1807-08.

Less than one fourth of the elements are common and abundant, among which are: oxygen, silicon, aluminium, iron, calcium, sodium, potassium, magnesium, hydrogen, chlorine, and carbon. Some of the elements are exceedingly rare, being more costly than precious stones. Radium, for example, sells for about $2,000,000 per ounce. Only about twenty of the elements are found free in nature, and about one half of them are encountered in substances commonly examined in chemical laboratories.

F. W. Clarke has made an estimate of the occurrence of the elements in the solid shell of the earth, in the sea and other waters, and in the air. An examination of Clarke's table shows that twenty elements constitute 99.5 per cent of the earth's crust. The other seventy elements are estimated to constitute 0.5 per cent. (Figure 3.)

Oxygen is by far the most abundant of the elements (about 50 per cent), followed by silicon (about 28 per cent). Aluminium is the most abundant metal (nearly 8 per cent), followed by iron (4.5 per cent).

CLARKE'S TABLE (Condensed)

	Solid shell 93 per cent	*Ocean 7 per cent*	*Average including atmosphere*
Oxygen	47.33	85.79	50.02
Silicon	27.74		25.80
Aluminium	7.85		7.30
Iron	4.50		4.18
Calcium	3.47	0.05	3.22
Magnesium	2.24	0.14	2 08
Sodium	2.46	1.14	2.36
Potassium	2.46	0.04	2.28
Hydrogen	0.22	10.67	0.95
Other elements	1.73	2.17	1.81
	100.00	100.00	100.00

When the materials constituting the human body and other living organisms are analyzed, only a limited number of elements are found in appreciable amounts. The four most abundant elements in organic matter are oxygen, carbon, hydrogen, and nitrogen, all of which are non-metals and three of which are gaseous elements. Calcium constitutes about 2 per cent of the human body and is the most important metal, for it is an essential constituent of bones. Magnesium, iron, phosphorus, potassium, sodium, and iodine are other essential constituents of the body. It is estimated that the average human body contains about 0.02 gram (20 milligrams) of iodine, about half of which is in the thyroid gland, near the Adam's apple. Small as the amount of iodine is, it is extremely important, for the proper amount of this element keeps the body so regulated that the diseases known as goiter and cretinism are prevented. The body is a marvelous chemical laboratory, and we are indeed "fearfully and wonderfully made."

The spectroscope, an instrument of unrivaled subtlety and sureness in the detection of chemical elements, has made it possible for us to study the composition of celestial bodies such as the sun and the stars. The elements aluminium, calcium, carbon, copper, helium, hydrogen, iron, nickel, nitrogen, oxygen, silver, and many others have been detected in the sun.

It is estimated that stellar temperatures vary from about 3,000° C. to 25,000° (45,032° F.), that of the sun being about 6,000° C. Metallic elements along with non-metals have been observed in the sun and cooler stars, while the very hot stars appear to be character-

ized by non-metals in the gaseous state. The metals are probably present also in the hotter stars, but they are more difficult to identify.

Masses of extraterrestrial matter which fall to the earth now and then, in the form of meteorites, are found to contain iron, nickel, phosphorus, carbon, oxygen, silicon, calcium, and hydrogen.

In general we may assume that the composition of the earth is somewhat similar to that of the sun; at least, the two bodies contain many elements in common.

2 Metals and Non-Metals; Alloys

More than a hundred years ago the elements were divided into metals and non-metals. This division has proved to be more or less arbitrary, for it is not possible sharply to divide the elements into these two classes. Metals and non-metals do have certain general characteristics, however. Metals—*e.g.,* silver and gold—possess a characteristic luster; they are malleable, ductile, and good conductors of heat and electricity.

The metals may be divided into light and heavy metals, the latter being five times or more heavier than an equal volume of water. The metals sodium and potassium are light enough to float upon water; and magnesium and aluminium are utilized in the production of light alloys. For example, one third of the weight of the Liberty motor was aluminium; and the metal is of prime importance in the construction of frames of airships and many parts of airplanes.

Of the heavy metals, gold, silver, copper, tin, lead, and iron have been longest known, owing to the fact that they occur free in nature, or can be easily prepared from certain of their compounds called ores. Gold is found chiefly in the free state, and it is more than nineteen times as heavy as an equal volume of water.

The metals chiefly used in the arts have been gold, silver, copper, tin (in bronze), iron, and lead. The advantages of gold, to illustrate, are durability, malleability, ductility, pliancy, and its susceptibility of being subdivided, which is of great value in gilding—an art mentioned by Moses.

Alloys are commonly obtained by melting together certain metals. Thus, bronze, an alloy of copper and tin, was of the highest importance to the ancients, the Bronze Age following the Stone Age.

The addition of a foreign metal increases the hardness and lowers the melting-point and also the conductivity for heat and electricity. Bronze, for example, possesses great fluidity when melted, and it is especially adapted for sharp and delicate castings. The ancient Egyptians, Assyrians, and Greeks knew how to temper bronze, so it was fashioned into various implements, such as knives, swords, hammers, daggers, and arrow-heads; it was also used in making splendid works of art.

In modern times, brass, an alloy of copper and zinc, has been much used instead of bronze, for it is cheaper; but in beauty, delicate surface, and durability it is much inferior to bronze. The "brass" of the Bible was probably bronze.

The engineering importance of alloys could hardly be exaggerated. Virtually nothing we use would be available without alloys. Alloys as a class are noted for the ease with which they can be shaped into various objects of superior strength—by casting, rolling drawing, forging, welding, or machining. The alloys of iron (steels) are superior in strength, and are relatively low in cost; but they are heavy and are subject to rusting. Where the weight is a disadvantage, alloys of aluminium are employed; and where resistance to rusting is required, the copper alloys find use.

Tin-plate is manufactured by dipping cleaned sheets of low-carbon steel or iron into molten tin. The coating of tin prevents or hinders corrosion. The resistance of the tin can to atmospheric corrosion and to the corrosion by organic acids of foods is of the highest importance; for modern life is greatly dependent upon it.

3 Chemical Compounds

The elements enter into union to form a very large number of chemical compounds. The most active non-metallic element is fluorine, a pale greenish-yellow gas, which is a member of the chlorine family. This element combines explosively with hydrogen, even in the dark; and many elements, such as sulphur, carbon, sodium, magnesium, and iron, burn spontaneously in fluorine.

The most active metals are the alkali metals, such as sodium and potassium, and for this reason they are preserved under oil to protect them from moisture. These two metals form a liquid alloy which has the ap-

pearance of mercury. An interesting story is told concerning this alloy and the late Sir Edward Thorpe, who was one of the leading British chemists. When a young man, Thorpe was a pupil of Roscoe, who had been a pupil of the celebrated Bunsen of Heidelberg. On the advice of Roscoe, young Thorpe decided to continue his chemical studies under Bunsen. Wishing to remember his old teacher, Roscoe had prepared beautiful specimens of crystallized potassium and sodium, which were inclosed in separate bottles and preserved under oil, and he requested Thorpe to present these to Bunsen. Being crowded for room, Thorpe placed the specimens in a single container. When the presentation was made to Bunsen, there were, much to Thorpe's surprise, no crystals but instead a liquid. At Bunsen's suggestion there was an investigation, which resulted in the discovery that potassium and sodium form a liquid alloy much like mercury in appearance. When a small piece of potassium is dropped upon water or put into a hole drilled in a lump of ice, the action is so lively and so much heat is formed that the liberated hydrogen catches fire spontaneously, and the metal and escaping gas burn on the surface of the water. This is a dangerous experiment, however, and should not be performed by the inexperienced.

Carbon is the element which enters into the formation of by far the largest number of compounds. It is a constituent of all organic matter. Many of the carbon compounds, such as the sugars, starches, cellulose, alcohol, ether, and chloroform, are of prime importance. For instance, the starches are the most abundant of foods.

It should always be borne in mind that a chemical compound has a constant composition. Thus, pure water, the world over, contains 11.19 per cent of hydrogen and 88.81 per cent of oxygen. A mixture, on the other hand, has a variable composition. For example, one can readily prepare a mixture of sea-sand and sugar, the amount of each component being varied at will. The sand and sugar are in intimate contact, but not chemically united, as may be seen by examining the material under a microscope; and the two components may be readily separated by the addition of water, in which the sugar is soluble. The dishonest grocer would hardly venture, therefore, to adulterate sugar with white sand.

Black gunpowder is a mixture of potassium nitrate (niter or saltpeter), charcoal (carbon), and sulphur; granite is a mixture of the minerals quartz, feldspar, and mica.

When compounds are formed or decomposed, the chemical changes may be represented by means of equations, every chemical equation being based upon the law of the indestructibility of matter. A chemical equation shows, therefore, weight relations, the weights of the factors being equal to the weights of the products. Thus, we have seen that when charcoal or carbon burns in air or oxygen, carbon dioxide is formed:

Carbon	+	Oxygen	=	Carbon dioxide
C		O_2		CO_2
12		16×2		44

The numbers below the symbols stand for parts by weight, which may be expressed in tons, pounds, or

grams. Now, the chemist generally employs the gram as the unit of weight, the grocer's pound being equal to 453.6 grams. Stated in words, the above equation may be read as follows: when 12 grams of carbon are burned or fully oxidized, 32 grams of oxygen are used up and 44 grams of carbon dioxide are produced. In other words, one atomic weight of carbon unites with two atomic weights (one molecule) of oxygen to form one molecular weight of carbon dioxide. The molecular weight of a substance may be found by summing up the weights of its constituent atoms; for a molecule is an aggregate of which the atoms are the units. It is clear, then, that the molecular weight of water, H_2O, is $(1 \times 2) + 16 = 18$, and that of alcohol, C_2H_6O, $(12 \times 2) + (1 \times 6) + 16 = 46$.

The formation of chemical compounds occurs according to definite laws and is in no sense haphazard. The synthesis and analysis of chemical substances have shown conclusively that a compound never contains fractions of atoms, which means that the number of each atom in a compound may be represented by an integer, or whole number, as in water, H_2O.

4 Valence

Experiment with the balance has enabled the chemist to decide that an atom of an element, say hydrogen, has the capacity to combine with one or more atoms of another element as shown below:

HCl	H_2O	H_3N (or NH_3)	H_4C (or CH_4)
Hydrogen chloride	Water	Ammonia	Methane

We say that a particular atom has a valence, the valence being a whole number which expresses how many atoms of hydrogen one atom of the particular element can hold in combination.

In the four compounds mentioned, we say that chlorine has a valence of 1, oxygen 2, nitrogen 3, and

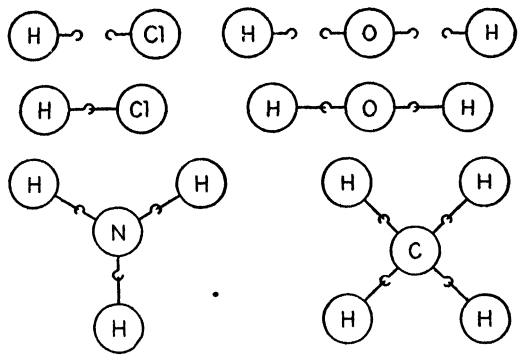
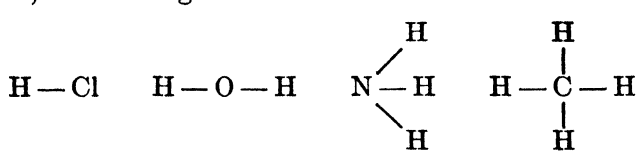


FIGURE 4
Diagram Illustrating Valence

carbon 4, *the valences of the elements being measured in terms of the numbers of hydrogen atoms uniting with one atom of each element.*

We may represent this graphically by imagining an atom to have a certain number of bonds, or lines of force, for holding on to other atoms:



We may picture the chlorine atom as dancing with one hydrogen partner, the oxygen atom with two, the

nitrogen atom with three, and the carbon atom with four. (Figure 4.)

Valence was rather humorously defined by one of the writer's pupils as "the number of hands an element has to hold hydrogen with, or the number of hooks an atom has to catch other substances with"; also, as the "appetite of an element."

CHAPTER V

OXYGEN · FIRE AND FLAME

A little fire is quickly trodden out; which being suffered, rivers cannot quench.—SHAKSPERE.

1 THE ATMOSPHERE AND OXYGEN

THE air we breathe is a mixture primarily of nitrogen, oxygen, and argon, which are present in almost constant proportions. Leaving out of consideration the minor components, the composition of pure, dry air is as follows:

	By volume	*By weight*
Nitrogen	78.06	75.5
Oxygen	21.00	23.2
Argon	0.94	1.3

The word atmosphere (Greek: vapor + a sphere) refers, of course, to the great ocean of aëriform fluid surrounding the earth and commonly called the air. The latter term was used by the older chemists in the same sense as we employ the word gas. Thus, oxygen was called "fire-air," and carbon dioxide, "fixed air."

The normal or standard pressure of the atmosphere is 1033.2 grams per square centimeter, or about 15 pounds per square inch; and the pressure supported on the body of the average man amounts to about 18 tons!

That the air has weight, or exerts pressure, may be shown most strikingly by boiling a small amount of water in a large tin can; when all the air has been

expelled by steam, the can is tightly stoppered and then immersed in ice-water, whereupon the steam condenses, followed by the collapse of the can, due to the great pressure of the surrounding atmosphere.

It has been known for centuries that the air contains at least two components—an active one and an inactive one. More than a thousand years ago the Chinese called the active component *yin* (oxygen). They knew that this active gas combined with sulphur, with charcoal, and with some of the metals.

Oxygen, then, is the active component of the air, of which it constitutes about one fifth by volume. In the free state it is exceedingly abundant and, therefore, widely distributed. Although it is an odorless, colorless, tasteless gas, we should soon suffocate if deprived of it. We are dependent upon oxygen for heat and light and even life itself. We could not make a fire without it, and the gas is consumed in every breath we take, from the moment of birth until the heart finally ceases to beat. Among gases it occupies the supreme place.

Joseph Priestley, an English chemist and clergyman, is usually regarded as the discoverer of oxygen. Priestley was endowed with an unusual gift for observing and experimenting, and he prepared and investigated many gases, such as oxygen, ammonia, sulphur dioxide, and hydrochloric acid gas. "A wandering life full of vicissitudes and even of persecutions was destined for Priestley, doubtless for the most part because of his relations to the English Church and his own intolerance." He spent some years as minister of a meeting-house in Birmingham; but in 1791 his house and laboratory were destroyed in the Birmingham riots,

and he was obliged to leave for London. In 1794 he emigrated to America, and lived at Northumberland, Pennsylvania.

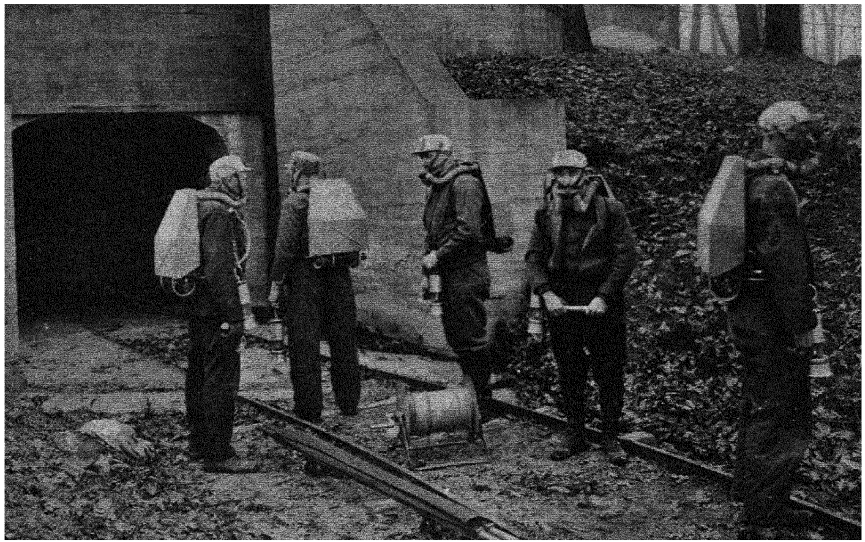
On August 1, 1774, Priestley prepared a specimen of pure oxygen by heating mercuric oxide, or "red precipitate (HgO)," confined over mercury in an elongated glass vessel, the heat being obtained by the concentration of the sun's rays by means of a lens. Priestley thrust a lighted candle into the gas and observed that it burned more brilliantly than in air.

Lavoisier, a renowned French chemist who is sometimes called "the father of modern chemistry," took up the study of the properties of oxygen, and in 1777 carried out his classical experiment to show the relation of the gas to air. By means of a charcoal fire he heated mercury confined in a retort, the neck of which passed up through a vessel containing mercury, into a bell-jar with air in it. The mercury and air were heated for twelve days, at the end of which he observed that *the air had lost about one fifth of its original volume.* The red powder formed was removed from the retort and heated in another vessel; it yielded a volume of an active gas equal to the decrease in the volume of the original air. This gas was, of course, oxygen. The gas left in the retort would not combine with mercury; it extinguished a burning candle, and a mouse was quickly suffocated in it. Lavoisier named it azote (nitrogen). The proof was now complete that *oxygen is a component of the air, and that combustion is dependent upon oxygen.* Subsequently, Lavoisier named the active gas oxygen.

Lavoisier was truly a remarkable man. Not only was

PRIESTLEY'S HOUSE AT BIRMINGHAM

Joseph Priestley spent some years as a minister of a meeting-house in Birmingham. In 1791 his house was attacked by a mob and he was obliged to leave for London.



Courtesy of United St[illegible] Bureau of M

GAS-MASKS

Self-contained oxygen-breathing apparatus is employed in fighting mine fires and in rescuing miners trapped by fire or poisonous gases.

he a great investigator and prolific writer, but he became associated with the Farmers General, a syndicate of financiers to whom the state leased the right to collect indirect taxes. During the French Revolution the Farmers General were put under arrest and were sent to trial, one of the principal charges against Lavoisier being that he had treated the soldiers' tobacco with water. He was unjustly put to death by the guillotine, the judge cynically remarking: *"La république n'a pas besoin de savants* [the republic has no need of savants]." The great wrong done was well expressed in the words of Lagrange: "It took them but a moment to cut off that head, though a hundred years, perhaps, will be required to produce another like it."

Oxygen not only occurs in the free state but is found most abundantly in the combined state, constituting by weight nearly 50 per cent of terrestrial matter, about 89 per cent of water, 65 per cent of the human body, and a very large part of such common substances as saltpeter, nitric acid, limestone, brick, and mortar.

Oxygen is usually prepared on a small scale by heating substances containing it, such as certain oxides or potassium chlorate. On a commercial scale it is obtained from liquefied air and by the electrolysis of water.

For laboratory experiments oxygen is very conveniently prepared by heating potassium chlorate, a white crystalline solid compound containing the elements potassium, chlorine, and oxygen:

Potassium chlorate = Potassium chloride + Oxygen

(potassium, chlorine, oxygen) = (potassium, chlorine)

The gas can be liberated by heating a small quantity of potassium chlorate in a hard glass test-tube (Figure 5). The crystals of the salt melt, and bubbles of oxygen are evolved. A glowing splinter thrust into the tube burns brilliantly.

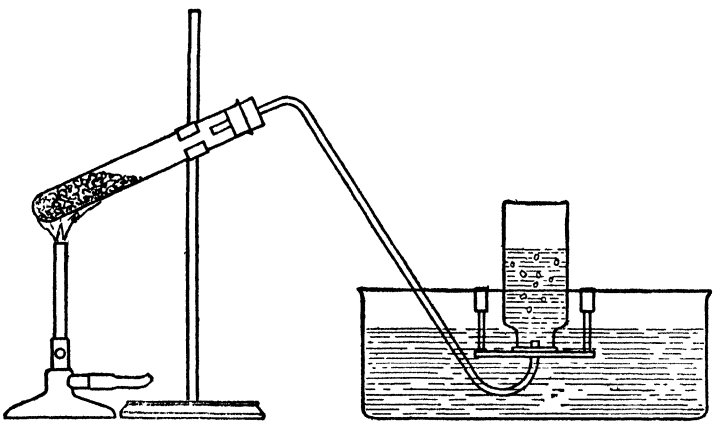


FIGURE 5
Preparation of Oxygen

Gases insoluble in water are very generally collected by placing the end of the delivery tube in the mouth of an inverted bottle previously filled with water. As the bubbles of gas rise, the water is displaced from the bottle.

The production of oxygen is greatly accelerated by mixing the potassium chlorate with manganese dioxide. The manganese dioxide undergoes no permanent change, and may be recovered at the end of the action by dissolving the potassium chloride in water. The mere presence, then, of manganese dioxide increases the

speed of the reaction, and the generation of oxygen is accomplished at a much lower temperature.

The presence of small quantities of certain substances alters the speed of many chemical actions. This sort of action is sometimes termed contact action, because the substances appear to act by contact. Berzelius proposed the name catalysis. A substance which alters the speed of a chemical action without itself undergoing permanent chemical change is called a catalytic agent, or catalyst. Catalysis is destined to play a greater rôle in chemistry, for it means the speeding up and cheapening of many processes.

2 Liquid Air

The commercial production of oxygen has undergone a remarkable development within the last quarter of a century, for the gas has many important uses, especially in metallurgy. This development is due largely to improved methods of liquefying air and separating it into its principal components, nitrogen and oxygen.

Liquid air is produced on a large scale by a method invented independently by W. Hampson and C. Linde. This method is based upon the fact that when a gas under high pressure is allowed to expand through a small orifice some of the heat energy of the gas is used up in overcoming the cohesion of the molecules and in separating them farther apart. The purified and highly compressed air is allowed to pass to a liquefier, the essential part of which consists of two concentric pipes wound in the form of a spiral and well protected by means of a non-conductor of heat (Figure 6). The

highly compressed air is pumped down the inner tube (C) and allowed to escape through a small orifice in the bottom. The gas therefore expands and drops in temperature. The cold gas now passes up the outer tube (D) and is again compressed and pumped back through the inner tube. While the gas is passing upward it cools

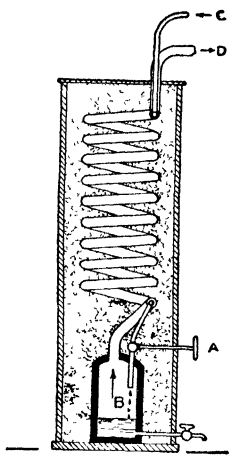


FIGURE 6
Liquefaction of Air

the compressed air passing down the inner tube, and the process is repeated until the temperature becomes so low that the gas liquefies. The liquid may be withdrawn from time to time by means of a valve. The liquid thus obtained contains about 21 per cent of oxygen; it has a pale blue color and boils at about —190° C., while the boiling-point of liquid oxygen is —182.5° C. and that of nitrogen —194° C. When liquid air evaporates, the more volatile nitrogen escapes first, and the residue becomes richer and richer in

oxygen. The gas is finally pumped into strong steel cylinders and thus stored for commercial use. It usually contains from 95 to 98 per cent of oxygen.

The chief use of liquid air is for the preparation of nitrogen, oxygen, and argon; it is also employed as a cooling agent, and with charcoal it forms a blasting explosive, for charcoal burns in liquid oxygen with great energy.

Liquid air is kept in Dewar flasks, which may be loosely stoppered with cotton. These flasks consist of one glass flask within another, the space between their walls being evacuated. The inner wall of the outer flask may be coated with silver or copper in order to reflect the radiant energy of surrounding bodies. The same principle is applied in the manufacture of thermos bottles.

Liquid air is, of course, extremely cold. When such substances as rubber, eggs, meat, and flowers are immersed in the liquid, they become almost as brittle as glass; and when the liquid is poured into a tea-kettle placed upon a block of ice, the liquid boils vigorously. An iron wire or steel spring, tipped with sulphur and ignited with a match, will continue to burn when dipped into liquid air; and when the liquid is heated over a burner in a small tin can, the air evaporates so rapidly that a coating of frost is formed on the outer surface of the can.

While liquid air is extremely cold, liquid hydrogen and helium are much colder. The former boils at about —252° C., and the latter at —268.5° C., which is not far from the absolute zero, namely —273° C. At the absolute zero a body would contain no heat. Scientists,

however, have not been able to cool any material to so low a temperature, but by the rapid evaporation of liquid helium a temperature within one degree of absolute has been reached.

All known gases have been liquefied. Any gas may be liquefied by cold and pressure, and it possesses what is known as a "critical temperature" and a "critical pressure." The critical temperature is the temperature to which a gas must be cooled before it can be liquefied; and the critical pressure is the pressure required to liquefy a gas at its critical temperature. The critical temperature of oxygen is —119° C., and its critical pressure is about fifty atmospheres. If the temperature of oxygen be above its critical temperature, it will remain in the gaseous state, no matter how great may be the pressure applied.

3 Properties of Oxygen; Oxidation

Oxygen is slightly heavier than air and is very sparingly soluble in water. Enough of the gas is in solution, however, to supply the needs of fish, which are cold-blooded. The most striking chemical property of oxygen is its great ability to support combustion. Charcoal, sulphur, phosphorus, and wood burn much more vigorously in oxygen than in air. Thus, when a small piece of white phosphorus is heated in a special spoon until it ignites, and then plunged into a jar of oxygen, it burns most brilliantly, giving off intense heat and light; hence this experiment is sometimes called the "phosphorus sun." All familiar metals, except the noble metals—silver, gold, and platinum—

when heated, combine with oxygen. Magnesium, for example, burns in oxygen, producing a dazzling light; and even iron will burn brilliantly in oxygen, as may be shown by coating the end of a bundle of fine iron wire with sulphur, igniting the latter, and then thrusting the bundle into a jar of oxygen. As the metal burns, accompanied by bright scintillations, it is converted into magnetic oxide of iron (Fe_3O_4), which occurs in nature as the mineral magnetite or lodestone, being identical in composition with the hammer-scale which flies from the blacksmith's anvil as he hammers red-hot iron. If the air did not contain nitrogen, our steel structures would burn much like wood in case they caught fire.

When an elementary substance burns in air, the product of combustion is an oxide. Many oxides occur in nature as valuable minerals and ores.

When a non-metallic element—*e.g.*, carbon, sulphur, or phosphorus—burns, the resulting oxide is called an acid anhydride (Greek: without water), for the oxide forms an acid when dissolved in water. For instance, carbon dioxide, formed by the combustion of carbon or charcoal, is often called carbonic anhydride, for it interacts with water to form carbonic acid:

$$\underset{\text{Water}}{H_2O} + \underset{\text{Carbon dioxide}}{CO_2} \rightleftarrows \underset{\text{Carbonic acid}}{H_2CO_3}$$

The arrows pointing in opposite directions mean that a molecule of water unites with a molecule of carbon dioxide to form a molecule of carbonic acid; and when a molecule of carbonic acid decomposes, or loses a

molecule of water, its anhydride (carbon dioxide) is formed. In other words, this is a *reversible action.*

An acid always contains hydrogen in chemical union with one or more other elements, one of which is frequently oxygen. Lavoisier had the notion that all acids contained oxygen, and for this reason he gave the element its name, which comes from two Greek words meaning acid-producer. The word oxygen is a misnomer, however, for there are many acids—*e.g.*, hydrochloric, HCl—that contain no oxygen.

All acids possess a sour taste and have the property of turning neutral or blue litmus-paper red.

When a metal—*e.g.*, calcium—burns in oxygen, the product is called a basic oxide; for the oxide, in case it is soluble, combines with water to form a base or alkali. Thus, calcium oxide or lime (CaO), formed by the combustion of calcium, unites with water to form calcium hydroxide, or slaked lime:

CaO	$+ H_2O \rightleftarrows$	CaO_2H_2
Calcium oxide (Lime)	Water	Calcium hydroxide

A water solution of a base or alkali has a caustic taste, a slippery feeling, and turns neutral or red litmus-paper blue. A solution of calcium hydroxide, or lime-water, is employed in almost every household; and it is well known to all that when a workman adds water to lime (or quicklime), the lime is converted into slaked lime, or calcium hydroxide, accompanied by much heat.

The chemical union of oxygen with a substance is known as oxidation, which is seen upon every hand.

Under the head of oxidation we have combustion, the rusting of metals, respiration, and, to a large extent, change and decay.

Combustion, in the popular sense, is the rapid chemical union of matter with oxygen, accompanied by the evolution of heat and light. Fire consists of heat and light produced by the rapid oxidation or combustion of fuel. The relation of oxygen to combustion can be shown by floating a burning candle, fastened to a cork, upon water, and inverting a glass cylinder over it. In a short while the light grows dim and the candle finally goes out, which means that the oxygen of the air is reduced so much that it will no longer support combustion.

When a candle or fuel burns, the chief products of combustion (in certain cases the only ones) are water and carbon dioxide. This may be demonstrated by inverting a dry glass cylinder or tumbler over a burning candle. In a short while water condenses upon the inside of the vessel, and by inverting it and adding some clear lime-water, followed by shaking, a white precipitate of calcium carbonate is obtained. This is a test for carbon dioxide.

That carbon dioxide is a product of respiration, may be shown by forcing the breath through a tube into lime-water.

4 Fire and Flame

The story of fire and flame is a fascinating one. Nobody knows just when man first kindled fire, but we do know that there was a time when he was unable to do so. Primitive man looked upon fire with wonder,

awe, and even reverence. The ancients thought that man was without fire until Prometheus, one of the most interesting creations of Greek mythology, stole it from the chariot of the sun. According to mythology, this great benefactor brought to mankind not only fire but certain arts depending upon it. It appears that human culture began with fire, and culture itself has increased with the uses of fire and the application of energy. We may say, therefore, that the use and application of fire and energy serve to differentiate man from the brute. Some one has defined man as "an animal that cooks his food."

The ancients had some very strange notions concerning fire. While its benefits were appreciated, its real nature was not understood. "Its warmth was agreeable in wintry weather; it served as a guide through trackless forests; it was of use in repelling the attacks of savage brutes; from its heat food was prepared and made more digestible and appetizing; clay vessels were fired; and metals were reduced and fashioned into various objects. Truly, the burning forest, the lightning-flash, and the fiery volcano must have filled the ancients with awe and veneration. Fire was regarded as a divinity, and worshiped."

There was much speculation on the part of the early philosophers concerning the nature of fire. Heraclitus of Ephesus, an early Greek philosopher, thought fire was the substantial principle of all things,—the divine spirit,—while Aristotle considered it to be one of the elements. As stated before, Stahl, a German physician, believed that all combustible substances contained a fire-stuff or fluid, termed phlogiston, which escaped as

the bodies burned. When a metal was burned, phlogiston escaped and a calx was formed. To illustrate, the formula for the combustion of copper was as follows:

$$\text{Copper (burned)} = \text{Copper calx} + \text{Phlogiston}$$

It was known that the product weighed more than the substance which was burned, but it was argued that phlogiston was so light that it buoyed the body up; consequently, when it lost phlogiston, it weighed more!

After the discovery of oxygen, Lavoisier solved the mystery of combustion by proving that it is rapid oxidation accompanied by the evolution of heat and light. The absorption of oxygen therefore accounted for the gain in weight.

As to fire-making by man, it is very ancient. Fire was no doubt the first chemical agent employed by man. According to the calculations of H. F. Osborn, fire has been in use for sixty thousand years. Svante Arrhenius, in his "Chemistry in Modern Life," says:

> In the famous cave-dwellings of that early period at Krapena in Croatia, Dr. Kramberger Gorgjanovic has uncovered, among the many layers, one which consists of a great fireplace with a mixture of broken human bones, no doubt the remains of a cannibalistic banquet.

It may be that man first kindled fire by the friction of two pieces of wood. It is certain that the fire-drill is very old. It is still employed by the South Sea Islanders. The Greeks employed a burning-glass, a method mentioned by Aristophanes in "The Clouds"; and the story of Archimedes employing a mirror to set

on fire the ships of Syracuse is familiar to every one. The Romans used concave mirrors for starting a fire.

Another ancient method for starting combustion was by striking together flint and iron pyrites ("fire-stone") in the presence of tinder, a method still employed by the South Sea Islanders.

The friction match is quite modern, having been invented by John Walker of England a century ago.

Natural fires—*i.e.*, fires not kindled by man—have originated in various ways. For instance, in connection with volcanoes, earthquakes, lightning, meteorites, friction, etc. During the earthquake at Bavispe, Mexico, in May, 1887, fires originated from the friction of falling stones. The oil-wells at Baku, on the Caspian Sea, have burned for many centuries; and as early as 600 B.C. the "eternal fires of Baku" attracted the fire-worshipers.

A globule of dew or balsam has started fire by focusing the sun's rays upon very combustible material. More than a quarter of a century ago the writer was delivering a lecture on chemistry at Richmond, Kentucky, when his attention was attracted by smoke a few yards away. There was a flask of water standing on a wooden table in front of a window through which the sun was shining brightly, and the conditions happened to be so favorable for concentrating the sun's rays that the table was scorched.

A material catches fire in air when it is heated to its kindling temperature. Ignition temperatures of different substances vary within wide limits. Thus, white phosphorus ignites at 35° C., carbon disulphide at about 150° C., and ordinary gases at much higher

temperatures. The ignition-point of a substance is not very definite, for it depends upon certain variables, such as the fineness of material, pressure, catalytic agents, etc.

Certain substances—*e.g.*, phosphorus and hydrogen phosphide—catch fire spontaneously when exposed to the air; they have very low kindling temperatures. Why do coal, haystacks, and greasy or oily rags sometimes ignite spontaneously? In case the combination of the material with oxygen proceeds slowly and the material is so exposed to the air that the heat rapidly escapes, the temperature does not rise to the ignition-point; but if the material is so exposed to the air that the heat accumulates, the temperature may rise until the ignition-point is reached. Now, such materials as piles of rags are poor conductors; furthermore, certain oils and fats have a tendency to absorb and combine with oxygen, producing heat. If combination with oxygen proceeds until the kindling temperature is reached, the material bursts into flame.

The beach-wrecked carcass of the whale has been known to take fire spontaneously, due to the union of oxygen with fat; and it is not uncommon for coal to ignite spontaneously in bunkers.

The amount of property destroyed by fire is enormous.

It is well known that when certain gases or very finely divided substances are mixed with the proper proportions of air or oxygen, they will explode if the mixture be ignited by a spark, match, or otherwise. An explosion is due to very rapid combustion of certain gaseous mixtures, such as illuminating-gas and air, or

to finely divided organic matter—charcoal, coal, flour, starch, etc.—suspended in air. The ignition of the mixtures usually starts at one point, and the speed of explosive combustion increases rapidly.

Some terrific explosions have occurred in flour-mills and other factories; so to-day the modern mills are equipped with elaborate dust-removing installations; and machinery likely to develop sparks of electricity by friction is grounded. Seventy lives and seven million dollars' worth of property were lost in 1919 as the result of dust explosions in factories.

There are also explosions which result from the breaking down of unstable compounds such as TNT (trinitrotoluene) and nitroglycerine—the basis of dynamite.

5 Decay and Respiration

Oxygen plays an important rôle in change and decay. Carbon and hydrogen of vegetable matter are oxidized to water and carbon dioxide. We oxidize fuel in order to obtain energy to carry on most of the work of the world. The oxygen dissolved in water is very important in the disposal of sewage. The latter is mixed with large volumes of water, not simply to dilute the sewage but for the object of having it undergo oxidation by coming in contact with dissolved oxygen. In Los Angeles water is purified by aëration. The aqueduct discharges water from a tunnel down a rocky cascade, and it comes into contact with much oxygen while flowing into a storage-lake. Slow oxidation takes place in the bodies of animals. The oxygen of the inspired air combines with the hemoglobin in the red-

blood corpuscles to form an unstable compound (oxyhemoglobin) which circulates throughout the body and oxidizes the carbon and hydrogen absorbed during digestion, to water and carbon dioxide. During this oxidation process heat is given out, which is of the greatest importance in keeping the body warm. We may compare the body to an engine, the material of which is burned up (oxidized), in each case furnishing power. Oxygen is the very "breath of life."

The rusting of iron may be shown by sprinkling iron filings over the inside of a wet test-tube, and then inverting it over water. In the course of time about one fifth of the mixture of gases confined in the tube disappears, and water rises to take its place. This experiment not only proves what rusting is, but shows incidentally that about one fifth of the air by volume is oxygen.

Oxygen is not only the most abundant element but the most useful; for life, heat, and light are largely dependent upon it. Oxygen is of the greatest use in the disposal of sewage and in the oxidation of waste matter in general. Considerable quantities of oxygen are used for cutting and welding metals by the oxyacetylene, the oxyethylene, or the oxyhydrogen blowpipe; in aviation, in submarines, and in tunneling; in medicine for treating cases of pneumonia and of gas-poisoning, and to mix with nitrous oxide (laughing-gas) when it is administered as an anesthetic; for enriching air in the blast-furnace and the steel-converter; etc.

Aviators flying at great heights need more oxygen than they can obtain from the air; therefore they are supplied with cylinders of compressed oxygen and with

breathing helmets. This prevents their becoming "dopey." Self-contained oxygen-breathing apparatus is employed in fighting mine fires and in rescuing miners trapped by fire or by poisonous gases.

The speed of oxidation of materials or substances varies greatly. In some cases it is so slow as to escape detection by ordinary means; in other cases it is so rapid that it is pronounced combustion or even explosion. Speed of oxidation depends not only upon the nature of the substance but upon conditions—temperature, concentration, fineness of material, and catalytic agents. The effect of temperature, concentration of oxygen, and fineness of material are well illustrated in the case of iron. An iron bar rusts slowly when exposed to air, which is about one fifth oxygen by volume; but when a bundle of iron wire is heated to a high temperature in contact with oxygen, the metal burns brilliantly. Finely divided iron may be burned by sprinkling it in the flame of a gas-burner. When matter is finely divided, a large surface is exposed to air or oxygen, and the chances of the particles of oxygen and iron coming into contact are greatly increased. Every one knows the value of shavings in kindling a fire. Again, finely divided platinum (catalytic agent) will cause a mixture of oxygen and hydrogen to explode.

6 Ozone

Ozone, an exceedingly active form of oxygen, appears to be present in very small quantity in the atmosphere. It is probably formed during thunderstorms, due to the action of electricity upon oxygen;

also by the action of ultra-violet light-rays upon oxygen. When electric sparks are passed through air or oxygen, a peculiar odor is noticed, which is due to ozone (Greek: smell).

Ozone (ozonized oxygen) is formed by subjecting oxygen to the action of electric waves. Many types of apparatus have been used, but one of the most convenient is Siemens' ozonizer. Two glass tubes are arranged coaxially, the smaller one being coated within and the larger one without with an electric conductor (silver or tin-foil). Each coating is connected with a wire from an induction machine, and dry, cool oxygen, circulating in the space between the tubes, is subjected to the action of electric waves. Ozonized oxygen contains, as a rule, 6 per cent to 7 per cent by volume of ozone. To prepare pure liquid ozone, the mixture of oxygen and ozone is cooled with liquid air.

Ozone is a blue gas possessing a sharp odor. It may be condensed to an indigo-blue liquid, boiling at —119° C. The weight of a liter of ozone gas is 2.140 g., so its specific gravity is 1.5 times that of oxygen, both gases being measured at 0° C. and 760 mm.

Ozone is a more active form of oxygen. What, then, is the exact relation of these two substances? When the chemist examines carefully the formation of ozone from ordinary oxygen, he finds that the latter absorbs energy and that the action is *reversible:*

$$\begin{array}{lll} \text{Oxygen} + & \text{Energy} & \rightleftarrows \text{Ozone} \\ 3O_2 & + 61{,}400 \text{ calories} & \rightleftarrows \ 2O_3 \end{array}$$

Three molecules of oxygen yield two molecules of ozone, but in either case there are six atoms, so the

weights are the same. The oxygen molecule is a cluster of two atoms, while the ozone molecule is a cluster of three atoms.

Ozone is a powerful oxidizing agent, attacking rubber, mercury, and even silver. The chief use of ozone is for the purification of water, mostly in European cities. The gas is bubbled through the filtered or settled water, in a long column. It is also used for the purification of the air of railway tubes, animal houses of zoölogical gardens, etc.; for bleaching-oils, waxes, ivory, flour, and starch. It is a good deodorizer and it oxidizes moist organic matter into harmless substances.

The relation of ordinary oxygen to ozone is an interesting one, for here is a case of two different substances containing only one elemental form of matter. In other words, there are two forms or modifications of the element oxygen. Substances thus related are called allotropic. Allotropy, as the term is ordinarily employed, may be defined thus: *That property by virtue of which one element may exist in two or more forms possessing different amounts of available energy (hence different properties) is called allotropy* (Greek: another way or mode). There are a number of common examples of allotropic forms: e.g., charcoal, the diamond, and graphite are carbon; white and red phosphorus. The less common form is sometimes called an allotropic modification of the other.

CHAPTER VI

THE SECRET OF THE FIREFLY: COLD LIGHT

The fireflies o'er the meadow
In pulses come and go.
—LOWELL.

Those who have seen the brilliant flashes of innumerable fireflies, filling the fields on a mid-summer night, or the sea a vivid sheet of flame when disturbed by some passing ship, cannot but marvel at the display. Slow is the imagination which will not inquire how and why this light is emitted, or whether we may not some day successfully develop a "cold light," modeled on Nature's plan.—E. N. HARVEY.

1 LIGHT-GIVING ORGANISMS AND BODIES

THE production of light by living creatures, such as the firefly, the glow-worm, and certain varieties of squid and fish, is known as bioluminescence; and since the light is accompanied by very little heat, it is called cold light. The quest for heatless illumination is a fascinating one, for cold light is efficient. If we can learn completely the secret of the firefly, we may be able to produce light at a price below that of warm light. At present the consumer of electricity for the production of light pays not only for the light, but also for the wasted heat which always accompanies light.

The bodies of animals are marvelous mechanisms, for living creatures possess methods of transforming matter and of producing heat and in certain cases light

and electricity as well. The processes differ from those of the furnace, the lamp, or the dynamo. During the life of an animal a steady fire burns within its body, with efficient heat-regulation, making the creature quite independent of cold. The firefly, or lightning-bug, is able to flash its light, luminescent bacteria shine with a steady glow, while electric fish can generate electricity enough to ring a door-bell. There are a great many luminescent organisms. At least forty orders of animals contain one or more light-producing forms, and two groups of plants—fungi and bacteria—are known to be luminescent. Among light-producing animals are fireflies and glow-worms, jellyfish, brittle-stars, mollusks, squid, and fish. Even the eggs of some animals are luminous. Light-producing animals are never found in fresh water; they are all either marine or terrestrial organisms. The great majority of luminescent marine forms are deep-sea animals. In 1810 a man named McCartney presented a paper to the Royal Society of London in which he concluded that the phosphorescence or "burning of the sea," which has been frequently observed, is caused by animals living in it. This conclusion of McCartney's proved to be correct. The so-called phosphorescence of the sea is always due to the presence of luminescent animals, most of which are microscopic.

It is well known that the glow of damp wood (called colloquially fox-fire) is due to fungi, a low order of plants to which mold and mildew belong; while the phosphorescence of dead meat or fish, sometimes observed in refrigerators, is caused by bacteria. The number of species of luminescent animals runs

into the tens of thousands. The light produced by dead fish was known to Aristotle, while both Aristotle and Pliny mention the glow of damp wood. It is only since the perfection of the microscope, however, that the phosphorescence of the sea, the shining of damp wood, and that of dead fish and meat have been proved to be caused by different forms of living things.

It is of interest to note that there are certain light phenomena which are not connected with living things. Thus, St. Elmo's fire, or the corposants of English sailors, is a glow which accompanies a slow brush discharge of electricity. This glow may be seen as a tip of light on masts of ships, particularly in winter during and after snow-storms.

The ignis fatuus (Latin: *ignis*, fire + *fatuus*, foolish), popularly called Will-o'-the-wisp, or Jack-o'-lantern, is a phosphorescent light that appears, in the night, over marshy grounds or stagnant pools. The pale bluish flame may be fixed or it may move from place to place. According to one theory, the light is due to the spontaneous combustion of phosphine (PH_3 and P_2H_4); but the production of phosphine is not known to accompany the decay of the vegetable matter of swamps. Another theory is that the phenomenon is caused by the combustion of marsh-gas or methane (CH_4), which is formed when organic matter decays. While methane burns with a pale bluish flame, it is not spontaneously inflammable; so it is not at all likely that this theory is correct. It may be that the phenomenon is electrical in nature.

Scientists make a distinction between incandescence and luminescence. An incandescent body—*e.g.*, a fila-

ment of an electric-light bulb—gives off much heat as well as light. Incandescence is a light which accompanies a high temperature—"hot light." In the production of light by means of incandescent bodies much energy is dissipated as heat. Certain forms of life are able to produce light without any appreciable accompaniment of heat, and are said to luminesce. Luminescence, as used in this connection, is therefore a light which is produced at a comparatively low temperature—"cold light."

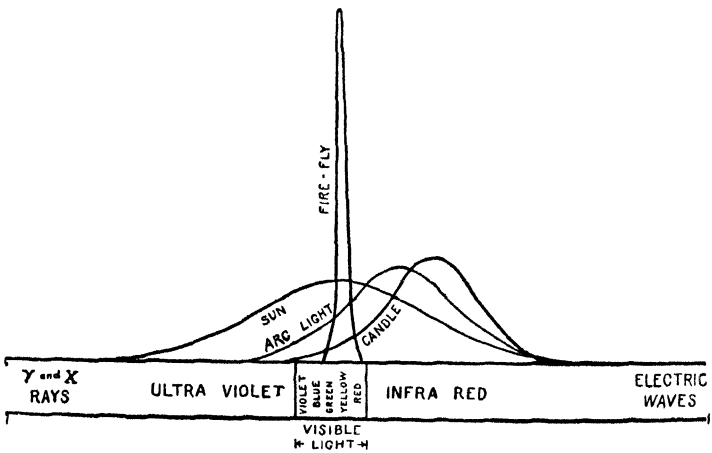
It might be well to state that animal light is not a fluorescence or a phosphorescence. When certain bodies are illuminated, they have the property of absorbing radiant energy of definite wave-lengths and of emitting this energy as waves having lengths entirely different from those which are characteristic of the exciting radiation. In case the body ceases to emit light after the illumination is cut off, it is said to fluoresce. Kerosene and uranium glass are fluorescent substances. In case the glow continues after illumination has ceased, the substance is said to phosphoresce. Thus, impure sulphides of calcium, strontium, barium, and zinc (CaS, SrS, etc.) phosphoresce for some time after exposure to strong illumination, such as sunlight. These sulphides have been employed in the production of luminous paints.

Fluorescence and phosphorescence are, therefore, essentially the same phenomenon, being differentiated only by persistence of luminescence.

It should be noted that bioluminescence (phosphorescence) has nothing to do with phosphorus.

2 Light-Waves; Low-Temperature Light

According to the physicist, light is believed to be due to a succession of wave-pulses produced in the ether by vibrating electrons, which are constituents of all atoms. Every solid body, provided its temperature is



Courtesy of Charles Scribner's Sons, New York

Figure 7

A schematic drawing of various kinds of radiant energy and the relative amount of the various kinds in the sun, arc, candle, and firefly light. The horizontal parallel lines represent the radiant energy of various wave-lengths broken up in the great spectrum of which the visible wave-lengths occupy the middle region. The curves show the properties of various wave-lengths present in the same amount of radiant energy from the four types of illuminants. Note that only visible wave-lengths are present in the firefly. X-rays, gamma-rays of radium, and electric rays are of the same nature as visible light, but the wave-length is different, very short in the case of X-rays and gamma-rays, and very long in wireless electric waves. —*From "Scribner's Magazine," Sept., 1922.*

above absolute zero (—273° C.) is giving off waves of different lengths, which travel at the same velocity

in vacuo, namely, 186,000 miles a second. If we represent the velocity by the symbol c, the wave-length by λ and the frequency by ν, we have

$$c = \lambda\nu$$

A wave is characterized when its length is known, for the velocity (c) is constant. (Figure 7.)

Bodies at relatively low temperatures give off long waves, which are known as heat-waves; they produce the sensation of warmth, but are not visible. With rise in temperature, however, the waves become shorter and shorter. In general, if the temperature is below 525° C., the body does not glow. When a solid body such as iron or platinum is heated to about 525° C., it becomes faintly red; *i.e.,* it gives off waves which are short enough to be detected by the eye. The length of this wave (λ) = 0.76 μ, in which μ = 0.001 millimeter,* known as a micron. As the temperature of a body rises, it emits light-waves of shorter and shorter length, as well as the longer heat-waves. At 900° C. the body changes to cherry red, at 1300° it becomes white-hot, while at 1400° or above it is blue-white. Above $\lambda = 0.4\mu = 4000$ Å, the waves are invisible, being known as ultra-violet rays. The lengths of these rays are from 4000 Å to 320 Å. The ultra-violet rays are of great aid in the treatment of certain diseases, as we shall see in a later chapter. They pass through clear fused quartz, which is now produced commercially, but

* It is now customary to express wave-lengths in *Angstrom units.* 1 micron (μ) = 0.001 mm = 1000 millimicrons ($\mu\mu$) = 10,000 Ångstrom units (Å). One Ångstrom unit = 10^{-8} centimeters = 10^{-7} millimeters, or one ten-millionth of a millimeter (1/10,000,000 mm.). 0.76μ = 7600 Å. There are 25.4 millimeters in an inch.

are stopped by ordinary window-glass. The infra-red rays are also invisible, but their waves are longer than those of visible light. The Röntgen rays, or X-rays, as well as radium rays, have wave-lengths shorter than the ultra-violet. The Hertzian electric waves, which are used in wireless telegraphy, are much longer than the other rays. The entire scale of wave-lengths extends from 10^{6} to 10^{-9} centimeters. A white-hot object emits radiant energy of many different wave-lengths, some of which produce heat, others light, and others (actinic rays) affect the photographic plate. But in order to produce the sensation of light, or to give visible radiation, the wave-lengths must run from 7600 Å to 4000 Å.

Some bodies give off light much below 525° C.—*i.e.*, below the temperature of incandescence. These bodies, as we have already seen, are said to be luminescent, and in this category belong luminous organisms such as the firefly and the glow-worm.

The production of light during a chemical change at low temperature is called chemiluminescence. Certain changes of this type depend upon the union of the substance with gaseous or dissolved oxygen, and may therefore be termed oxyluminescence. The glowing of phosphorus is the best-known example of chemiluminescence; it is slow oxidation.

According to a recent statement in "Science," chemiluminescence is the term applied to a new kind of light caused by chemical reactions which involve no burning or combustion. The practical application of this principle, according to advices received in London, has been worked out in a factory in Hungary,

where a tube has been devised in which chemiluminescent reactions can be carried out in a vacuum,

The materials which have thus far proved most successful in this capacity are chlorine gas and sodium vapor. These two elements brought together in this form combine to produce sodium chloride, or common table salt, giving off in the process a brilliant yellow light. About one tenth of the energy involved in this reaction is converted into light.

It is expected that such tubes will find practical use for special scientific experiments and among surgeons, due to the fact that the light they give off is of only one color, and not composed, like ordinary daylight, of all the colors of the spectrum.

3 Luminous Creatures and Their Organs

The light of luminous organisms is not essentially different from other light, except in mode of production. The spectrum of the firefly lies entirely within the visible range. The spectra of luminous animals are similar to those produced by chemiluminescent change. In general, luminous animals depend upon oxygen for light-production, the light being due to the oxidation of some substance produced in the cells; therefore, chemiluminescence and bioluminescence are similar phenomena.

Many false reports of luminous organisms have been made, so great care has to be exercised to discover the luminous form among a large number of non-luminous forms. It is a well-known fact that all luminous organisms, with the exception of fungi, bacteria, and

a few fish, flash only when stimulated, the animal being lost to view between flashes. If, however, a little ammonia be added to the sea-water, the organisms slowly die, and any luminous forms glow with a steady light. It should be borne in mind that non-luminous forms may become infected with luminous bacteria, in which case the luminescence is purely secondary. E. N. Harvey tells the following remarkable story concerning a luminescent frog:

> I remember once while collecting luminous beetles in Cuba, I was astounded to find a frog which was luminous. Expecting this animal to be of great interest, I examined it further, only to find that the frog had just finished a hearty meal of fireflies, whose light was shining through the belly with considerable intensity.

Before the time of aseptic and antiseptic surgery, it was not uncommon for wounds to glow at night, due to the presence of luminous bacteria; and it was believed by surgeons of that period that luminous wounds were more apt to heal. There may be some foundation for this view, owing to the fact that luminous bacteria are not the cause of disease, and it seems possible that such bacteria may have crowded out the pathogenic organisms. According to Robert Boyle, no harm has come from eating luminous meat which was free from disease-producing organisms.

Various forms of luminous organisms have been carefully studied in the attempt to solve the mystery of cold light, among which are bacteria, fireflies, squid, fish, and a little form called cypridina. Luminous bacteria have the advantage of emitting a steady light,

but they are the smallest luminescent creatures, a single organism having a diameter of perhaps one twenty-five-thousandth of an inch. Luminous bacteria are so small that it is not possible to see the light from a single individual.

The firefly season is not long enough to supply material for the year round. It has been discovered, however, that the firefly can be dried, and when the dried material is moistened, the glow returns. In Japan fireflies may be bought in large quantities. The schoolchildren collect the flies by the thousand, and in the evening on certain days of the year the insects are released and rise in the air, filling it with a marvelous, flitting glow. The whole population turns out on the lakes in boats and punts to take part in these firefly festivals. While fireflies possess more cold light than bacteria, they are not very satisfactory for experiment.

Squids also are plentiful and cheap in Japan. From these the light-giving tips are cut off and investigated.

The most important luminous animal in Japan is the above-mentioned cypridina, a tiny crab-like creature about one eighth of an inch long. The cypridina, like the clam, has a shell. This organism has been most helpful in the study of cold light.

Luminous fish and a luminous centipede are found in the East Indies. Some of the luminous organs of animals are most interesting from a structural standpoint, for they are veritable lanterns. They have been quite thoroughly investigated by Professor Ulric Dahlgren of Princeton University. In many respects a luminous organ resembles an eye. Both contain a lens, but that of the luminous organism is employed in directing

the light, while the lens of the eye receives light and converges it on the retina. The production of light is, therefore, the converse of the detection of light. Some luminous organs are provided with reflectors which throw the light forward and out through the lens. Since strong light tends to destroy living tissue, some luminous organs are provided with screens also, which protect the tissues from the strong light of the organism. Some organs have color-screens, which allow only light of certain wave-lengths to pass, giving rise to different colors, such as blue, violet, and red. It is reported that a certain South American insect has not only white luminous organs but red ones as well; and since the white lights are at the head of the insect and the red ones at the tail, it is known as the "automobile bug."

Two luminous fishes in the Dutch East Indies have developed a large organ, just under the eye, which is designed for the support of luminous bacteria. These bacteria live in companionship with the fish, and will not grow anywhere else; for this reason they are called symbiotic bacteria. The partnership is a most interesting one, for the fish are supplied with light, while the bacteria in turn have free board and lodging. Now, luminous bacteria shine continually; therefore these fish have developed a screen to cut off the light. The screen consists of a fold of black pigmented skin, which can be drawn over the luminous organ to shut off the light. Owing to the resemblance of the screen to an eyelid, the fish is called photoblepharon (Greek: light eyelid). According to Harvey, the fishermen of Banda cut off these luminous organs and, removing the screen,

use them on hooks for bait. The cypridina has a gland near its mouth which produces the light it emits. In general, the light of luminous organisms is associated with granules.

4 The Use of the Light of Organisms

There has been a good deal of discussion concerning the use of the light of luminous organisms. In certain cases the light may be of no use whatever, as in luminous bacteria, fungi, and certain marine forms. It appears that their existence is not dependent upon luminescence.

The light may serve as a warning to scare away animals which would otherwise prey upon the luminous creatures. The sea-pens, for instance, live in the mud or sand at the bottom of the sea, and it has been conjectured that they flash on their light for self-protection when fish come along. It may be that animal light is employed in certain cases as a lure to attract other forms of life on which the luminous animals prey; but this also is a mere guess.

There is along the Italian coast a squid, the heteroteuthis, which throws out a luminous secretion. This secretion is produced in a gland corresponding to the ink-sac in which the surface squid or cuttlefish produces the blackest fluid known. It is startling to see the cuttlefish surround itself with a jet-black fluid; but it is marvelous to see the heteroteuthis envelop itself in a cloud of "fire," which glows in sea-water for some time.

Certain fish possess luminous organs which "are ar-

ranged in rows on the sides or bottom of the fish, giving it the appearance of a ship with all its port-holes illuminated. Sometimes the organ is dangled on the end of a stalk projecting from the head of the fish, a Diogenes of the deep in search of an honest meal." It is possible, then, that certain animals use their luminous organs as lanterns or search-lights. Most of these forms are found in the depths of the sea, where there is perpetual darkness.

Finally, the light may serve as a means of recognition or a sex signal to bring the sexes together for mating. This is true in the case of the firefly. Indeed, each species of firefly has a peculiar light, which is recognized by an expert.

It is also interesting to know that luminous organisms have been utilized by man. For instance, tropical fireflies are used by the natives of the West Indies and South America for adornment and for bait in fishing; also, luminous bacteria have been employed for certain purposes in the laboratory. "Bacterial lamps" have been prepared, but they are too feeble to be of practical use.

5 The Secret of Cold Light

Considerable progress has been made in finding out the chemical nature of animal luminescence.

Our chemical knowledge of luminescence has advanced in four important steps:

(1) Robert Boyle, in 1667, placed a small piece of luminescent wood in an air-pump and found that it ceased to glow when the air was removed, and reap-

peared when air was admitted again. Luminescence, therefore, occurs in the presence of oxygen.

(2) Lazaro Spallanzani, an Italian, discovered in 1794 that all luminescence required water. When luminescent tissue is dried rapidly, it can be preserved for a long time; but when water is added, the light reappears.

(3) The Frenchman R. Dubois showed in 1865 that two substances (in addition to oxygen and water) are necessary in the production of luminescence—luciferin and luciferase. The former is oxidized in the animal (or plant), and the latter is a catalytic enzyme which induces oxidation.

(4) When luciferin is oxidized to oxyluciferin, light is produced. E. N. Harvey has shown that the oxyluciferin is then reduced—*i.e.*, loses oxygen—to form luciferin. When the firefly flashes its light, oxyluciferin is produced; but between flashes oxyluciferin is reduced to luciferin. The reaction is reversible and is essentially as follows:

$$\text{Luciferin} + \text{Oxygen} \rightleftarrows \text{Oxyluciferin} + \text{Water}$$

Note that this is a very economical process, for the animal first burns an "oil," which is re-formed between flashes, ready to be re-burned; or, as Harvey says, "Like the Phenix of old, luciferin is recreated from its ashes to pass through the cycle of another life."

Luciferin and luciferase can be prepared and experimented with like any other chemical substances, but their exact structure is not yet known. Luciferin appears to be one of the simpler members of the proteins, such as the peptones or proteoses; while lucif-

erase is related to the albumins. In case chemists should succeed in synthesizing proteins and discovering the structure of their molecules, it is quite likely that they would be able to produce the substances concerned in the production of luminescence, and this would perhaps lead to heatless illumination. Ceilings might be painted with the luminescent material, and when darkness fell the paint would begin to glow. By increasing or decreasing the painted area, the light could be made stronger or weaker. Just as different organisms give off light of different colors, different lights might be produced by artificial means; and the light could be regulated by means of screens or coverings. Heatless light would be most welcome in hot weather. When the chemist can write the structural formula—*i.e.*, the arrangement of the atoms in the molecule—of the photogenic substance found in the cells of living organisms and explain exactly how its oxidation is produced, the problem of light-production by living creatures will be solved; the secret of the firefly will be known. This seems quite as reasonable as the aëroplane and the automobile seemed fifty years ago.

CHAPTER VII

HYDROGEN AND WATER

Water is the mother of the vine,
The nurse and fountain of fecundity,
The adorner and refresher of the world.
—CHARLES MACKAY.

1 HYDROGEN

HYDROGEN is the lightest substance known, and its atom, represented by the symbol H, is the simplest, consisting of one proton and one planetary electron. If we arbitrarily fix its atomic weight as 1, that of oxygen is nearly 16.

The English chemist Henry Cavendish established the elementary nature of the gas in 1766, just eight years before Priestley discovered oxygen. Subsequently, Cavendish burned hydrogen in air and proved that water was the sole product; hence Lavoisier named the element hydrogen, from two Greek words meaning water-producer.

Hydrogen occurs very widely distributed in nature. In the free state it is present in certain volcanic exhalations and in the intestinal gases of many animals; it is also a component of illuminating gas and of water-gas. The spectroscope reveals the presence of hydrogen in the sun and in most stars. The chromosphere of

the sun, a region of the sun's gaseous envelop which lies close above the photosphere, owes its name to the fact that as seen for an instant, during a total eclipse, it is of a bright scarlet color, the color being caused by glowing hydrogen which is one component of the chromosphere. According to C. A. Young, it is from five thousand to ten thousand miles thick, and in structure is very like a sheet of scarlet flame. Its appearance has been compared to that of "a prairie on fire."

In the combined state hydrogen constitutes over 11 per cent of water, and it is an essential constituent of all acids, hydrocarbons (compounds of hydrogen and carbon only, such as methane and benzene), and of such compounds as the sugars, the alcohols, starch, and cellulose.

Hydrogen is prepared from water or acids. Some of the hydrogen for industrial uses is obtained by the electrolysis of water. When sodium hydroxide, or caustic soda, is added to water contained in an iron tank and a current of electricity passed through the solution, hydrogen is liberated at the cathode and oxygen at the anode. Hydrogen is obtained as a by-product when a solution of common salt, or brine, is subjected to electrolysis.

When the alkali metals sodium and potassium are brought into contact with cold water, hydrogen is evolved with great energy. The gas is also liberated when steam is passed over hot magnesium or iron, the metal uniting with the oxygen of water to form an oxide. Heated magnesium will burn, therefore, in the presence of steam. Hydrogen for industrial use is prepared by passing steam over red-hot iron:

Iron + Steam = Magnetic oxide of iron + Hydrogen

The active and moderately active metals, such as magnesium, iron, and zinc, interact with dilute acids to form hydrogen. The metals commonly used are zinc and iron, and dilute sulphuric or hydrochloric acid is generally employed. The hydrogen of the acid is displaced by the metal. For experimental work zinc is usually treated in a small bottle with sulphuric acid. The acid is poured through a funnel-tube, and a delivery-tube leads from the generator to the water-pan, or pneumatic trough, where the gas is collected over water as in the case of oxygen. All joints must be fitted carefully, for a mixture of hydrogen and air explodes violently when ignited!

Hydrogen is a colorless, odorless, tasteless gas. An equal volume of air weighs about 14.4 times as much as hydrogen. The extreme lightness of the gas may be shown by pouring it upward from one vessel to another. As hydrogen is combustible, the gas poured upward may be ignited by bringing a burning taper to the mouth of the inverted vessel.

Owing to its extreme lightness, hydrogen has been long used for inflating balloons. For instance, the ZR-3, now the *Los Angeles,* one of the world's biggest airships, was inflated with hydrogen before sailing from Germany, in October, 1924. This enormous Zeppelin landed at Lakehurst, New Jersey, having covered five thousand miles in eighty-one hours. Due to the great inflammability of hydrogen, helium is sometimes substituted for it in airships. This extraordinary gas was discovered in the sun in 1868, and owes its name to a

Greek word, meaning the sun. The red "flames" which are so prominent during a total eclipse of the sun consist of hydrogen and helium.

The gas-fields of the Southwest are the chief source of helium, the Petrolia fields of Texas yielding about 1 per cent. The inflammable components of the natural gas are liquefied by means of liquid air, the helium remaining gaseous. Helium is non-inflammable and has about 92 per cent of the lifting power of hydrogen for a balloon floating in air. A few years ago helium cost about two thousand dollars a cubic foot, but now the price is only a few cents per cubic foot, which is, of course, much more expensive than hydrogen.

When hydrogen gas is subjected to a very low temperature and high pressure, it forms a colorless liquid which boils at —252.5° C., and when the liquid is allowed to evaporate rapidly it freezes to a white solid, melting at —259° C. Many marvels of low temperature may be produced by the application of liquid hydrogen. All other known gases, except helium, solidify easily when led into a vessel surrounded by liquid hydrogen. Liquid helium has the lowest boiling-point (—268.5° C.) of any known substance, being within 4.5° C. of absolute zero.

When hydrogen is allowed to impinge upon finely divided platinum exposed to the air, so much heat is generated by the absorption of the gas that it catches fire. This is the principle involved in the construction and action of the Döbereiner lamp and of certain automatic cigar-lighters.

When pure hydrogen burns in air or oxygen, water is produced. This may be shown by allowing a jet of

burning hydrogen to impinge upon a glass flask or beaker containing cold water. Water condenses upon the surface of the cold vessel. When hydrogen burns, an immense quantity of heat is liberated. The heat of the oxyhydrogen blowpipe is so intense that platinum (melting-point 1740° C. = 3364° F.) may be readily melted, and a steel spring burns brilliantly in the flame. The oxyacetylene blowpipe or torch has largely displaced the oxyhydrogen blowpipe, for the temperature is much higher—about 3300° C., or 5972° F., which is only a few hundred degrees below that of the electric furnace or arc. The oxyacetylene flame is employed extensively for cutting and welding metals. For example, it is used for welding pipe-lines and for cutting thick armor-plate. It will cut through sixteen-inch metal plate quite as readily as a saw cuts wood.

In this connection it is of interest to note that Dr. Irving Langmuir, of the General Electric Company, is able to produce atomic hydrogen (H) by passing ordinary hydrogen (H_2) into an electric arc. When the monatomic hydrogen is burned, it yields a flame with an extremely high temperature, even higher than the oxyacetylene flame, which will be of very great value in welding metals. Minute flames of atomic hydrogen can be produced and maintained, thus making it possible even now to weld sheets of metal as thin as five one-thousandths of an inch.

According to Langmuir, iron can be melted in the flame of atomic hydrogen without contamination by carbon, oxygen, or nitrogen. As atomic hydrogen has reducing action,—*i.e.*, a tendency to remove oxygen,—alloys containing chromium, aluminium, silicon, or

manganese can be melted without fluxes and without surface oxidation. The oxyethylene flame is also excellent for cutting and welding metals.

When hydrogen is passed over certain hot oxides of metals, the oxides are robbed of oxygen, forming metals and water. We say, therefore, that hydrogen is a reducing agent, because it robs certain compounds of oxygen. Thus, when hydrogen is passed over black copper oxide (CuO) the oxide is reduced to the red metal, copper, accompanied by the formation of water:

$$\text{Copper oxide} + \text{Hydrogen} = \text{Copper} + \text{Water}$$

Reduction is the converse of oxidation.

Much hydrogen is now used for transforming certain liquid fats, or oils, into solid fats. To illustrate, when cotton-seed oil is treated with hydrogen, in the presence of such a catalyst as finely divided nickel, the oil combines chemically with the gas to form a solid fat. Large quantities of Crisco are produced by the chemical addition of hydrogen to vegetable oils, the process being known as hydrogenation.

The manufacture of solid fats is a safeguard against a shortage of such food in time of war, and is one of the triumphs of catalysis in modern chemistry.

2 Water and Its Properties

We have seen that water may be synthesized by burning hydrogen or by reducing hot copper oxide by hydrogen. Water may also be synthesized by passing an electric spark through a mixture of hydrogen and oxygen. This experiment was performed as far back as

1781 by Cavendish, who passed a spark through a mixture of the two gases which were contained in a long graduated glass tube fitted with platinum terminals at the top, the lower end of the tube being immersed in mercury. The tube is called a eudiometer (Greek: *eudios,* fine air + *metron,* a measure).

Careful experiments show that two volumes of hydrogen combine with one volume of oxygen to form water. If this experiment be performed in a eudiometer incased in a steam-jacket, it is found that the volume of steam produced in the eudiometer is equal to the volume of hydrogen and to double the volume of oxygen used up. This fact may be summarized thus:

Hydrogen	+	Oxygen	=	Steam
2 volumes		1 volume		2 volumes

This is a good illustration of the law of Gay-Lussac, which was enunciated in 1808: *When gases combine chemically, they do so in volumes which bear a simple ratio to one another, and to the volume of the product, if gaseous.*

Shortly after the discovery of Gay-Lussac's law, Avogadro propounded his hypothesis, which runs as follows: *Equal volumes of different gases at the same temperature and pressure contain an equal number of molecules.* This hypothesis is now accepted as a law, and is one of the most important principles of chemistry. It means that equal volumes of such gases as oxygen, hydrogen, and carbon dioxide contain an equal number of molecules. Nature, therefore, appears to assign the same average space to gaseous molecules no matter what their nature may be.

Hydrogen forms two oxides—hydrogen monoxide or water, H_2O, and hydrogen dioxide or peroxide, H_2O_2.

Water is the most abundant and useful hydrogen compound. It covers about three fourths of the earth's surface, the greatest depth of the ocean being about six miles. It is an important component of the air, and even "dry" land contains considerable quantities of water. It constitutes about 62 per cent of beef, 87 per cent of milk, 92 per cent of watermelons, and 95 per cent of cucumbers. When we buy normal milk, we pay for about 87 per cent of water.

The presence of water in organic matter may be shown by heating pieces of apple or potato in a clean test-tube.

Pure water is a clear, tasteless, odorless liquid; it is colorless in moderate quantity, but possesses a bluish-green color when viewed in bulk. Water is a poor conductor of electricity and leaves no residue when evaporated to dryness. As natural water contains matter in solution, it is a conductor of electricity and leaves a residue upon evaporation. We often experience a shock when we touch an electric wire with wet hands.

When water is heated or cooled at temperatures above 4° C., it follows the general law that bodies expand when heated and contract when cooled. When cooled from 4° to 0°, it expands. On being heated from 0° to 4°, water contracts, reaching its maximum density at 4°. One cubic centimeter of water at 4° C. weighs one gram, which is the unit of density. The abnormal behavior of water between 4° and 0° has a marked influence upon climate and therefore upon life. If water followed the general law of liquids be-

tween 4° and 0°, our large bodies of fresh water would be converted into solid masses of ice during long, cold winters, which the warmth of summer would not be sufficient to melt.

The amount of heat required to raise one gram of water 1° C. is called a calorie; therefore, when one gram of water cools one degree, a calorie is liberated. This means that when large bodies of water cool down, much heat is liberated, which tempers the climate in the vicinity of the ocean.

Water has a powerful solvent action upon many substances, being the best solvent known to man. Some solids, such as sugar and salt, are very soluble in water; others—*e.g.*, sea-sand and silver chloride—are so slightly soluble that they are called insoluble substances. There appears to be no material or substance absolutely insoluble in water, even finely divided glass, quartz, gold, and platinum dissolving in minute amounts. In general, water is a better solvent for inorganic compounds than for organic. Ether, the alcohols, carbon disulphide, and benzene dissolve many substances which are virtually insoluble in water. For instance, ether is a good solvent for fats and oils, the alcohols for resins, and carbon disulphide for phosphorus.

A solution is homogeneous to the eye,—*i.e.*, one portion is like any other portion,—but it may, of course, be highly colored. A small crystal of potassium permanganate will color several gallons of water a fine purple. Exceedingly minute quantities of dyes have very great coloring power. Arrhenius relates the following amusing incident:

The late Emil Fischer, German chemist of considerable fame, in fact a scientist who contributed more than any other of his day to the development of organic chemistry, at one time worked with various fluorescin dyes. In this period he once went to a public bath and took a dip in the big swimming-pool. As he left the water he overheard other bathers complaining of the dirtiness of the water of the pool. It had acquired a powerfully fluorescent yellow-green color. Fischer, who believed that the color must have come from some flecks of fluorescin which had probably fallen in his hair while in the laboratory, forebore from giving any scientific explanation to the group—and he suddenly decided to return to his laboratory as soon as possible.

3 Natural Waters; the Purification of Waters

No water found in nature is pure. When rain falls, various gases and solids are dissolved, and insoluble matter, such as particles of dust, pollen grains, bacteria, etc., are carried down. Moreover, when water percolates through the soil it has a solvent action upon the various substances, such as limestone and calcium sulphate. The water finding its way into the rivers, lakes, and ocean contains not only matter in solution but suspended matter. Even clear spring-water and rain-water are not pure. The impurities found in water can be divided into two classes: mechanically suspended impurities and soluble impurities. Suspended impurities may be removed either by filtration or by allowing the suspended matter to settle.

On a large scale, the process of filtration is carried out by means of beds of sand and gravel (Figure 8). Most of the suspended matter, including bacteria, is removed.

The household filters which were formerly used extensively are not very efficient in removing disease-producing organisms. Boiling the water for ten or fifteen minutes is much more effective. If necessary, the water can be boiled a second time.

Water is also run into large settling-tanks, and small amounts of alum or other substances are added. A slimy precipitate is formed; and suspended matter, including microörganisms, attaches itself to the gelati-

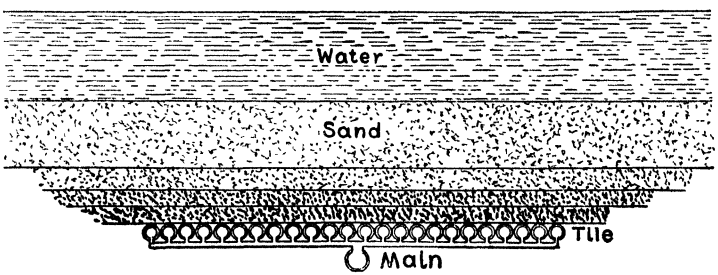


FIGURE 8
Filtration of Water

nous precipitate and is finally carried to the bottom of the tank.

Even after filtration or the coagulation treatment, water still contains some bacteria. To make it safe for drinking, small quantities of germicides are added, such as chlorine or bleaching powder. Water is also treated with ozone and ultra-violet light. Water may be purified by distillation. The Liebig still is quite generally employed in laboratories for distilling liquids.

Waters containing soluble impurities may be divided into soft and hard waters. Soft waters are comparatively free from mineral salts. They are found in dis-

tricts where sand, sandstone, and quartz occur. Soft waters form a lather readily with soap. This is well illustrated in rain-water. Hard waters contain in solution such mineral salts as those of calcium and magnesium. They occur in limestone and dolomite districts; also where gypsum is found. Hard waters are objectionable, for they consume large quantities of soap and often form boiler-scale, which means that a larger amount of fuel is required to generate steam. It has been estimated that a layer of scale one quarter of an inch thick on the boiler tubes requires 50 per cent more fuel in generating steam. It is difficult to remove boiler-scale; and now and then the thick scale cracks, thus exposing very hot iron to steam, causing an explosion.

Waters containing in solution the bicarbonates of calcium and of magnesium may have the "hardness" removed by boiling, the metals being thrown out of solution in the form of carbonates.

When water comes into contact with gypsum (calcium sulphate), it becomes "permanently" hard, for the salt cannot be removed by boiling the water. Such waters are particularly objectionable in industrial operations, for calcium sulphate forms a very hard, porcelain-like scale. Permanently hard waters are softened by chemical means.

In early times the laundress by the river softened the water and cleansed her clothes by the addition of wood-ashes and soap, but without any knowledge of the chemical principles involved. Dr. Thomas Clark, an English chemist, treated water with lime in order to remove calcium and magnesium carbonates. Subse-

quently, Dr. J. H. Porter, another chemist, treated water with washing-soda, or sodium carbonate, in order to remove the permanent hardness. In this case the sulphate of calcium interacts with sodium carbonate to form the insoluble carbonate of calcium.

The permutit process is a modern one for softening water. The water is filtered through the permutit, an artificial preparation which is employed in the form of coarse sand. When the permutit has been used for twelve hours, it is covered with a 10-per-cent solution of common salt and allowed to remain out of use for another twelve hours, after which it is ready for further employment. It is claimed that the life of a charge is over twenty years. Permutit is a complex sodium silico-aluminate. When hard water filters through it, the calcium and magnesium of the hard water are exchanged for sodium.

Effervescent waters are rich in carbonic acid, so when the gas escapes the waters are said to effervesce. The Seltzer and Apollinaris waters are well-known examples.

Sulphur waters contain hydrogen sulphide (H_2S) and other sulphur compounds: *e.g.*, the White Sulphur Springs and the waters of Harrogate. They possess a disagreeable odor and are used for skin disorders.

Alkaline waters contain very appreciable quantities of such salts as sodium bicarbonate, sodium chloride, and sodium sulphate. Large quantities of Vichy waters (France) are used in the treatment of certain diseases, such as acidosis. The alkali salts neutralize the acids of the body. The temperature of the springs at Vichy is about 45° C., or 111° F.

A pure water-supply is essential for the health of a city or community. In recent years so much attention has been given to the subject that typhoid fever is almost negligible in large cities. Water which is apparently pure may contain disease-producing organisms, germs of typhoid, cholera, or anthrax. To insure its purity, water for drinking should be examined frequently by the biologist and the chemist. The object of a bacteriological examination is to detect the numbers and kinds of organisms present. The detection of disease-producing organisms is a matter of considerable difficulty. Such an examination of water is valuable chiefly as a test of the efficacy of the processes used in its purification.

Chemical analysis of a water is more rapid than a bacteriological examination, and, while it leaves much to be desired, it affords valuable indications. Thus, if a water contains much nitrogen either in the form of albumin or albuminous matter or as decomposition and oxidation products—ammonia, nitrites, or nitrates —it shows pollution with animal matter, likely sewage. A high content of chlorine as sodium chloride usually indicates sewage pollution. Wherever animal matter or sewage is present, disease-producing bacteria may be present also.

Boiling water for a few minutes greatly diminishes the number of bacteria contained in it, but does not usually entirely destroy them.

It is well known that salt water freezes at a lower temperature than fresh water. Blagden, as long ago as 1787, stated a law governing the freezing point of solutions, which runs as follows: *The depression of the*

freezing-point of a solution is proportional to its concentration. This law has a familiar application in the prevention of the freezing of water in the radiator of an automobile. By the addition of a soluble substance, such as alcohol or glycerine, the freezing-point of the liquid is lowered. Forty-six grams of ethyl alcohol dissolved in one thousand grams of water, lower the freezing-point about 1.85° C., or 3.3° F. The principle finds further application when we throw salt upon ice to melt it, and when we employ a salt-ice mixture in making ice-cream.

It is also of interest to know that such a substance as salt, when dissolved in water, raises the boiling-point of the liquid, for the salt molecules interfere with the formation of water vapor, or steam. It requires more heat, therefore, to boil a salt solution, or brine, than pure water. This may be readily demonstrated by immersing the bulb of a thermometer, first in boiling water, and then in a concentrated boiling salt solution.

4 Hydrogen Peroxide

Hydrogen peroxide is twice as rich in oxygen as water. These compounds illustrate an important law of chemistry, known as the law of multiple proportions, which was formulated by John Dalton at the beginning of the last century. The relative proportions (approximately) by weight of hydrogen and oxygen in the two oxides of hydrogen are as follows:

	Hydrogen	Oxygen
Water, H_2O	1×2	16
Hydrogen peroxide, H_2O_2	1×2	$16 \times 2 = 32$

It is clear that water contains 2 parts by weight of hydrogen to 16 parts by weight of oxygen, while hydrogen peroxide contains 2 of hydrogen to 32 of oxygen. The law may be stated thus: *When two elements unite to form more than one compound, the weights of the second element which unite with a fixed weight of the first element, are to each other in the ratio of whole numbers.* In the language of the chemist, a molecule of water contains 2 atoms of hydrogen and 1 atom of oxygen, while a molecule of hydrogen peroxide contains 2 atoms of oxygen to 2 of hydrogen.

Hydrogen peroxide has a strong tendency to give off oxygen, which is perhaps its most interesting and useful property. Like ozone, it is therefore a good oxidizing agent. When a molecule of the peroxide loses an atom of oxygen, it is reduced to water. The ordinary household peroxide solution contains about 3 per cent of hydrogen peroxide. When the dilute water solution is free from impurities, it keeps fairly well. Many substances, however, accelerate its decomposition. For example, finely divided metals, free alkalis, and even any rough surfaces on the inside of the containers act as catalysts, and thus hasten the formation of oxygen. Traces of acetanilide, on the other hand, lessen its decomposition; acetanilide functions as a negative catalyst.

Hydrogen peroxide is used for bleaching silk, wool, hair, feathers, and ivory; for restoring color or brightness to old oil paintings; and in medicine as an antiseptic and cleansing agent. As it has long been employed for changing dark hair to blonde, an old name for the substance is "golden fluid."

The restoration of color to old paintings is due to the fact that the white-lead used by the artist is gradually converted into black lead sulphide (PbS) by the action of the hydrogen sulphide of the air; but when the film of sulphide is treated with a solution of hydrogen peroxide it is oxidized to white lead sulphate ($PbSO_4$). While hydrogen peroxide is a germicide, its effect as such has been overestimated by the public. It is particularly serviceable for expelling pus, for loosening dried bloody bandages, and when a mild oxidizing agent is needed. Tincture of iodine, corrosive sublimate, carbolic acid, and mercurochrome are much more powerful germicides.

CHAPTER VIII

A NATURAL FAMILY OF ELEMENTS· THE HALOGENS

The graduation in characters which the halogens show with increasing weights from fluorine to iodine yield an almost perfect family series—J. W. MELLOR.

1 NATURAL FAMILIES OF ELEMENTS

THE chemical elements may be arranged in families the members of which are closely related. Among the metals we have the alkali metals, such as sodium and potassium, which are constituents of the alkalis, sodium hydroxide and potassium hydroxide, so important in the manufacture of soap. The alkali metals are the most active of metals; we have already seen that they decompose water with great energy, and are preserved under mineral oil to prevent their interaction with oxygen and water.

Fluorine, chlorine, bromine, and iodine constitute a remarkable family of non-metallic elements. These elements have properties which are least like those of the metals. The group as a whole is often called the halogens—from two Greeks words meaning sea-salt and to produce. They were given this name because they occur in sea-water, and the sodium salts are similar to sea-salt, or sodium chloride. The graduation in properties which these elements exhibit with increasing atomic weight, from fluorine to iodine, fur-

nishes a most interesting family series. Their symbols, atomic weights, and colors are as follows:

Fluorine	F	19	pale greenish-yellow gas
Chlorine	Cl	35.5	greenish-yellow gas
Bromine	Br	80	brownish-red liquid
Iodine	I	127	steel-gray solid

These elements have a very strong tendency to unite with metals and with hydrogen to form compounds known respectively as fluorides, chlorides, bromides, and iodides, which are often termed the halides; they contain two elements, one of which is a halogen. Some of the halides, such as sodium chloride, potassium chloride, and silver bromide, are of the highest importance.

2 Chlorine, Bleaching, and Disinfecting

Since chlorine is the most abundant and important of the halogens, it will receive first consideration. This element occurs most plentifully as chlorides. Sodium chloride is the most abundant soluble salt, constituting the chief part of the total solids obtained by the evaporation of sea-water. Then, too, there are vast beds of rock-salt, or common salt, some of which are of enormous thickness, those of Sperenberg, Germany, having a thickness of four thousand feet. There are salt-mines in Galicia said to be five hundred miles long, twenty miles broad, and twelve hundred feet thick. There are also vast deposits of salt in Louisiana. It is estimated that if all the sodium chloride in the sea could be recovered it would form a layer one hundred

feet thick over the entire surface of the earth. The most valuable salt-deposits in the world occur at Stassfurt, Germany. These beds contain a mixture of many salts, including potassium chloride and sodium chloride. They are the chief source of potassium compounds, so vital in agriculture.

Chlorine is produced industrially by subjecting a solution of sodium chloride, or brine, to electrolysis, the other products being hydrogen and sodium hydroxide, both of which are also very valuable:

$$\text{Sodium chloride} + \text{Water} + \text{Electricity} = \text{Hydrogen} + \text{Chlorine} + \text{Sodium hydroxide}$$

The United States Government built a very extensive chlorine plant at Edgewood Arsenal, in Maryland, for the production of chlorine during the recent war. This plant had a capacity of one hundred tons of chlorine and one hundred and ten tons of sodium hydroxide every twenty-four hours.

Chlorine may be generated readily by adding hydrochloric acid to manganese dioxide, which occurs in nature as the mineral pyrolusite.

Chlorine is a greenish-yellow gas possessing a very disagreeable smell. When breathed it has an excessively irritating action upon the membranes of the nose and throat, producing coughing, inflammation, and even death; hence it is appropriately called "poison gas." Chlorine may be easily condensed to a golden-yellow liquid, and as such stored in strong lead-lined cylinders holding from about forty to sixty pounds. Great quantities of chlorine and chlorine compounds were used in the World War. The first attack was made by the

Germans on April 22, 1915. They previously stored the substance in steel cylinders containing forty-four pounds each. These were concealed in the trenches, and the substance was employed in the form of gas "clouds." As chlorine gas is about two and a half times as heavy as air, the clouds were carried over the ground by the wind. Chlorine is a powerful respiratory irritant. In high concentration, it affects the eyes also. In a concentration of one part of chlorine to ten thousand parts of air, the struggle for breath becomes acute, and a man would probably be incapacitated in five minutes.

Chlorine is an exceedingly active substance, even more so than oxygen. It unites directly with most of the other elements, the chemical changes often being accompanied by the evolution of heat and light. A jet of chlorine will burn in an atmosphere of hydrogen, forming hydrochloric acid gas, thus proving that we may have fire and flame without oxygen. This may be readily shown by lowering a jet of burning hydrogen into a jar of chlorine.

When a mixture of hydrogen and chlorine is kept in the dark, there is almost no union between the gases at ordinary temperatures; in diffused light the union is very slow; but when exposed to the light of burning magnesium or direct sunlight the mixture explodes at once.

Chlorine combines readily with all the common metals except gold and platinum. Finely divided antimony, thin leaves of copper, and sodium burn in the gas to form chlorides.

The combustion of antimony may be shown by

sprinkling a little of the powdered metal into a jar of chlorine.

When chlorine and the metals are thoroughly dried, they do not combine; but when a trace of water is admitted, combination occurs. Water plays the rôle of a catalyst. We thus see that certain chemical changes are promoted by light and by moisture.

Chlorine is more active than bromine, iodine, or sulphur, but not so active as fluorine. To illustrate, when a very dilute solution of potassium iodide is mixed with starch and then treated with two or three drops of chlorine water, iodine is set free, and it colors the starch a magnificent blue—a very delicate test. Furthermore, if a tuft of cotton-wool is dipped into hot turpentine and then thrust into a jar of chlorine, so much heat is formed that combustion occurs, accompanied by the liberation of carbon (soot), which is one of the constituents of the hydrocarbon turpentine.

When a mixture of carbon monoxide and chlorine is exposed to light, the gases unite to form phosgene ($COCl_2$). This compound is a volatile liquid, and was used very extensively in gas warfare. It is manufactured by passing carbon monoxide and chlorine over porous charcoal, which serves as a catalyst.

Phosgene is highly poisonous. When inspired it interacts with water to form hydrochloric and carbonic acids in the lungs. Phosgene is chiefly a respiratory irritant, being more poisonous than chlorine.

Immense quantities of chlorine are used in bleaching and disinfecting. Either free chlorine, in the presence of water, is employed, or the bleaching and disin-

fecting are accomplished by means of hypochlorites or chloride of lime, which are active chlorine compounds.

The bleaching action of chlorine may be shown by lowering moistened strips of colored cotton cloth into jars of chlorine. A strip of dry cloth lowered into a cylinder of chlorine standing over concentrated sulphuric acid is not bleached, however, for the acid in the bottom of the cylinder absorbs the moisture.

Chlorine water bleaches ordinary writing-ink (ferrous tannate), but not printer's ink (carbon).

Why does chlorine act as a bleaching agent? In the presence of water, hypochlorous acid (HClO) is formed, which readily loses oxygen to form hydrochloric acid (HCl), and the oxygen serves to destroy dyes or bacteria.

Bleaching powder, or chloride of lime, which is employed in almost every household, is produced by absorbing chlorine in dry slaked lime. It was first prepared more than a century and a quarter ago, and is used extensively for bleaching vegetable fibers for the textile and paper industries and as a disinfectant.

Sodium hypochlorite may be prepared by treating a solution of sodium hydroxide with chlorine, the solution being sold under the name Javelle water, or "chlorizone." Javelle water is used for bleaching or for removing stains. Dakin's and Carrel's solutions, which are similar to Javelle water, were used extensively in the war for cleansing deep wounds.

Vegetable fiber (cotton, linen, or wood-pulp) may be bleached by first saturating the material with a solution of bleaching powder and then passing it into a

bath containing a *dilute* mineral acid, which liberates hypochlorous acid and more or less chlorine. The excess of chlorine is removed from the goods by the use of a solution of such a substance as sodium sulphite, which is called an antichlor.

Vegetable fiber, after appropriate preliminary treatment, is also bleached by saturating the material with a solution of bleaching powder and then piling it loosely in the air. Carbonic acid interacts with the bleaching powder, yielding hypochlorous acid.

It is used for bleaching cotton and linen goods and wood-pulp, but is too active for silks and woolens.

3 Hydrochloric Acid

One of the most important compounds of chlorine is hydrochloric acid gas (HCl). A water solution of this compound is called hydrochloric acid, and it was prepared as far back as the middle of the seventeenth century by Glauber, who obtained it by treating common salt with sulphuric acid, the method still in use. Commercially, it is often called muriatic acid.

Hydrochloric acid gas occurs in the exhalations of certain active volcanoes, such as Vesuvius. Hydrochloric acid is formed in the waters of several of the South American rivers which rise in the volcanic districts of the Andes. It is an important component of the gastric juice of man and of animals, the gastric juice of man containing from 0.2 to 0.4 per cent, while that of dogs contains about 0.6 per cent. The acid plays an important rôle in digestion.

Hydrochloric acid gas is colorless and possesses a

very sharp odor. With moist air it forms a cloud which consists of droplets of hydrochloric acid. The gas is extremely soluble in water; at the melting-point of ice one volume of water dissolves over five hundred volumes of the gas. Concentrated hydrochloric acid usually contains about 35 per cent of the active substance and 65 per cent of water.

Hydrochloric acid is one of the most useful of the acids. It is a powerful solvent, dissolving many metals and compounds of metals to form an important class of salts known as chlorides, the most common of which is sodium chloride. Ammonium chloride, or sal ammoniac, is a white salt which may be obtained by treating hydrochloric acid with ammonia. This salt is similar to common salt, but decomposes when heated. When sal ammoniac is employed in soldering, the hot iron decomposes the salt, and one of the products—hydrochloric acid gas—removes the coat of oxide from the surface of the metal.

When an electric current is passed through a solution of hydrochloric acid, equal volumes of hydrogen and chlorine are set free.

4 Bromine

Bromine was discovered a century ago by the French chemist Ballard, who named the element bromine—from a Greek word meaning stench. The element occurs as bromides, particularly as magnesium bromide and sodium bromide. These salts are found in the Stassfurt deposits, in certain mineral springs and in

the upper layers of some of the beds of rock-salt. Before the beginning of the present century, Germany produced most of the bromine; but for a good many years the average annual production in the United States has been about 1,000,000 pounds. In 1924, over 2,000,000 pounds were produced, the largest portion coming from the brines of the Saginaw Valley, Michigan. The demand for bromine will depend largely upon the extent to which tetraethyl lead is added to gasoline. About two cubic centimeters of ethylene bromide are added to each gallon of leaded gasoline (ethyl gasoline). The ethylene bromide is used to furnish bromine for transforming the lead of the tetraethyl lead into lead bromide; otherwise the free lead would alloy with the ignition-points, thus injuring them. The consumption of gasoline in the United States in 1925 was approximately 11,200,000,000 gallons, and if this entire amount were treated with tetraethyl lead and ethylene bromide about 90,000,000 pounds of bromine would be required. Even if only 10 per cent of this quantity of gasoline were so treated, 9,000,000 pounds of bromine would be required, which is more than four times our production in 1924.

Realizing that there might be a shortage of bromine, the Ethyl Gasoline Corporation in coöperation with the DuPont Company has conducted experiments for the recovery of bromine from the bromides of sea-water. Sea-water contains on an average about 0.0064 per cent of bromine, which means that about 1800 gallons of the water must be treated to secure a pound of bromine. To recover bromine from sea-water, a

vessel was equipped capable of recovering 100,000 pounds of the element per month. It has been reported that the trial trip of this "bromine ship" was quite successful; indeed, the production was beyond the rated capacity. This is another of the marvels of modern chemistry.

At Midland, Michigan, the brine pumped up from the underlying salt-beds is concentrated to crystallize out common salt, and the remaining liquor, known as bittern, is subjected to electrolysis, bromine being set free at the anode.

Bromine is also obtained by treating solutions of bromides with the more active element chlorine.

Bromine is a dark-red fuming liquid, and is more than three times as heavy as water. The vapor not only has a most disagreeable odor, but attacks the eyes very painfully and produces great irritation when inhaled. It is a corrosive poison; and when brought into contact with the skin, it produces sores which are difficult to heal. Like chlorine, it is moderately soluble in water, both solutions being employed as oxidizing agents.

In its chemical behavior bromine is very similar to chlorine, but is less active. Bromine unites with hydrogen to form hydrobromic acid (HBr), which is analogous to hydrochloric acid (HCl).

Bromides are similar to chlorides. Those of potassium and sodium are used in medicine as sedatives and in preparing silver bromide, which is used extensively in photography as the sensitive material on the plate. A considerable quantity of bromine has been used of late in the manufacture of "tear-gases," or lachrymators.

5 Iodine; Goiter

Iodine was discovered in 1812 by Courtois, a manufacturer of saltpeter, near Paris, who obtained it from the mother-liquor of salts produced from burnt seaweed, or kelp. The liquid was heated with sulphuric acid in a retort, "a vapor of a superb violet color" being obtained, which condensed in the form of brilliant crystals. Shortly after this discovery, Gay-Lussac proposed the name iodine—from a Greek word meaning violet.

Iodine occurs in combination in small quantities, but widely distributed, both in the organic and inorganic kingdoms. It occurs in sea-water, in sea-plants and sea-animals, and in the thyroid gland of man and of animals. Formerly the only commercial source of iodine was seaweed, which was collected along the rocky coasts of Scotland, Ireland, and France. Certain sea-plants, in growing, extract iodine from water. Thus, the giant sea-plants, known as kelp, which grow along the Pacific coast, contain not only potassium chloride but a small quantity of iodides. For some years most of the iodine of commerce has been obtained from sodium iodate, which is found in small quantity in Chile saltpeter, or crude sodium nitrate.

In general, the methods employed in preparing iodine are similar to those used for bromine; it is not prepared, however, by electrolysis. Crystals of iodine in the form of brilliant plates may be obtained by gently heating a mixture of potassium iodide, manganese dioxide, and sulphuric acid in a glass beaker,

the element being condensed upon the bottom of a small flask containing cold water.

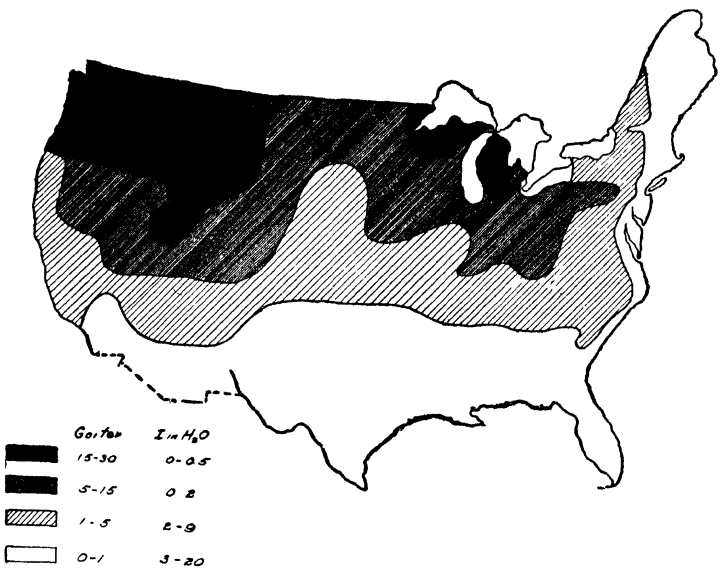
Iodine is a shining, blackish-gray solid, which is nearly five times as heavy as water. When a small crystal is heated, it gives a magnificent violet vapor. Tincture of iodine consists of iodine and potassium iodide in alcoholic solution. An alcoholic solution of iodine is brown in color, while a chloroform solution is a lovely violet. When a small amount of chloroform is poured into a dilute solution of potassium iodide and then treated with a few drops of chlorine water, followed by shaking, the heavier layer of chloroform takes on a fine violet color, due to liberated iodine. A mere trace of iodine colors starch solution a deep blue, which is an exceedingly delicate test for the element.

Iodine in its chemical properties resembles the other halogens but is the least active. It unites directly with many other elements to form iodides. When it is brought into contact with white phosphorus the latter soon bursts into flame.

Iodine is used in the manufacture of certain coal-tar dyes, iodoform, potassium iodide, and sodium iodide; in medicine, and in photography. Tincture of iodine is effective in reducing swellings and as a germicide, but in the latter capacity it has been displaced to some extent by a 1-per-cent to 2-per-cent aqueous solution of mercurochrome which "does not irritate, burn or injure the tissue as iodine does."

Iodine is an essential constituent of the animal body. It is estimated that there are approximately twenty milligrams in the body of a normal adult, about one-half of which is in the thyroid gland near the Adam's

apple. It is very important to keep the iodine content of the body well regulated. A subnormal secretion of iodine may give rise to simple or fibrous goiter or to cretinism, which is accompanied by lowered muscular activity and dullness of mind. There is apparently a



Courtesy, J. W. Turrentine, United States Department of Agriculture

FIGURE 9

Goiter Map of the United States. Distribution of goiter and comparison of iodine water-supplies: goiter rate per thousand population; iodine in parts per billion of representative rivers.

close connection between the prevalence of goiter and cretinism and the deficiency of iodides in drinking-water and foodstuffs. Goiter and cretinism are prevalent in the central Alps and in the regions of the Great Lakes and of the Rocky Mountains, due, it is believed, to the insufficiency of iodides. (Figure 9.)

Iodides are present in sea-water and therefore in sea-salt. Now, sea-salt in the form of very fine dust, may be carried many hundreds of miles inland before being washed down by rains. In case the iodides fail to reach certain districts or are leached out of the soil, there is an insufficiency in the drinking-waters or in the plants which are used as food. It has been estimated, for example, that a person would require a thousand years to drink water enough of Lake Superior to supply the iodine necessary for the thyroid gland. Some form of goiter among school-children is prevalent in certain districts, being more common among girls than boys. In thirteen localities in Minnesota, 4061 children were examined, and it was found that about 41 per cent of the boys and 72 per cent of the girls were afflicted.

It is now quite common to add a small quantity of sodium iodide to table salt in order to supply the body with sufficient iodine to prevent goiter. Some time ago it was decided that the salt-manufacturers of Michigan should add 0.02 per cent of sodium iodide to common salt. J. W. Turrentine, of the United States Department of Agriculture, has suggested the use of dried kelp, which contains an appreciable amount of iodine compounds. Iodine is supplied by certain foods, such as spinach, lettuce, string beans, butter, and milk.

Some years ago Dr. E. C. Kendall, of the University of Minnesota, isolated and identified the active principle of the thyroid gland, which is called thyroxin; it is a complex organic compound, the constituents of which are carbon, hydrogen, oxygen, nitrogen, and iodine. As the result of much patient and careful research, its constitution is known, and it is possible that

the compound may be synthesized instead of having to be extracted from the thyroid glands of animals, such as sheep.* Thyroxin appears to be a powerful catalyst. When an injection of only 1 milligram is made, the increase in the output of carbon dioxide from the body is enormously increased, amounting to about 400,000 milligrams. Thyroxin has been administered with considerable success in the treatment of goiter.

There is another form of goiter, known as exophthalmic goiter, which is the result of an excessive absorption of iodine. The symptoms of this affliction are an enlarged thyroid gland, accompanied by protruding eyeballs, palpitation of the heart, and anemia; it is known as Basedow's disease.

Iodine, like the other halogens, unites with hydrogen to form a colorless, gaseous compound, its water solution being known as hydriodic acid. This acid is much less stable than the other halogen acids, however; the colorless solution, when exposed to the air, becomes brown, owing to the liberation of iodine. Potassium iodide is used in medicine and silver iodide in photography. Mercuric iodide has a magnificent scarlet color, while lead iodide is a brilliant yellow.

6 Production of Smoke Screens

All the halogen compounds of phosphorus are unstable in the presence of water, and therefore fume violently when exposed to moisture. Indeed, many other compounds are decomposed in the presence of

* Since this was written Dr. C R. Harington of University College Hospital (London) has synthesized thyroxin.

water, the chemical change being known as hydrolysis (Greek: water + to loosen). Hydrolysis may be defined, therefore, as double decomposition in which water is one of the interacting substances. Thus, when a bottle containing phosphorus trichloride (a colorless liquid) is uncorked, fumes of hydrochloric acid appear, due to the action of water vapor upon the chloride. Hydrolysis plays an important part in the production of certain smoke screens or curtains. Titanium chloride, for instance, may be carried by an airplane, and when the compound is sprayed into the air it interacts with water vapor, producing a screen.

7 Fluorine; Etching Glass

The remaining halogen—fluorine—occurs abundantly in the minerals fluorspar and cryolite; it also occurs in very small quantities in bones and teeth, and traces have been detected in the blood, milk, and brains of animals. The element was named fluorine, owing to the use of fluorspar as a flux (Latin: meaning flow) in metallurgy.

Fluorine, being the most active element known, was not prepared until 1886. This difficult task was accomplished by a brilliant French chemist, Moissan, who also produced diamonds from sugar charcoal. He obtained the element by the electrolysis of a fluorine compound in a U-tube constructed of platinum, or of an alloy of platinum and iridium, the tube being surrounded by methyl chloride which boiled and kept the temperature at about —23° C. Fluorine was evolved at the anode. It was learned subsequently that

copper vessels may be employed instead of those constructed of the very expensive metals.

At present, fluorine is prepared by the electrolysis of molten potassium hydrogen fluoride (KHF_2) or the analogous sodium compound. The elementary substance is of no practical importance

Fluorine is a pale greenish-yellow gas which may be condensed to a pale-yellow liquid. It resembles chlorine, but is paler in color and much more active. Fluorine combines explosively with hydrogen, even in the dark; and many other elements, such as sulphur, phosphorus, carbon, and silicon, catch fire spontaneously in fluorine. Most metals also burn in fluorine. Fluorine displaces chlorine from chlorides, bromine from bromides, and iodine from iodides; also oxygen from water, ozone being formed. It is an interesting fact that fluorine and oxygen do not interact. Fluorine has the most pronounced non-metallic properties of any known element, and it possesses great chemical activity at the lowest temperatures attainable.

One of the most useful compounds of fluorine is hydrofluoric acid (HF), which is analogous to the other halogen acids, but the most stable. It may be prepared by treating fluorspar, or calcium fluoride, with concentrated sulphuric acid in a platinum or a lead vessel. The vapor may be condensed to a colorless liquid, or absorbed in water. The acid may be preserved in bottles made of ceresin or gutta-percha.

Hydrofluoric acid fumes are *poisonous*, and the acid also produces wounds, when brought into contact with the body, which heal with difficulty. Great care must

be used, therefore, in handling this acid. Professor Nicklés, of Nancy, died, in 1869, from accidentally breathing the vapor of the acid while trying to prepare fluorine.

Hydrofluoric acid is used for etching glass. In etching, the surface of the glass is first covered with paraffin or beeswax, some of the wax being removed by a sharp instrument so as to expose the glass to the acid. The etching may be accomplished either with the vapor or by applying the aqueous solution with a feather. The vapor yields a rough surface, while the solution makes smooth depressions.

CHAPTER IX

ACIDS AND ALKALIS

As vinegar to the teeth, and as smoke to the eyes, so is the sluggard to them that send him.—Proverbs x. 26.

1 Acids

There is an important class of hydrogen compounds the water solutions of which possess a sour taste and have the property of turning blue litmus, a dyestuff extracted from certain lichens, red. A dyestuff or substance which undergoes a change in color upon the addition of an acid or alkali, is called an indicator. The nature of an indicator is amusingly presented in the following jingle from "Metrical Stories in Chemistry and Natural Philosophy" of the long ago:

Within a glass of water put
A fair blue violet,
Blue cabbage leaves, or radish root,
A clear, bright blue you get.
Then pour sulphuric acid in,
And all the blue is fled,
You'll see the change will quick begin,
Till all is turned to red.

The most common acids are sulphuric, hydrochloric, nitric, carbonic, and acetic. Acetic acid is the active component of vinegar, which has been used in one form

or another for thousands of years. For instance, in the Old Testament (Numbers vi. 3) we read: "He shall separate himself from wine and strong drink, and shall drink no vinegar of wine, or vinegar of strong drink." When wine and other alcoholic liquids undergo acetous fermentation, or sour, in the presence of the catalyst "mother of vinegar," acetic acid or vinegar is formed. When the Roman soldiers were in camp, they drank a sour wine called *acetum,* or vinegar, both in its pure state and diluted with water. Many fruits—*e.g.,* the apple, grapefruit, lemon, and gooseberry—owe their agreeable flavor, in part, to acids, such as malic, citric, and tartaric.

In connection with oxygen it was pointed out that certain oxides of non-metals (anhydrides) interact with water to form acids. Acids always contain hydrogen and frequently contain oxygen:

Hydrochloric acid, HCl
Sulphuric acid, H_2SO_4
Nitric acid, HNO_3
Carbonic acid, H_2CO_3

Carbonic acid occurs in natural waters, and certain soils are naturally acidic or become so as the result of the application of fertilizers. Soda-water and other soft drinks contain carbonic acid. When carbonated waters are exposed to air, they effervesce, due to the escape of carbon dioxide.

Inasmuch as all acids contain hydrogen, this element may be obtained by treating magnesium, iron, zinc, or other active metals, with aqueous solutions of acids. This may be readily shown by dropping a pinch of

magnesium powder into dilute hydrochloric or sulphuric acid. Brisk effervescence shows that a gas is set free. Hydrochloric acid gas may be obtained by pouring strong sulphuric acid upon salt. The gas is extremely soluble in water, the solution being known as hydrochloric acid, which may be purchased at any drug store. The concentrated acid fumes when exposed to air, owing to the escape of hydrochloric acid gas (HCl). The acid is used as a solvent, for the preparation of hydrogen and chlorine, for cleansing the surfaces of metals, etc.

Concentrated sulphuric acid, or oil of vitriol, contains about 5 per cent of water. When the strong acid is poured into water, an enormous quantity of heat is generated. Oil of vitriol chars wood, paper, sugar, etc., because it has such great affinity for water, or for the elements of water—hydrogen and oxygen. Cane-sugar, for example, contains carbon, hydrogen, and oxygen in chemical union; and when strong sulphuric acid is poured into a syrup of sugar, the sugar turns black and froths violently, owing to the fact that hydrogen and oxygen are abstracted from the sugar to form water, leaving black carbon. Vast quantities of sulphuric acid are manufactured, for nearly all chemical industries demand its use.

Pure nitric acid is a colorless liquid. Concentrated nitric acid contains about 68 per cent of the active substance and 32 per cent of water. The ancients called the acid *aqua fortis* on account of its powerful solvent action; and they mixed it with hydrochloric acid, the mixture being known as *aqua regia,* due to the fact that it dissolves the noble metal gold. Nitric acid is a

powerful oxidizing agent, and may therefore set fire to straw or fine shavings.

When strong nitric acid is brought into contact with the skin it produces painful wounds, being used in surgery as a powerful cautery. The dilute acid colors the skin, nails, wool, and many other organic bodies a yellow tint. There is a great demand for this acid in the manufacture of explosives and fertilizer.

Carbonic acid, formed by the interaction of carbon dioxide and water, occurs in nature. While a weak, unstable acid, it plays an important part in certain natural processes. Thus, it is a solvent for calcium carbonate or limestone, and gradually dissolves carbonate rocks to form caves.

2 Alkalis; Soap-Making

When water is carefully treated with metallic sodium, one atom of hydrogen is set free from each water molecule, forming sodium hydroxide (NaOH) which remains in solution in the excess of water. When the solution is tested with neutral or red litmus-paper, the paper turns blue, and the solution has a caustic taste and a slippery feeling. Now, sodium hydroxide belongs to the class of compounds known as alkalis or bases. These compounds may be formed by treating the very active metals (or their oxides) with water; they are hydroxides of metals; *i.e.*, an alkali or a base contains a metal in union with definite weights of hydrogen and oxygen. The most important substances belonging to this class of compounds are as follows:

Sodium hydroxide or Caustic soda, NaOH
Potassium hydroxide or Caustic potash, KOH
Calcium hydroxide or Slaked lime, $CaO_2H_2 = Ca(OH)_2$
Ammonium hydroxide or Ammonia water, $(NH_4)OH$

Acids and alkalis possess very dissimilar properties; the properties of an acid may be destroyed or neutralized by the addition of an alkali.

Sodium hydroxide is a white solid compound, which may be prepared in the form of long sticks. It is extremely soluble in water, the solution being frequently called lye.

Sodium hydroxide is used on a very large scale in the manufacture of hard soap. This is accomplished by heating fats or certain oils, such as palm-oil and cocoanut-oil, with the alkali:

Fat + Sodium hydroxide (Lye) = Soap + Glycerine

Soap-making is therefore a chemical reaction carried out on a large scale. It was learned by certain of the ancients that grease could be removed from the hands by washing them with wood-ashes. The Gauls prepared a sort of crude soap by mixing wood-ashes, water, and goat's tallow; and with this they washed their hair and beards in order to give them a fiery-red color which they regarded as becoming. The Romans no doubt learned something from the Gauls, and they were perhaps the first civilized people to prepare real soap.

Years ago, in our own country, soap-making, like weaving and spinning, was one of the household arts or industries. Soap was made by dissolving the potash out of wood-ashes by means of water or lime-water, the

solution being known as lye. The fat, or soap-grease, saved by the housewife was heated in iron kettles with potash lye, soft soap being obtained.

In case sodium hydroxide, or caustic soda, was purchased at the grocery and substituted for potash, hard soap was obtained.

At present, however, soap is made chiefly by large manufactories. Let us see how this is accomplished. The first process of soap-making takes place in huge kettles two or three stories in height and arranged in parallel rows. The stock—that is, the oil obtained from fats—is brought to the top of a kettle by means of a pipe. Lye and water are also brought to the kettle until it is filled. A single kettle holds enough stock to make from 200,000 to 300,000 pounds of soap. Steam is blown in at the bottom of a kettle and its contents are thoroughly agitated and boiled until a pasty mass of soap is obtained. In the next operation salt is added, which causes the globules of glycerine and water to sink to the bottom of the kettle and the clear soap curd to form a layer on top. The water and glycerine are withdrawn from the bottom and the soap curd pumped into large stirring-bowls called crutchers, where it is stirred until it is smooth. The soap is next emptied into frames, which are similar to boxes, but with detachable sides, where it is allowed to cool. The large blocks of soap are finally cut by machinery into small cakes, dried, stamped, and wrapped.

Sodium hydroxide solution is also used for removing skins from fruits, such as the peach, which is done by dipping the fruit into a boiling solution for a short while.

When a piece of pure woolen cloth is boiled in a 10-per-cent solution of lye, the material dissolves completely, whereas cotton is insoluble. Sodium hydroxide is therefore used in testing goods for cotton or other vegetable fiber.

Potassium hydroxide is very similar to sodium hydroxide, but is more expensive.

Calcium hydroxide is used on a large scale in mortar. It is also used for whitewash, in preparing lime-water, and as a test for carbon dioxide. When carbon dioxide comes into contact with calcium hydroxide, the gas enters into chemical combination forming calcium carbonate:

$$\underset{\text{hydroxide}}{\text{Calcium}} + \text{Carbon} = \underset{\text{carbonate}}{\text{Calcium}} + \text{Water}$$

As calcium carbonate is insoluble in water, it renders the lime-water turbid. A lime-sulphur orchard spray is prepared by adding sulphur to calcium hydroxide.

Magnesium hydroxide is similar to calcium hydroxide, but is less soluble in water. Milk of magnesia consists of a very dilute solution of magnesium hydroxide in which magnesium oxide, or magnesia, is suspended. It is used in medicine as an antidote for poisoning by acids and as a laxative.

Ordinary household ammonia, which is formed by dissolving ammonia gas (NH_3) in water, contains ammonium hydroxide, and possesses the properties of a base. The solution is employed on a large scale as a cleansing agent and for neutralizing acids. Red acid stains may be removed by the application of dilute ammonia water.

Oxides of metals are called basic oxides: for example, calcium oxide, or quicklime. By treating the basic oxide with water, a base (alkali) is formed:

CaO	$+$	$H_2O =$	CaO_2H_2
Calcium oxide		Water	Calcium hydroxide, or Slaked lime

3 Salts and Their Names

When a base or an alkali is treated with an acid, the characteristic properties of each are destroyed or neutralized, a salt and water being formed:

Alkali + Acid = Salt + Water

In case sodium hydroxide is treated with hydrochloric acid, sodium chloride and water are the products:

$NaOH$	$+$	HCl	$=$	$NaCl$	$+$	H_2O
Sodium hydroxide		Hydrochloric acid		Sodium chloride		Water

Such a chemical change as this is known as neutralization, for the product (salt) does not have any effect upon indicators such as litmus. In other words, a water solution of common salt is neutral toward indicators. By exactly neutralizing caustic soda, or sodium hydroxide, with hydrochloric acid, and then evaporating off the water, pure sodium chloride may be obtained. An alcoholic solution of phenolphthalein, a complex carbon compound, is a most delicate indicator for an alkali, for a purplish-red tint is obtained by treating a dilute solution of the alkali with two or three drops of a solution of the indicator.

Hundreds of salts may be prepared by treating various bases with acids. In case the acid contains two replaceable atoms of hydrogen in the molecule, two salts may be formed from each acid. Carbonic acid (H_2CO_3) has two sodium salts—a normal salt and an acid salt:

Carbonic acid, H_2CO_3 { Normal sodium carbonate, Na_2CO_3 / Sodium acid carbonate or Bicarbonate, $NaHCO_3$

Normal sodium carbonate is used in the laundry, being known as washing soda, while the acid salt, or bicarbonate, is called baking soda. The latter is employed on a large scale in the manufacture of baking-powders; it is termed an acid salt, for it contains hydrogen which may be replaced by a metal.

The following simple rules are to be followed in naming salts:

(1) Salts derived from acids containing two elements have names ending in *-ide.*

(2) If the acid contains oxygen and its name ends in *-ic,* the name of the salt ends in *-ate.*

(3) If the acid contains oxygen and its name ends in *-ous,* the name of the salt ends in *-ite.* Thus:

Name of Acid	*Formula of Acid*	*Formula of Sodium Salt*	*Name of Salt*
Hydrochloric acid	HCl	$NaCl$	Sodium chlor*ide*
Sulphuric acid	H_2SO_4	Na_2SO_4	Sodium sulph*ate*
Sulphurous acid	H_2SO_3	Na_2SO_3	Sodium sulph*ite*

Salts are a large and exceedingly important class of compounds. Many of these substances occur in solution in sea-water and constitute a considerable portion of the earth's crust.

4 Some Natural Salts

In our study of chlorine we saw that common salt is the most abundant soluble salt, rock-salt sometimes occurring in beds thousands of feet thick. Salt has been used for thousands of years as a condiment and as a preservative for food. One writer estimates that each person uses about twenty-nine pounds of salt per annum. It was employed in Canaan and adjacent regions in the preservation of food, for ice was almost unknown there. Salt was perhaps the only antiseptic used at the time to preserve food. Under the ancient law salt was presented with offerings of various kinds. In the second chapter of Leviticus, the third verse, we find: "And every oblation of thy meat offering shalt thou season with salt." We read in Chapter V of St. Matthew: "But if the salt have lost his savour, wherewith shall it be salted?"

Now, pure salt is sodium chloride, a definite chemical compound. Is it possible, therefore, for salt to lose its savor or taste—*i.e.*, its characteristic quality? Pure sodium chloride as prepared by the chemist is a definite chemical compound and cannot lose its characteristic properties so long as it does not change chemically. "Salt," as used in the Sermon on the Mount, did not mean pure sodium chloride; it was a mixture of sodium chloride and other matter, no doubt largely earthy. Salt of poor quality could be scraped up along the shore of the Dead Sea, after the water had evaporated, or be cut from the neighboring cliffs. As this salt was a mixture, it was possible for the sodium chloride to be removed by solution in water, the insoluble matter being

left as a residue. This earthy matter, which possessed none of the characteristics of sodium chloride, was good for nothing except for the construction of walks as we employ gravel or stone. It is a well-known fact that the impure salt of Syria, when exposed to rain or stored in damp houses, is apt to lose its taste and become worthless. Such "salt" is "good for nothing, but to be cast out, and to be trodden under foot of men."

The greatest known salt-deposits are at Stassfurt, in the province of Magdeburg, Germany. The Stassfurt salt-beds contain immense quantities of compounds of potassium, sodium, magnesium, and calcium, which occur largely as chlorides and sulphates. Salt springs were known in this region as early as the thirteenth century, but borings were not made until about the middle of the nineteenth century, rock-salt having been mined. The material excavated with the rock-salt was thrown away, for it was thought to be worthless. Rose and Rammelsberg investigated this refuse thoroughly, and discovered that it was rich in potassium and magnesium salts, which led to the great potash industry of Germany. One of the most valuable salts obtained is potassium chloride, the first works for its extraction having been erected in 1861. It is estimated that the Stassfurt deposits yield about five million tons of crude potassium salts annually.

The Stassfurt salt-beds are about three thousand feet deep and were no doubt formed as the result of the evaporation of sea-water extending over a period of many thousand years. The volume of sea-water evaporated represents a total depth of thirty miles. France

has very large deposits of potassium salts in Alsace, which were acquired as a result of the war. The potash-producers of Germany and France effected an agreement in May, 1925, according to which the export market is to be divided on the basis of 70 per cent to German production and 30 per cent to French. This means, of course, that Europeans are in a position to control the potash market. In Germany the potash syndicate has complete control of the industry.

Niter or saltpeter (Latin: *sal,* salt + *petra,* a rock) is a highly important salt, the chemical name being potassium nitrate. Niter, in ancient times, meant sodium carbonate or potassium carbonate, a solution of which was employed in washing clothes. Thus, Solomon in one of his proverbs (xxv. 20) refers to the commotion which resulted when vinegar was mixed with niter. For hundreds of years, however, the term has stood for potassium nitrate, the potassium salt of nitric acid. This important salt occurs in nature, being especially abundant in the vicinity of certain Oriental villages, where nitrogen-bearing organic matter undergoes decay in contact with air and alkalis such as wood-ashes. Potassium nitrate is now produced on a large scale by treating a concentrated solution of sodium nitrate, or Chile saltpeter, with one of potassium chloride. This method for the production of potassium nitrate, a compound essential for the manufacture of black gunpowder, was introduced during the Crimean War, because of the insufficient supply. Potassium nitrate, or saltpeter, is a good oxidizing agent, which tells us why it is so important as a component of black powder: it burns the sulphur and carbon, producing

immense volumes of gases at a temperature of over 2000° C. (3632° F.). Potassium nitrate has been administered internally, but it was found to have a depressant action upon the heart. When heated, a molecule of the nitrate (KNO_3) loses an atom of oxygen, forming potassium nitrite (KNO_2). It is well known that nitrites relieve asthmatic attacks because they cause a relaxation of involuntary muscular fiber. Asthmatic attacks are sometimes relieved by soaking blotting-paper in a solution of potassium nitrate; the paper is then dried and burned in a jar, and the fumes inhaled.

One of the most useful salts found in nature is sodium nitrate, or Chile saltpeter. This salt occurs in beds extending about two hundred and fifty miles along the West Coast of South America. The average width of the beds is over two miles, while the average depth is about five feet. The salt occurs in a rainless zone, and is locally known as caliche. The better grades of the crude material contain from about 50 to 75 per cent of sodium nitrate and from 20 to 40 per cent of sodium chloride. Other salts also are present, as well as some organic matter: *e.g.*, guano. Caliche is treated with hot water, and the insoluble matter allowed to settle. The liquid is then run into cisterns, where much of the sodium chloride crystallizes out. From the mother liquor sodium nitrate is obtained by crystallization.

Over 55,000,000 tons of Chile saltpeter have been mined since its discovery early in the last century. It is of very great economic importance, for it is not only a source of nitric acid, but is an excellent fertilizer. In

1825 the first ship-load of Chile saltpeter was taken to Europe, but was dumped into the sea, for nobody would buy it. In 1914 the United States was importing about 500,000 tons annually, and Germany about 700,000 tons.

The origin of Chile saltpeter is not known with certainty, but it may have been formed by the decomposition and oxidation of sea-plants and animals.

There are hundreds of other salts, some of which are of great economic importance: *e.g.*, calcium carbonate, which occurs as limestone, marble, chalk, and coral. Magnesium carbonate also occurs in very large quantity, and when associated with calcium carbonate, the rock is known as dolomite, or magnesium limestone, a valuable building material. When limestones are heated, they lose carbon dioxide, leaving lime and magnesia, which are basic oxides of prime importance in industry.

5 Crystals

Salts, as a rule, may be obtained in crystalline forms, some of which are very beautiful. Crystals are formed by the solidification of a substance or by its deposition from solution. Thus, in winter, when the weather is cold, frost appears upon our window-panes, and snow-flakes of exquisite loveliness appear. A great many salts may be prepared in crystalline form by allowing a hot saturated solution to stand in a glass crystallizing dish, or by coating a piece of glass with a little of it. As the solution cools, crystals form, which may be examined with a pocket lens or by means of a microscope. Crystallization may be shown most beautifully by placing

a drop or two of silver nitrate solution on a clean glass slide and then adding a *small* piece of copper filing or very fine copper wire. When examined, crystals of silver are to be seen—the so-called "silver tree." The smallest crystal which makes its appearance has the same form as a large crystal. Crystals are formed, therefore, by growth. Many crystalline substances occur in nature, such as the diamond, the emerald, quartz, sulphur, and calcite.

Crystals differ much in appearance. Common salt crystallizes in cubes, Epsom salt in the form of four-sided prisms, and ammonium chloride may be viewed under the microscope as exquisite crosses and fern-like forms. While crystals appear to assume an almost infinite variety of forms, they may be classified in six systems.

Substances may be divided into two classes—amorphous and crystalline. Under amorphous substances we have liquids and glassy solids, in which the arrangement of the particles is chaotic—*i.e.*, not arranged according to a definite pattern. The arrangement of particles may be likened to trees growing in a natural forest. A crystalline substance, on the other hand, is one in which the particles are arranged in definite order, like trees in a nursery or garden, or soldiers on parade. Crystals, therefore, have a structure, and many of them possess cleavage, as illustrated in mica. This mineral may be split into sheets of inconceivable thinness; indeed, it is estimated that a single sheet may be only two molecules in thickness! While some crystals are microscopically small, others are very large. A natural crystal was found which measured

3 feet by 6 feet by 42 feet in length, thirty-seven tons of spodumene having been quarried from a single crystal. Artificial crystals do not reach these dimensions, but very long metallic crystals have been prepared. Thus, when plastic tungsten is drawn through a die at such a rate that the particles have time to arrange themselves in definite order, crystals a mile or more in length may be prepared.

CHAPTER X

ELECTRICITY IN THE SERVICE OF CHEMISTRY

Amber was used by the ancient world as a jewel and for decoration. Its color and luster reminded the fanciful Greeks of the virgin gold which glistened in the sands of Pactolus, even as the brilliant metal had itself recalled to them the yellow sunshine. Afterward they applied the same name to the compounds of metals which, when burnished, gave a golden glow. They were all children of "Elector," reflecting in miniature his radiance. Thus, in common with native gold and the silver-gold alloys, the amber, in Hellenic speech, came to be called "electron."—PARK BENJAMIN.

1 AMBER AND ELECTRICITY; LIGHTNING

ELECTRICITY owes its name to the fact that the first electrical effects ever observed were produced by rubbing amber (Greek: *electron*). Trade in amber—a yellowish, hard, brittle, resinous material—must have been carried on in prehistoric times, for amber beads have been discovered in royal tombs of great antiquity.

Amber was employed in spinning, the oldest handiwork known to the human race. Spinning was done by means of the distaff, and in the case of the women who could afford the luxury the spindles were made of the much-prized amber. The spinner called her spindle the clutcher, due no doubt to the fact that as the spindle descended and whirled around, it rubbed against the loose feminine garments, thus becoming electrified, and

on nearing the ground, it attracted bits of chaff or leaves.

Aside from the observations of the ancients that rubbed amber had the power to attract light objects, no further knowledge was gained on the subject of electricity until 1600 A.D., when Gilbert, surgeon to Queen Elizabeth, discovered that when a glass rod and about twenty other substances are rubbed separately with silk, the bodies, like amber, become electrified. Many years later it was observed that when sealing-wax was rubbed with cat's fur, the wax assumed an electric charge, which differed from that of the glass. Two kinds of electricity were therefore recognized—vitreous and resinous. About the middle of the eighteenth century Benjamin Franklin introduced the terms positive and negative to distinguish the two kinds of electrification. It is interesting to know that there were no electrical theories before the time of Franklin, who, while flying a kite on a rainy day, discovered electricity in the clouds, and proved "the sameness of lightning and electricity." According to Franklin, any body is positively electrified if it is repelled by a glass rod which has been electrified by silk, and negatively electrified if repelled by sealing-wax which has been rubbed by cat's fur. These definitions of the two kinds of electrification are still in use.

It was early proved that when a glass rod is rubbed with silk, the latter takes up a negative charge exactly equal to the positive charge of the glass; so, in general, we may state that positive and negative charges of electricity always appear simultaneously and in exactly equal quantities.

What is electricity? Various hypotheses have been advanced to explain the nature of electricity, most of which proved to be unsatisfactory: *e.g.*, the two-fluid theory. Franklin advanced a one-fluid theory, which was essentially a material one. Franklin unquestionably believed in the existence of an electrical particle or atom, for he says: "The electrical matter consists of particles extremely subtle, since it can permeate common matter, even the densest, with such freedom and ease as not to receive any appreciable resistance." The atomic theory of electricity was to Franklin a pure speculation, as was the atomic theory of matter to the Greek philosophers. It is only within the last thirty years that the electron theory has been developed. The atomic theory of electricity was clearly stated by G. Johnstone Stoney, in 1874, and he first suggested, in 1891, the word electron as a name for the natural unit of electricity. The modern view is that negative electricity consists of electrons, the free negative electron having a mass which is 1/1845 of that of the hydrogen atom. As stated in a previous chapter, matter is probably granular and electrical in nature. There is convincing evidence to show that the hydrogen atom consists of one positive electron (proton) and one negative electron, which is usually called the electron.

What we call an electric current is now held to be merely a movement of electrons through a wire; and it is believed that good conductors of electricity, such as gold, silver, and copper, have a good many electrons loosely held. In the case of non-conductors, it seems probable that there are not many free electrons.

When a glass rod is rubbed with silk, the negative

charge taken on by the silk is explained by supposing that some free electrons are rubbed off the glass; while the glass, having lost electrons, assumes a positive charge. In general, we may assume that a neutral body takes on a positive charge when it loses electrons, and a negative charge when it gains electrons.

Charging by induction is readily explained by the electronic theory. If the end of a positively charged rod be brought near the end of a neutral rod, the end of the rod near the first is always negatively charged, while the opposite end is positively charged. This is explained by assuming that free electrons are attracted by the positively charged rod, leaving one end of the other rod positively charged.

Lightning may also be explained in terms of electrons. Electrons, or charged molecules of air, serve as nuclei around which moisture of the air may condense. In the course of time the droplets increase in size until they fall as rain-drops; and it appears that they carry down large numbers of stray electrons, the final result being that a tremendous potential is developed, followed by the passage of a "bolt" between the cloud and the earth.

> The earth is rocking, the skies are riven—
> Jove in a passion, in god-like fashion,
> Is breaking the crystal urns of heaven.
>
> —ROBERT BUCHANAN.

2 THE ELECTRON AND THE IONIC THEORY

R. A. Millikan captured the electron on a tiny droplet of oil, and after certain observations were made

the electronic charge was calculated. The proof is now complete that electricity exists as granules, the electron being a unit granule.

In general, an atom of a metal has a tendency to lose one or more electrons, becoming positively charged; while an atom of a non-metal has a tendency to take on one or more electrons, thus assuming a negative charge. An atom or group of atoms bearing an electrical charge is known as an ion. To illustrate, representing an electron by the symbol $\ominus$, we have in the case of sodium the following:

$$\underset{\text{Sodium atom}}{Na} - \ominus = \underset{\text{Sodium ion}}{Na^+}$$

When an atom of chlorine takes on an electron, it has unit negative charge:

$$\underset{\text{Chlorine atom}}{Cl} + \ominus = \underset{\text{Chlorine ion}}{Cl^-}$$

Water solutions of salts, acids, and alkalis conduct the electric current and are decomposed by it; they are known as electrolytes, and the decomposition of the compound under the influence of the current is termed electrolysis. Other classes of compounds, in general, when dissolved in water, do not conduct electricity, so they are called non-electrolytes. Thus, when sugar or alcohol is dissolved in water, the current will not go through the solution, nor is the compound decomposed. Furthermore, a solution of cane-sugar has a normal freezing-point and boiling-point, while a solution of common salt of identical concentration has a lower

freezing-point and higher boiling-point than the corresponding sugar solution. Now, why does a solution of salt exhibit an abnormal behavior in these and certain other respects, and why does it conduct the electric current?

The first satisfactory answer to this question was given by Svante Arrhenius, a distinguished Swedish chemist, in 1887. He propounded a theory which is known as the ionic theory, or the theory of electrolytic dissociation. Stated briefly, this theory assumes that molecules of salts, acids, and alkalis, in the presence of water, partially break down or dissociate into electrically charged particles called ions, as soon as the compound is dissolved in water. The metals and hydrogen carry positive charges, and are known as cations, while the non-metallic ions are negatively charged, being called anions. The following may serve as illustrations:

$NaCl$	$\rightleftarrows$	Na^+	$+$	Cl^-
Sodium chloride		Sodium-ion		Chloride-ion
HCl	$\rightleftarrows$	H^+	$+$	Cl^-
Hydrochloric acid		Hydrogen-ion		Chloride-ion
$NaOH$	$\rightleftarrows$	Na^+	$+$	OH^-
Sodium hydroxide		Sodium-ion		Hydroxide-ion

These actions are reversible. When more water is added, the action goes to the right; *i.e.*, more ions are formed. But when water is evaporated off, more molecules are formed by the union of ions; *i.e.*, the action goes to the left. These actions in the opposite directions are shown by the arrows.

The number of charges carried by the ion corresponds to its valence, and the positive charges exactly

balance the negative charges, so the solution as a whole is electrically neutral.

Ordinarily, a majority of salts dissociate into ions to the extent of 80 to 90 per cent. The more dilute the solution, the greater the degree of ionization. All acids furnish the hydrogen-ion (H^+), so they possess a sour taste and turn litmus red. All alkalis yield the hydroxide-ion (OH^-), and have, therefore, the property of turning litmus blue.

The properties of electrolytes are largely dependent upon the nature and concentration of the ions. Thus, the lead-ion (Pb^{++}) is highly poisonous, which explains why lead salts as a class are poisonous.

The freezing-point of a salt solution is lower than that of a sugar solution of equivalent concentration, because each molecule of salt that dissociates yields two particles, thus increasing the total number of particles.

3 Electrolysis

Electrolytes are conductors, for the ions serve as transports for electricity. When the current is turned on, the ions are piloted or directed to the electrodes, namely, the cathode and the anode, where they are discharged. Thus, when the current is passed through a solution of copper sulphate or blue vitriol ($CuSO_4$) the copper-ion (Cu^{++}) is attracted to the negative electrode (cathode), where it takes on two electrons and is deposited as metallic copper:

Copper sulphate		Copper-ion		Sulphate-ion
$CuSO_4$	=	Cu^{++}	+	$SO_4^{=}$
$Cu^{++} + 2\ominus$	=	Cu (metallic copper)		

In the refining or electrodeposition of a metal, therefore, the electrons which circulate from cathode to anode are required for the discharge of the metallic ion.

Electrolysis has played a very important rôle in the development of chemistry. Early in the last century, for example, it enabled Humphry Davy to decompose certain alkalis, leading to the discovery and isolation of such metals as potassium, sodium, and calcium. Davy placed some caustic potash in a silver dish, heated it to fusion, then introduced the two poles of a battery into the molten mass. Much to his surprise, he observed that silvery-white globules were formed at the cathode and ignited spontaneously. It is needless to say that he was almost overcome with excitement. According to his cousin Edmund, "When Humphry saw the silver globules which caught fire, his joy knew no bounds and he began to dance and it was some time before he could control himself to continue his experiments."

This calls to mind a story concerning Sir Isaac Newton, so well related by Sir P. C. Rây:

> Newton, on the eve of completing the calculations from his Law of Inverse Squares, found that the numerous observations made by Kepler went to establish his theoretical deductions. He grew so nervous and restless that he could not proceed further and a friend of his had to finish the calculations. He was conscious that he was on the threshold of an epoch-making discovery. Such is the ecstasy that a scientific worker feels on the occasion of making great discoveries.

In 1833-34, Michael Faraday discovered a very

fundamental law governing the electrolysis of solutions, which runs as follows: *When different compounds are decomposed by the same current, equivalent quantities of the various products are obtained* (Figure 10). According to this law, the same current which will deposit in a definite time from a solution of a silver salt a weight of silver equal to its atomic weight (107.88) will deposit from a solution of copper sulphate in the same time a weight of copper exactly

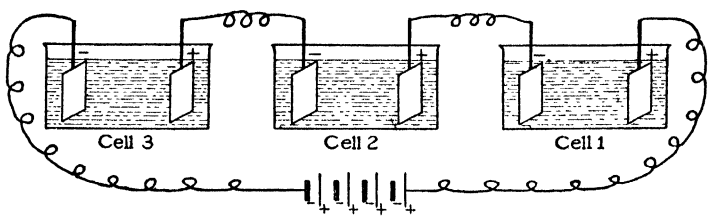


FIGURE 10

Diagram Illustrating Faraday's Law Governing Electrolysis

equal to half of its atomic weight ($63.57 \div 2$). This shows that the copper-ion (Cu^{++}) carries in solution just double the charge carried by the silver-ion (Ag^{+}). In other words, the copper-ion carries two positive charges, or it needs two electrons in order to form metallic copper. Ions therefore bear charges which are directly proportional to their valences.

The ionic theory furnishes an excellent explanation of electrolysis. It should be pointed out that the electrical conductivity of a solution depends upon the nature and concentration of its ions. Strong acids, such as hydrochloric and nitric, furnish a high concentration

of the hydrogen-ion, while a strong alkali furnishes a high concentration of the hydroxide-ion.

In the formation of a salt by the interaction of an alkali and acid—*i.e.*, when neutralization is carried out —we have the union of the hydrogen-ion and the hydroxide-ion to form water:

$$H^+ + OH^- = H_2O$$

Water is a neutral substance in the presence of an indicator, such as litmus, and it is virtually non-ionized and a non-conductor of electricity. The dissociation of water at room temperature is so slight that we need about 10,000,000 liters of water to supply 1 gram of the hydrogen-ion and 17 grams of the hydroxide-ion, or only 1 molecule of water out of about 550,000,000 is ionized.

Stated another way, 100,000 barrels of water would be required to yield 1 gram of the hydrogen-ion.

4 Ions in the Human Body

The hydrogen-ion concentration can be measured, which is of great importance—*e.g.*, in connection with the fluids of the body. The saliva is nearly neutral, while the gastric juice contains a considerable quantity of hydrochloric acid. This acid is of higher concentration in the gastric juice of the dog, which is able to digest bone. The term hyperacidity is employed to denote an excess of acid, while hypoacidity means that there is a scanty secretion, as in anemia, cancer, gall-bladder, heart disease, and in beri-beri and pellagra. Certain bacteria cannot exist in media which are too

acid; consequently they are conspicuous by their absence in the stomach, but are present in vast numbers in the intestines. The hydrogen-ion concentration of the blood is virtually constant.

The calcium-ion (Ca^{++}) is important in the chemistry of the blood. In cases of rickets and certain other diseases it may be much reduced. Other ions, such as the sodium, potassium, magnesium, and chlorine, are also delicately balanced in the blood. Too high a concentration of potassium-ion (K^{+}) may produce paralysis of the heart, the rate of heart-beat dropping to zero; while an excess of calcium-ion (Ca^{++}) is very toxic. We see, therefore, that the ionic theory is very important in the field of medicine.

5 The Production and Uses of the Electric Current

An electric current may be produced by chemical change, the source of the electricity being the chemical energy stored in the interacting substances such as zinc and sulphuric acid. When zinc is dissolved in dilute sulphuric acid, hydrogen is liberated along with heat. It is possible, however, to carry out this chemical reaction so as to make electricity appear instead of heat. This may be accomplished by immersing one end of a rod of zinc (Zn) in sulphuric acid and connecting the other end of the zinc rod by means of a copper wire to one of the binding posts of a galvanometer, the other post of which is connected with a piece of platinum (Pt) foil, which is also immersed in the dilute sulphuric acid (Figure 11). The needle of the galva-

nometer is deflected, showing that a current of electricity is produced. In other words, we have a simple electric cell. Zinc dissolves to form the zinc-ion (Zn^{++}), each atom of the metal losing two electrons, which flow through the zinc rod, the wire and galvanometer, around to the platinum, at the surface of which bub-

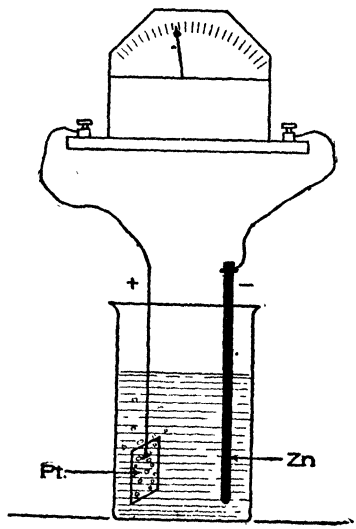


FIGURE 11
Production of an Electric Current

bles of hydrogen are liberated. The circulation of electrons constitutes an electric current. In an electric cell, therefore, chemical energy is transformed into electricity.

In order to produce an electric current by means of chemical change, the reactions are carried out in cells (voltaic or galvanic), which are commonly called bat-

teries. (Strictly speaking, a battery is a collection of cells.) Volta, in 1800, produced a current of electricity by introducing a plate of zinc and one of copper into dilute sulphuric acid, and then joining the plates by means of a wire. The voltage of this cell is about 0.74. Davy employed a battery of these cells in 1807 for the electrolysis of the alkalis.

It was found that the copper plate of the Volta cell was rapidly attacked by the chemical reagents, so in practice it has been displaced by a plate of carbon, which is much more resistant. To remove hydrogen, which accumulates on the carbon electrode, the latter is surrounded by an oxidizing agent, such as manganese dioxide, which is used in dry batteries. The zinc plate may be protected from too rapid disintegration by amalgamation—*i.e.*, by coating the metal with a thin layer of mercury.

In the storage-battery, or lead-accumulator, plates of leaden gratings are prepared, one of the gratings being filled with spongy lead and the other with lead dioxide (PbO_2). Pairs of these plates are placed in a cell and dilute sulphuric acid (specific gravity about 1.2) is added. When the plates are connected by means of a wire, a current is produced as the cell is discharged The specific gravity of the acid decreases as the cell or battery runs down, as automobilists know; hence it is wise to test the acid from time to time with a hydrometer. The exhausted battery is charged by passing through it a current from a dynamo, the current being passed in the opposite direction to that produced by the battery. Sulphuric acid is regenerated, and the specific gravity of the liquid therefore increases; while the

filling of the plate (lead sulphate) is changed into lead dioxide. The battery has thus stored up energy and may be discharged again by connecting the wires of the plates. The chemical changes occurring both on discharge and charge are as follows:

$$\underset{\text{dioxide}}{\text{Lead}} + \text{Lead} + \underset{\text{acid}}{\text{Sulphuric}} \rightleftarrows \underset{\text{sulphate}}{\text{Lead}} + \text{Water}$$

Discharge $\longrightarrow$ $\longleftarrow$ Charge

The application of electricity in the field of chemistry has become more and more important ever since the two Englishmen Nicholson and Carlisle succeeded, in 1800, in decomposing water into its constituents (hydrogen and oxygen) by the electric current. Many important substances such as the alkali and alkaline earth metals, aluminium, chlorine, hydrogen, oxygen, and sodium hydroxide, are obtained by electrolysis. Copper and other metals are refined by electrolytic methods; and many articles are plated with gold, silver, nickel, and other metals. Thus, copper may be refined by arranging large ingots of impure copper as anodes in electrolytic tanks, while the cathodes are thin sheets of pure copper, each anode being arranged opposite a cathode. The electrolyte is a solution of copper sulphate and sulphuric acid. When a properly regulated current is passed through the solution, copper is carried from the anode to the cathode where it is deposited. Certain impurities, such as silver and gold, collect on the bottom of the tank as mud or slime, which is worked over for the precious metals. Selenium, tellurium, and other by-products are sometimes obtained in the refining of copper.

A copper electrotype of a page of type is made by preparing a plaster-of-Paris, wax, or gutta-percha cast of the type, after which it is coated with graphite and then employed as a cathode in an electrolytic cell containing a solution of a copper salt.

Silver-plating and gold-plating may be accomplished by employing as electrolyte a compound of the metal in the form of a cyanide. The article to be plated is the cathode, a plate of the metal serving as anode.

Electrometallurgy is now a large and growing department of metallurgy; for the electric current is employed not only for electrolytic separation or deposition of metals from solutions, but as a source of heat in smelting, refining, annealing, and welding.

There are many valuable products of the electric furnace, among which may be mentioned carborundum, graphite, phosphorus, calcium carbide, and alundum. In the electric furnace electricity is transformed into heat, the temperature rising to about 3500° C., or over 6300° F. At the temperature of the electric furnace very refractory substances, such as platinum and quartz, melt almost as readily as butter.

The Cowles Electric Smelting and Aluminium Company of Cleveland first employed (1885) the electric furnace on a large scale. Moissan, of Paris, employed the furnace, in 1893, in the preparation of artificial diamonds from sugar charcoal, or carbon. The charcoal was packed in a graphite crucible with iron, the crucible placed in an electric furnace, and a powerful arc formed between carbon electrodes. At the extremely high temperature, the carbon dissolved in the molten iron. The fiery crucible was then rapidly cooled, and

the carbon in the inner part of the vessel was subjected to enormous pressure. When the iron was removed with acids, very small diamonds were found in the residue, some of which were colorless and others black.

Graphite, a form of carbon, is manufactured at Niagara Falls, where abundant water-power means cheap electricity. Coke or anthracite coal is heated in the Acheson electric furnace, the charge being covered with a mixture of sand and carbon. In the course of time the coal or coke is transformed into artificial graphite, which can be used for virtually any purpose to which natural graphite, or plumbago, is put.

Carborundum, or silicon carbide (SiC), also is produced at Niagara Falls by the Acheson process. Sand, coke, and common salt are heated in an electric furnace for thirty-six hours, the charge being packed around a horizontal core of granulated coke. The crystals obtained often have a beautiful, iridescent luster. Carborundum is harder than corundum and is a very stable substance. It is used extensively as an abrasive. Without abrasives it would be impossible to manufacture modern machinery such as the automobile.

The first carborundum furnace produced only a quarter of a pound per day, which sold at eighty dollars a pound. A modern furnace can produce sixteen thousand pounds in thirty-six hours, which sells for about fifteen cents a pound. The annual production is about thirty thousand tons. This is an excellent illustration of the possibilities of utilizing the heat of the electric furnace. Electrochemistry is one of the most important branches of chemistry.

CHAPTER XI

THE MAGIC AND MYSTERY OF CATALYSIS

A pompous word will stand you instead
For that which will not go into the head.
—GOETHE.

1 THE MEANING OF CATALYSIS

IT was known to Berzelius, a great Swedish chemist, nearly a century ago, that the presence of relatively small quantities of certain substances alters the speed of chemical changes, the substances themselves undergoing no permanent change. Berzelius proposed the pompous name catalysis (Greek: down + to loosen) for this sort of action, and the agents employed are known as catalysts or catalyzers.

To illustrate, everybody who has studied chemistry knows that oxygen may be prepared by heating potassium chlorate to a high temperature (about 700° F.); but when manganese dioxide is mixed with potassium chlorate, the latter yields up its oxygen at a much lower temperature, and the dioxide is unchanged at the end of the action. The mere presence, then, of manganese dioxide increases the rate at which oxygen is liberated and a lower temperature is required; or, in other words, the dioxide is a catalyst in this action.

Ostwald, the celebrated German chemist, compares the action of a catalyst with the influence of oil on

the wheels of a machine. The similarity is indeed marked. For instance, the catalyst is unchanged in weight and composition at the end of a chemical action; the lubricating-oil is not burned up or changed chemically when a machine is in operation. Moreover, the catalyst speeds up the chemical change very much as a lubricant lessens friction and accelerates the working of the wheels of a machine. As expressed by E. J. Holmyard, "If oil be added to a machine making paper bags, the machine will continue to make paper bags and not packets of cigarettes."

As a rule a chemical change is not started by a catalyst; it merely affects the rate or speed of change.

Chemists employ the terms positive catalyst and negative catalyst. The former term may be compared to lubricating-oil on a machine, while the latter may be likened to the action of grit in a machine. Thus, hydrogen peroxide, which is familiar in the household, gradually breaks down into water and oxygen; so in order to lessen its decomposition a small quantity of acetanilide, a coal-tar derivative, is added as a negative catalyst. On the other hand, water functions as a positive catalyst in many chemical reactions; indeed, it is doubtful if any chemical change will take place in the complete absence of water. *Perfectly dry carbon or charcoal, for example, will not burn in perfectly dry air or oxygen;* but when a trace of water is introduced, the action proceeds vigorously, carbon dioxide being produced.

Tetraethyl lead, which is employed as an "anti-knock" in gasoline, may play the rôle of a catalyst. The compound is unstable, breaking down into lead

and the very reactive ethyl group (C_2H_5). The precise way in which tetraethyl lead produces smooth combustion is not known.

2 Enzymes

It is marvelous to observe the effect of certain catalysts, or to watch them at their work. Somebody has referred to them as "chemical parsons." It is of interest to know that the organic catalysts, called enzymes or ferments, work independently: one splits starch, another splits proteins, and still another splits fats. They remind us of the different branches of a great labor union, a member of one branch refusing to do the work of a member of a different branch.

The catalytic effect of yeast upon dough is perhaps the earliest recorded example of the phenomenon of catalysis. According to St. Paul, "A little leaven leaveneth the whole lump."

Enzymes are present in all living organisms, and they play an essential part in life-processes. Their rôles are important in digestion, fermentation, oxidation, and decay. Payen and Persoy isolated diastase in 1833, and pepsin was isolated by Schwann the following year. The production of enzymes by bacteria was observed by Wortmann in 1882. While enzymes are found in all plants and animals, certain organs produce them in large quantity. Thus, in plants the seeds are the principal seat of enzyme activity, while in animals enzymes are produced in certain glands, such as the salivary glands and the pancreas. It is also true that enormous quantities of enzymes, so important in

digestion, are secreted by the mucous membrane of the stomach and intestines. Very little progress has been made in synthesizing enzymes. In 1896 Buchner expressed from yeast a liquid containing the enzyme known as zymase. Yeast consists of microscopic cells belonging to a low order of plants. It was found that zymase would act as a catalyst in transforming a solution of glucose into alcohol and carbon dioxide, thus showing that alcoholic fermentation may be brought about without the presence of the living cells or plants. Yeast will ferment a solution of cane-sugar or molasses, for it contains two important enzymes—sucrase (invertase) and zymase. Sucrase first transforms cane-sugar into glucose and fructose, and these simple sugars are then fermented by the catalyst zymase.

Diastase, an enzyme contained in sprouting grain, or malt, converts starch into dextrine and maltose, a sugar; it is capable of transforming more than 2,000 times its own weight of starch. Sucrase, an enzyme present in yeast, will transform 100,000 times its own weight of cane sugar into the simpler sugars, glucose and fructose. Rennet, an enzyme obtained from the stomach of the calf, will coagulate over 250,000 times its own weight of casein in milk, and is therefore of great importance in the manufacture of cheese.

Normal butyl alcohol, now used in the manufacture of butyl acetate, a valuable solvent, is produced on a large scale by the fermentation of carefully sterilized corn mash. The mash is inoculated with spores of Weizmann bacteria, which ferment starch to normal butyl alcohol and acetone, both important substances.

This is an outstanding example of biological engineering. In conducting the process, air must be excluded and foreign organisms prevented from gaining access to the starch. The corn mash circulates through pipes previously sterilized by high-pressure steam, and the circulating pumps have pistons which pass through loose packings wet with a solution of carbolic acid. Most careful provision is made for isolating a single spore of the necessary micro-organism, and then propagating from this a pure culture in sufficient quantity to ferment the contents of a vat twenty feet deep and twenty feet in diameter. This is truly a marvelous process.

The digestive ferments play a great rôle in the transmutation of the food into products capable of being assimilated, and therefore useful in the production of energy and in the building up of tissues. The saliva contains a ferment called ptyalin, which converts starch into sugar and dextrin. Ptyalin is very important, for the food is not brought into contact with starch-splitting enzymes again until it reaches the intestines. When food reaches the stomach it comes into contact with pepsin and a curdling enzyme found in rennet. This ferment curdles milk, or causes a separation of casein. Pepsin is the enzyme which transforms the proteins, or complex nitrogenous bodies, into simpler substances. Pepsin therefore plays a useful part in the digestion of meat and eggs.

Trypsin is a protein-splitting enzyme found in the pancreatic juice of the small intestine; it breaks down proteins into amino-acids. Other very important enzymes which aid in digestion, are amylase, a starch-

splitting enzyme, and steapsin or pancreatic lipase, which splits up fats into glycerine and fatty acids; these acids then diffuse through the intestinal wall to recombine, forming fat in the blood. In case of jaundice, bile is prevented from reaching the intestine, so the utilization of fat is strikingly diminished.

Various diseases, such as gout, result when certain enzymes do not function.

Thrombin (Greek: a clot) is an enzyme in the blood; in shed blood it transforms soluble fibrinogen into insoluble fibrin, which collects at the wound the red corpuscles and platelets. In other words, a clot is formed, or the flow of blood is stayed.

3 Other Applications of Catalysis

It will be of interest to study other processes in which catalysts play an important part.

The modern process for the manufacture of sulphuric acid, known as the contact process, is dependent upon the use of finely divided platinum as a catalyst. Sulphur dioxide, produced by burning sulphur, is mixed with air (or oxygen) and passed over heated asbestos or other material covered with finely divided platinum. In contact with the platinum the sulphur dioxide (SO_2) and oxygen unite to form sulphur trioxide (SO_3), the anhydride of sulphuric acid, which means that sulphuric acid is obtained by allowing sulphur trioxide to interact with water. Several million tons of "contact" sulphuric acid are produced annually in the United States. Since the minutest amounts of arsenic, dust, and certain other materials "poison" the

platinum, the sulphur dioxide is carefully purified before it is allowed to come in contact with the catalyst. This process for the industrial production of sulphuric acid has been a great success.

Another very successful application of catalysis is in the manufacture of solid fats from vegetable and animal oils, the process being known as the hydrogenation of oils. Hydrogen, in the presence of the catalyst nickel, may be added chemically to certain liquid fats and oils. Thus, when cotton-seed oil is so treated, a solid fat is obtained. Crisco and other substitutes for lard are produced by hydrogenation. This process is adding $20,000,000 annually to the value of our cotton-seed oil, and the amount of solid fat produced each year is equal to that obtained from 7,000,000 hogs. About 300,000,000 pounds of oils are hydrogenated annually in the United States. Due to hydrogenation, there is an enormously expanded whaling industry in Arctic and Antarctic seas, and new tracts of cocoanut plantations have been developed in tropical countries.

In adding hydrogen to oils, the gas, under several atmospheres of pressure, is passed through the liquids in the presence of finely divided nickel; for, this being a contact process, the largest possible surface of metal is needed. A ton of fat requires from 500 to 5,000 cubic feet of hydrogen.

Catalysis is also of the highest importance in the fixation of atmospheric nitrogen. Before the recent war, Professor Haber, of Germany, perfected a method for the chemical addition of one atom of nitrogen to three atoms of hydrogen to form each molecule of ammonia

(NH_3). This is accomplished by passing a mixture of nitrogen and hydrogen, at a pressure of 150 atmospheres or more, over a suitable catalyst, such as some form of iron, at a temperature of about 500° C. (932° F). This synthetic method for the production of ammonia is the leading one for the fixation of nitrogen. Over 300,000 tons of nitrogen were fixed by this method in 1921, most of which was done in Europe. The production of synthetic nitrogen products is increasing very rapidly. During the fertilizer year ending with May, 1926, Germany's production of synthetic nitrogen products is estimated to have been about 400,000 tons of nitrogen. In the year 1925 Germany exported over $20,000,000 worth of Haber products.

Ammonia is not only used in the production of fertilizers, but it may be oxidized to nitric acid, of prime importance in the manufacture of explosives. No nitric acid, no explosives. Before the war, Ostwald brought to completion a method for the transformation of ammonia into nitric acid. A mixture of ammonia and air is passed through nickel tubes containing layers of glowing platinum gauze, the platinum serving as catalyst for the oxidation of ammonia. This process enabled Germany to produce great quantities of nitric acid after the supply of Chile saltpeter was exhausted, thus prolonging the war.

Until recently all our methyl (wood) alcohol, or methanol, was obtained by the destructive distillation of wood. For about two years, however, synthetic methanol has been produced on an industrial scale in Europe. Methyl alcohol is formed when a mixture of hydrogen and carbon monoxide, under high pressure,

is passed over suitable catalysts. The process is somewhat similar to that employed in the Haber process for ammonia. The product is pure, and it is reported that it can be produced more economically than from wood.

In writing about synthetic products, Hugh Farrell says:

> In most cases the chemist not only succeeds in duplicating the product of Nature's laboratory; he actually improves upon the natural product—makes a stronger, a purer and a more lasting thing than Nature can make. The chemist can even make more beautiful things than Nature can make—his colors, or some of them, have no counterpart in Nature and are vastly more brilliant and enduring.
>
> If you don't know about what the chemist is doing you are due to receive some startling information, especially if you have your money invested in some industry or other, which is running the risk of having its product matched or bettered in the laboratory at a production cost which the concern in which you are interested cannot meet.
>
> Some such thing as this recently happened to the distillers of wood alcohol. This industry with more than $100,000,000 invested and an annual production valued at something around $35,000,000 a year, has been dealt a very hard blow.

Catalysis, for several years, has played an important part in the production of industrial acetic acid. When lime and coke are heated to a high temperature in an electric furnace, calcium carbide is formed, which yields acetylene when treated with water. Now, acetylene in the presence of a suitable catalyst such as mercuric sulphate combines with water to form acetaldehyde, which in the presence of the catalyst manga-

nese sulphate unites with oxygen to form acetic acid, the acid flowing out of the reaction chamber like soft ice as thick as the arm of a man. Large quantities of calcium carbide are manufactured at Shawinigan Falls, Canada, and enormous quantities of acetic acid have been produced from the acetylene derived from the carbide.

Now and then important discoveries are made by accident. An interesting story is told concerning the discovery of mercury as a catalyst for transforming naphthalene (familiar as moth-balls) into phthalic acid. Years ago, in the Badische works in Germany, where they were working on synthetic indigo, phthalic acid was needed as an intermediate substance. At that time the compound was expensive, but there appeared to be every reason why one should be able to prepare it by treating naphthalene with fuming sulphuric acid. Trial after trial was made, but the results were most discouraging. One day, while an experiment was being conducted with naphthalene, a laboratory boy was told to read the mercurial thermometer. By accident he broke the instrument and a small amount of mercury fell into the reacting mass, whereupon the material began to seethe and in the course of time phthalic acid was formed in quantity. Mercury was just the catalyst needed. It worked like magic.

Within twenty years catalysis has largely transformed industrial and commercial life. Synthetic indigo, for instance, has displaced the natural product; so the indigo plantations of India are no more. Indeed, the story of the accomplishment of the catalytic chemist reads like a romance.

We might go on almost indefinitely telling the marvelous story of catalysts, but sufficient has been written to show that they not only are adding greatly to the wealth of nations, but are most intimately connected with life-processes themselves.

4 The Mechanism of Chemical Reactions

Very little is known about the precise way in which catalysts do their work or about the true nature of enzymes. Various hypotheses have been advanced, most of which are untenable.

In one type of chemical change there is evidence that the catalysts form unstable intermediate compounds which break down, leaving the catalysts unchanged. In the case of potassium chlorate and manganese dioxide there is evidence that manganese dioxide reacts with potassium chlorate to form potassium permanganate, the latter compound then decomposing to form manganese dioxide and other substances.

In another type of chemical change the catalyst appears to act by contact: *e.g.*, platinum in the contact process for sulphuric acid.

Professor H. S. Taylor and his co-workers, of Princeton, have carried out a great deal of experimental work on catalysis and the mechanism of chemical reactions, and a theory of the catalytic surface has been developed. It has been shown that a catalyst surface, such as that of nickel, shows a *varying capacity* to absorb gas and to promote catalytic change. While the body of a granule of the cataylst is crystalline,—*i.e.*, has an ordered arrangement of atoms,—it appears that

here and there, on the surface of a mainly crystalline granule, there are groups of atoms in which the process of crystallization is not yet complete. It is believed that certain atoms at the surface of the catalyst are in a state of unsaturation relative to the main body of the catalyst material, and it is these unsaturated atoms which are effective in absorbing gases; that some of the diatomic hydrogen molecules (H_2) in the presence of nickel and of copper, yield atoms (H) which are very active; also that nitrogen molecules (N_2) and hydrogen molecules (H_2) in the presence of the catalyst iron tend to dissociate to form atoms, or monatomic molecules, which are very reactive.

CHAPTER XII

SULPHUR, A PILLAR OF INDUSTRY

> Quickly, O nurse, bring fire that I may burn
> Sulphur, the cure of ills.
>
> —HOMER.

1 THE OCCURRENCE, PRODUCTION, PROPERTIES, AND USES OF SULPHUR

EVERYBODY is more or less familiar with sulphur, an old name for which is brimstone.

> From his brimstone bed, at break of day,
> A-walking the Devil is gone.

This element was well known to the ancients. Thus, we find in Genesis that "the Lord rained upon Sodom and upon Gomorrah brimstone and fire." The element is also mentioned in the writings of Homer. Sulphur was burned in ancient times for the purpose of fumigation; and according to Paracelsus it was one of three constituents of the human body, salt and mercury being the others. The alchemists believed sulphur to be the principle of fire, which accounts for the saying: "Where there is fire and heat, there is sulphur."

Sulphur, together with the less familiar elements selenium and tellurium, belongs to the oxygen family. While there is a chemical relationship between sulphur and oxygen, they differ widely in many respects,

as do their corresponding compounds. To illustrate, water (H_2O) is analogous to hydrogen sulphide (H_2S), the latter of which confers part of the disgusting odor upon decaying eggs. Carbon dioxide (CO_2) and carbon disulphide (CS_2) are also analogous, but the latter is a very inflammable liquid with a disagreeable odor. Indeed, sulphur probably forms more evil-smelling compounds than does any other element.

Sulphur occurs abundantly and widely distributed in nature. In the free state it is found in volcanic districts of Italy, Sicily, Iceland, Mexico, and other countries. Native sulphur is especially abundant in Sicily and in the United States, Louisiana and Texas being noted for their large and remarkably pure deposits of the element. Before 1900, Sicily furnished about 90 per cent of the world's supply of sulphur; but in 1918 the United States mined 1,353,000 tons, which was 65 per cent more than the world's production in 1913.

The precise way in which native sulphur is formed is not known. Volcanic gases, such as those of Vesuvius and of Mount Ætna, generally contain sulphur dioxide and hydrogen sulphide, and when these moist gases come together they mutually decompose, sulphur being deposited. Deposits of this type are being formed at the present time. The formation of sulphur may be shown by bringing mouth to mouth two bottles, one filled with hydrogen sulphide and the other with sulphur dioxide. Much of the native sulphur may have been formed by the reduction of calcium sulphate, or gypsum.

Sulphur in the combined state is much more abun-

dant and widely distributed than native sulphur. It occurs principally as sulphides and sulphates. Sulphides contain sulphur and one other element, usually a metal. Many sulphide minerals are of great industrial importance, such as iron pyrites, copper pyrites, zinc sulphide or blende, lead sulphide, or galena, and mercuric sulphide, or cinnabar. Iron pyrite has somewhat the appearance of gold; therefore it is appropriately called "fool's gold." Hydrogen sulphide, or sulphuretted hydrogen, is present in the so-called sulphur waters and in certain volcanic gases. The water from one of the sulphur springs in Iceland is said to be ejected to a height of several feet, accompanied by a hissing noise.

Sulphates, or salts of sulphuric acid, are found in very large quantities, both in the crust of the earth and in sea-water. Among these compounds some of the most important are calcium sulphate or gypsum, barium sulphate or heavy spar, strontium sulphate or celestite, and magnesium sulphate or Epsom salts. Millions of tons of gypsum are mined annually; it is used in agriculture and in the manufacture of plaster-of-Paris and wall-plaster and as a filler of paper.

Sulphur compounds are also found broadly distributed in the vegetable and animal kingdoms. Sulphur is therefore an essential constituent of certain forms of life. Sulphur compounds are present in garlic, onions, hair, wool, the blood, bile, etc. About one per cent of the element is contained in all the albuminous substances, which are so important in the animal body. Proteins are the only source of sulphur in a form suitable for use by the tissues. Sulphur is a constituent

of hemoglobin, each red blood-cell containing billions of molecules of this complex substance, the formula for which is supposed to be $C_{758}H_{1203}N_{195}S_3FeO_{218}$. Sulphur is also present in petroleum and in coal. The element is a great nuisance in fuel, for it injures boilers and grate-bars. Likewise, it is very objectionable in iron ores, for it makes iron "red short"—*i.e.*, brittle when hot.

In Sicily, sulphur occurs mixed with earthy matter, from which it may be separated by heating the ore and allowing the molten sulphur to flow away from the impurities. This is usually done in kilns. The crude sulphur thus obtained is purified by distillation from iron retorts, the vapor passing into a large chamber where it condenses, at the beginning, to form "flowers of sulphur." When the chambers become heated above the melting-point of sulphur, the liquid element is drawn off and then cast into slightly conical wooden molds, "roll sulphur" being obtained.

In 1787 some workmen in one of the Sicilian sulphur fields accidentally ignited the sulphur, and the fire raged for two years, while the pit was filled with suffocating sulphur dioxide, which caused the abandonment of the mine. Subsequently and quite suddenly the mountainside opened up, emitting dense yellow fumes, and a torrent of molten sulphur poured into the river below, the mass of the pure element amounting to about forty thousand tons. This extraordinary phenomenon was similar to the crude method employed in Sicily for producing sulphur.

In the United States, sulphur is produced by a highly successful process invented by Herman Frasch.

In Louisiana and Texas the element occurs several hundred feet below clay, rock, and quicksand. There is one deposit in Louisiana which is over half a mile in diameter and is estimated to contain many million tons. The early attempts to mine the sulphur met with failure until Frasch solved the problem of reaching the deposit and of extracting the sulphur. An outline of this process is as follows:

Borings are made through the overlying material until the beds of sulphur are reached, and three concentric pipes are then driven through the holes. Superheated water (temperature about 325° F.) is pumped down the outside pipe to the sulphur formation, which melts, the liquid sulphur collecting at the foot of the well. Compressed hot air is forced to the bottom of the well through the smallest pipe and it forces the liquid sulphur through the other to the surface, where it is collected in sumps. The sulphur is now pumped into large vats, where it solidifies and is subsequently broken down for shipping. The sulphur thus obtained is sold with the guarantee that it is at least 99.5 per cent pure. A single well often produces 500 tons of sulphur daily, and the most productive wells are said to have yielded more than 100,000 tons. A single block of the element has contained over 1,000,000 tons.

Sulphur, like oxygen, carbon, phosphorus, and tin, exists in different forms. Native sulphur occurs in the form of large yellow crystals, known as rhombic sulphur. This form of the element may be obtained by allowing the substance slowly to crystallize from solution in carbon disulphide. Another form of the ele-

ment, known as monoclinic sulphur, may be prepared by allowing melted sulphur to cool until a crust is formed on the surface. By breaking the crust and pouring out the sulphur still in the molten condition, the vessel will be lined with long, lemon-yellow crystals. What is the relation of rhombic to monoclinic sulphur? Sulphur is dimorphous; *i.e.*, there are two distinct crystalline forms. Rhombic sulphur is stable between 96° and 119° C., its melting-point. Ninety-six degrees is called the transition-point, for these two forms of sulphur are in equilibrium at this temperature. When monoclinic sulphur is cooled below 96°, it gradually changes to rhombic sulphur, the form occurring in nature.

There are two common modifications of tin, called gray tin and white tin, the latter modification being the common form of the metal. When white tin is exposed to low temperature for some time, it slowly changes to a gray powder. For instance, A. L. Erdmann observed, in 1851, that some of the tin organ pipes in the church at Zeita crumbled to a gray powder. During the winter of 1867-68 blocks of tin in St. Petersburg underwent a similar change. Tin medals and buttons of military uniforms have also been known to crumble to powder. This transformation of white tin to the gray form is called the "tin pest." The transition point is 18° C. (64.4° F.). Above 18°, the white modification is stable, while below this temperature the change to the gray form occurs. Excepting in warm weather, ordinary white tin is in what is known as a metastable condition; but the speed of change to the gray form is very slow at ordinary temperatures.

When melted sulphur is poured in a thin stream into cold water it forms a gummy, elastic mass, known as plastic or amorphous sulphur. It is so viscous that it can be drawn out into long threads; but on standing it gradually changes to a hard, brittle lump. Plastic sulphur is insoluble in carbon disulphide. It is, indeed, an extraordinary substance.

The allotropic forms of sulphur and of tin remind us of the two forms of oxygen—the ordinary oxygen of the air and ozone. This element has, therefore, a dual character. The deportment of some forms of matter is strikingly like the behavior of persons who have a dual or multiple personality, as portrayed in "Dr. Jekyll and Mr. Hyde."

When sulphur is cooled to a very low temperature by means of solid carbon dioxide, or "carbonic acid snow," its color changes from yellow to white. On removal from its icy environment, however, it reverts to its original color. This reversal of color with change in temperature is not uncommon. For instance, zinc oxide is white when cold, but yellow while hot.

2 Sulphur Dioxide

Sulphur burns in air or oxygen, forming sulphur dioxide, a colorless gas with a sharp odor, which has many important uses, such as fumigation, bleaching, and the manufacture of sulphuric acid and sulphites. Liquid sulphur dioxide for commercial purposes is stored in metal cylinders. Sulphur dioxide is employed for bleaching many materials, such as straw, paper, silk, and wool. It is much milder in its action than

chlorine, which injures silks and woolens. The bleaching action of sulphur dioxide may be shown by introducing a colored flower, thoroughly moistened with water, into a bell-jar containing sulphur dioxide, or sulphur burning in oxygen. A red rose or carnation thus bleached may have its color restored by dipping it into moderately concentrated nitric acid. Dried fruits, cherries, and corn for canning may also be bleached by means of sulphur dioxide. Its use as a food preservative is questionable.

Sulphur dioxide dissolves in water, forming sulphurous acid (H_2SO_3), the salts of which are termed sulphites. When sulphurous acid is exposed to the air, it slowly unites with oxygen, each molecule of the acid combining with an atom of oxygen to form a molecule of sulphuric acid (H_2SO_4).

Sulphur may be appropriately called a pillar of industry, for it has so many important uses, such as the manufacture of sulphuric acid, sulphur dioxide, and carbon disulphide. It is also employed in vineyards to destroy fungi, as well as red spiders on hops. The lime-sulphur spray is used extensively in orchards. Refined sulphur is used in black gunpowder and in fireworks and for vulcanizing rubber. During the World War there was a large demand for sulphur in the manufacture of mustard gas ($C_4H_8Cl_2S$), which produces serious burns, and in severe cases attacks the larynx, bronchial tubes, and lungs.

3 Sulphuric Acid

Sulphuric acid is the most important and useful acid known. Next to water, it is the fluid most widely em-

ployed in the chemical industries, and is appropriately called the "king of chemicals," the "old horse of chemistry," and the "vital fluid of the nation's industries." The acid plays such an important part in industrial chemistry that it has been said that a country's prosperity and civilization may roughly be estimated from its output of sulphuric acid. Without this acid, commerce, manufacturing, transportation, as well as many affairs in the home, would be paralyzed. There is scarcely an article of clothing or a household utensil or fixture which is not dependent either directly or indirectly upon sulphuric acid. It is employed in almost every art and trade. Thus, it is utilized in the production of other acids, such as nitric and hydrochloric; it is employed extensively in petroleum refining, in metallurgy, and in the manufacture of steel, leather, alums, and blue vitriol.

Deprived of this acid, we could not operate our lead storage-batteries, manufacture explosives, or transform insoluble phosphate rock or bone-ash into soluble acid phosphate, so necessary in agriculture. Through the agency of sulphuric acid, starch is transformed into glucose, an important sugar, and copper is refined by electrolysis; also, a form of sugar may be formed from paper or sawdust, and from this sugar alcohol may be produced. Immense quantities of the acid are combined with ammonia to form ammonium sulphate, one of the most important fertilizers. The world's output of sulphuric acid in 1907 was about 4,000,000 tons; but just before the war the production was about 8,000,000 tons, over one fourth of which was manufactured in the United States. On November 1, 1918, the

domestic manufacturing capacity was 6,000,000 tons annually. While there is an enormous demand for the acid in time of peace, it is much greater in time of war.

The acid was obtained in the fifteenth century by heating ferrous sulphate, otherwise known as copperas or green vitriol, with sand; hence the name oil of vitriol, or vitriolic acid. About the middle of the eighteenth century, Ward, a quack doctor of England, manufactured sulphuric acid by burning a mixture of sulphur and saltpeter in ladles suspended in glass globes containing small quantities of water. The capacity of the globes was from forty to fifty gallons. The acid was crude and expensive, selling for 13 shillings ($3.25) per pound. Shortly afterward lead chambers were substituted for the glass globes, and a great process for the manufacture of the acid, still known as the lead-chamber process, was developed. Such chambers were first constructed at Birmingham in 1746.

In the lead-chamber process a mixture of sulphur dioxide and air is passed into lead-lined chambers into which oxides of nitrogen and steam are also sent. Since all the interacting substances are gaseous and the reactions not speedy, large chambers are required. The oxides of nitrogen are needed only in small quantities, and may be regarded as a catalyst in oxidizing sulphur dioxide and water to sulphuric acid. The chamber acid thus obtained usually contains about 68 per cent of sulphuric acid (H_2SO_4). A more concentrated acid may be produced by distillation. The product of distillation is a heavy oily liquid, which generates an enormous amount of heat when poured into water. The acid is a powerful solvent and dehydrating agent. Its great af-

finity for the elements of water may be shown by dipping strips of wood into the acid. Hydrogen and oxygen are abstracted to form water, leaving carbon, which is black. Within the last quarter of a century, the contact process has become more and more important in the manufacture of sulphuric acid. In the year 1920, the United States produced about 40 per cent of the acid in contact-acid plants. The use of platinum as catalyst in the manufacture of sulphuric acid was referred to in Chapter XI.

In the production of sulphuric acid, sulphur dioxide is required; and it is obtained either by burning sulphur or by roasting or burning a sulphide, such as iron pyrites (FeS_2). By the oxidation of sulphur dioxide, sulphur trioxide (SO_3) is formed. This oxide is the anhydride of sulphuric acid; *i.e.*, it yields the acid by uniting with water:

$$H_2O + SO_3 = H_2SO_4$$

Sulphur trioxide is readily soluble in concentrated sulphuric acid. The production of fuming sulphuric acid or oleum is accomplished by passing sulphur trioxide into strong sulphuric acid.

The contact process yields acid of a high degree of purity; and all concentrations of acid, including oleum, may be produced without costly lead chambers and oxides of nitrogen. There is a great demand for oleum in the manufacture of dyes.

It is worthy of note that sulphuric acid was first manufactured in the United States by John Harrison, of Philadelphia, in 1793. He produced about a carboy of acid a day, or approximately twenty tons a year.

Many years ago the founders of the Chemical National Bank of New York undertook the manufacture of sulphuric acid, but owing to various difficulties they gave up the task and made use of their charter in founding a bank, which has grown to be a powerful and useful institution.

In the year 1838 the King of Naples leased to a Marseilles firm the monopoly for producing sulphur in Sicily, which is the only European country possessing large deposits of sulphur. Owing to the monopoly the price of sulphur rose from £5–10 to £15 per ton. At that time almost all the sulphuric acid factories were in England, so the English were greatly disgruntled, and there was danger of a sort of sulphur war; the monopoly was withdrawn.

4 Sulphides

Sulphur forms many sulphides, which are analogous to oxides.

The formation of hydrogen sulphide, or sulphuretted hydrogen, by the decay of organic matter has been referred to. This useful compound may be prepared by treating iron sulphide (FeS) with dilute sulphuric acid. It is a colorless gas with a sweetish taste and a most disagreeable smell. When hydrogen sulphide is inhaled, it acts as a powerful poison. It is said that one part of the gas to two hundred parts of air is fatal to mammals, and smaller animals are still more sensitive. Very dilute chlorine gas, obtained by sprinkling bleaching powder on a towel moistened with acetic acid, may be employed as an antidote.

Hydrogen sulphide is readily soluble in water, the solution having weakly acid properties. Its salts are called sulphides, many of which occur in nature. Some of them were no doubt formed by the interaction of metals with hydrogen sulphide. Illuminating gas usually contains hydrogen sulphide as an impurity, and this accounts for the black film of silver sulphide (Ag_2S) which forms on household silver. This film may be removed by carefully rubbing the surface with a finely divided abrasive, such as diatomaceous earth (electro-silicon). When the dry polish is moistened with ammonia, the latter serves as a solvent and therefore aids in cleaning the metal. Silver may also be cleaned by placing it in a solution of baking-soda, or sodium bicarbonate, contained in an aluminium dish. A voltaic cell is produced, the silver being the positive pole, aluminium the negative pole, and the solution serving as electrolyte. Hydrogen is formed on the surface of the silver and unites with sulphur to form hydrogen sulphide, thus restoring the silvery luster. Hydrogen sulphide is of the greatest utility in chemical analysis, since it enables the chemist to separate the metals into groups and to identify some of them by the colors of their sulphides: *e.g.*, antimony sulphide is orange, zinc sulphide is white, lead sulphide is black, and manganese sulphide is flesh-colored.

Carbon disulphide (CS_2) is a most useful compound. It is prepared by the direct union of highly heated carbon (charcoal) and the vapor of sulphur. Carbon disulphide, when pure, is a colorless liquid with a pleasant odor; it is not very stable, however, so it ordinarily smells disagreeable. The compound is ex-

ceedingly inflammable and its vapor is poisonous. Great care must be exercised, therefore, in handling it. Carbon disulphide is a good solvent for fats, resins, rubber, sulphur, and iodine. It is employed extensively as a solvent, for the manufacture of artificial silk (rayon), for the extermination of burrowing animals, such as the rat and the prairie dog, and as an insecticide: *e.g.*, in destroying the household moth and its eggs.

5 Selenium and Tellurium; the "Electric Dog"

Selenium and tellurium are related to sulphur, both being non-metallic elements.

Selenium, Se (Greek: the moon), occurs in certain sulphides and in some specimens of native sulphur. Selenium is obtained as a by-product in the electrolytic refining of copper and lead.

Selenium, like sulphur, may be prepared in several allotropic modifications.

When selenium is carefully annealed, it conducts electricity, its conductivity increasing on exposure to light. Graham Bell made use of this property of the element in the construction of a photophone, and Joel Stebbins (1914) constructed a delicate photometer for measuring the relative intensity of the light of stars. J. H. Hammond, Jr., utilized selenium in the construction of a curious machine called the "electric dog," which is a little four-wheeled wagon equipped with a battery, selenium being placed back of glass lights to represent eyes. When exposed to a bright light, the selenium resistance coils become a conductor,

the "dog" speeding forward after the light. The apparatus is propelled by a storage-battery, the light causing the selenium coils to conduct the current from the battery to the motor.

Selenium may also be employed in automatic devices for lighting buoys at night and for cutting off the flow of gas at daylight. Pictures and drawings may be telegraphed by means of selenium, and wireless telephones and army signaling employ the effect of light on the conductivity of the element.

Selenium is used to color glass red; it neutralizes the greenish tint of ferrous iron, and can be employed instead of manganese dioxide in decolorizing glass. In 1918, when the supply of manganese dioxide was limited, twenty thousand pounds of selenium were used in the United States for this purpose. The supply is now above the demand. It is possible that selenium will have a great future in the world of commerce.

Tellurium, Te (Latin: *tellus*, the earth) is obtained as a by-product in the electrolytic refining of copper and lead. It resembles antimony, being a silver-gray, metallic-appearing substance. The United States has facilities for the annual production of about 125,000 pounds, but at present it is of no great importance. There is a small demand for the element in radio sets. To-morrow, due to research, it may become of great value.

CHAPTER XIII

NITROGEN, FERTILIZERS, AND EXPLOSIVES

Every scrap of nitrogen in our bodies once floated in the primeval atmosphere ages before man or beast or plant arose. Every particle of nitrogen in every living thing that creeps upon the earth, in every flower that nestles on the ground, in every tree that grows aloft to heaven, once streamed in the primeval winds of our planet. There is no atom of nitrogen in the air that has not at some time or other in the course of its existence throbbed through the tissues of a living plant or animal, not once but many times.—GEOFFREY MARTIN.

1 HISTORY, OCCURRENCE, PREPARATION, AND PROPERTIES OF NITROGEN

NITROGEN is an indispensable element, for all life is dependent upon it. While this is true, it is also a fact that neither animals nor plants, with the exception of certain families of micro-organisms, possess the faculty of taking nitrogen directly from the air, of which it constitutes about four fifths by volume. While nitrogen does not appear to play an active rôle in the air as does oxygen, it is essential; for animal life in an atmosphere of pure oxygen would soon pass into an abnormal state and die.

Nitrogen was recognized as a distinct element in the year 1772 by Dr. Rutherford, Professor of Botany in the University of Edinburgh. He put small animals

in closed vessels, and in the course of time dissolved the gaseous product of respiration (carbon dioxide) in caustic potash. The residual gas not only extinguished a burning candle but failed to support the life of animals which were brought into it. Rutherford also removed oxygen from air by means of such substances as phosphorus and heated charcoal, and dissolved the products of combustion in alkalis. Lavoisier named the element azote, the name still used by the French. Subsequently it was named nitrogen (Greek: niter + to produce), because it is a constituent of saltpeter, or niter. The Germans very appropriately call it *stickstoff* (suffocating stuff).

Nitrogen occurs in the air in the free state and in enormous quantity. There are about 20,000,000 tons of nitrogen above each square mile of the earth's surface. Since there are 640 acres in a square mile, a farmer owning this amount of land may lay claim to nitrogen enough to supply necessary nitrogen compounds to the whole world for fifty years at the present rate of consumption. From 20,000,000 tons of nitrogen, 120,000,000 tons of pure Chile saltpeter, or sodium nitrate, could be produced, which at the abnormally high war price of $250 per ton would be worth $30,000,000,000, or about 50 per cent more than our total war debt.

The great abundance of free nitrogen is due to its inertness under ordinary conditions and to the further fact that many nitrogen compounds are more or less unstable, and therefore tend to give up nitrogen to the atmosphere. Moreover, nitrates, ammonia, and certain other nitrogen compounds are soluble in water

and do not therefore enter into the composition of the outer crust of the earth as do many compounds containing such elements as oxygen, silicon, calcium, aluminium, and iron. Clay, or aluminium silicate, for instance, is insoluble and very abundant.

Nature cannot construct a cell without nitrogen. The marvelous properties of all living matter depend in part upon the presence of the element. Furthermore, it is an essential constituent of all commercial explosives such as guncotton and trinitrotoluene (TNT), as well as of valuble fertilizers such as Chile saltpeter and ammonium sulphate; also of nitric acid, ammonia, certain useful drugs and medicines, and dyes of lovely colors. In spite of its apparent inertness and lack of odor, color, or taste, all life would sicken and die if deprived of nitrogen or of nitrogenous compounds. Bountiful harvests and vigorous growth of grass, flowers, and trees are obtained only when the soil contains proper nitrogenous fertilizers.

Impure nitrogen may be obtained by passing air over heated copper, which unites with oxygen to form copper oxide (CuO); or by confining air in the presence of white phosphorus, an easily oxidizable substance, the latter unites with the oxygen to form an oxide of phosphorus, readily soluble in water. The removal of oxygen from the air may be demonstrated by placing a small piece of white phosphorus in a small saucer or porcelain crucible, which is then floated on water by the support of a cork. The phosphorus is ignited by touching it with a hot rod, and the whole covered with a glass bell-jar. Water rises in the bell-jar to take the place of the oxygen consumed. Nitro-

gen thus prepared contains about one per cent of argon, besides smaller amounts of other inert gases, such as helium and neon.

Pure nitrogen for laboratory use may be prepared by heating ammonium nitrite, or a mixture of sodium nitrite and ammonium chloride. Like oxygen and hydrogen, it may be collected over water. For industrial uses, nitrogen is obtained from liquid air. This liquid is allowed to evaporate and the more volatile nitrogen passes off first, leaving a residue richer and richer in oxygen.

It was discovered by Lord Rayleigh, the eminent English physicist, that a liter of nitrogen obtained from air weighed slightly more than a liter of the gas prepared from different nitrogen compounds. Lord Rayleigh adopted the hypothesis that the atmospheric nitrogen is a mixture of chemical nitrogen and an unknown gas of greater density. This led to the discovery of argon, in 1894, by Lord Rayleigh and Sir William Ramsay.

Argon (Greek: idle, lazy) is a colorless, odorless, tasteless gas, which has a valence of zero; *i.e.*, no compounds of the element are known. Argon is used for filling tungsten electric-light bulbs, for it produces greater brilliancy and prolongs the life of the bulbs. The discovery of argon was soon followed by the discovery of the rare, inert atmospheric gases—helium, neon, krypton, and xenon. They may be obtained from liquid air. The gases of the helium family give characteristic spectra and exhibit resemblances and gradations in physical properties such as are seen in other families of elements.

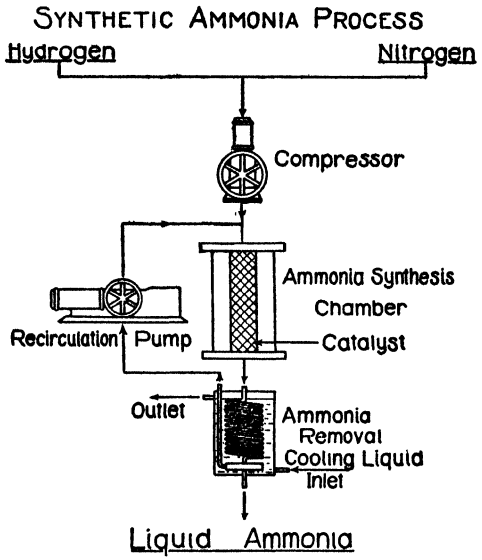
2 The Fixation of Nitrogen

Under ordinary conditions nitrogen is quite inactive; but at high temperatures it combines directly with oxygen to form nitric oxide (NO). The union of nitrogen and oxygen occurs during thunder-storms, due to lightning. Arrhenius has estimated that 400,000,000 tons of fixed nitrogen fall annually into the earth and sea as the result of electrical action. Nitrogen thus fixed is a valuable source of nitrogenous food for growing plants. The fixation of atmospheric nitrogen is of vast economic importance, owing to its use in the production of fertilizers and explosives, which are needed in time of peace as well as in war. Sir William Crookes, in his famous address delivered before the British Association in 1898, had the prevision to state that there would be a shortage of nitrogenous fertilizer, so necessary for the growth of wheat, unless the chemist should devise ways and means of bringing about the chemical union of nitrogen with other substances. The following words are from his address, entitled "The Wheat Problem":

> The fixation of nitrogen is vital to the progress of civilized humanity, and unless we can class it among the certainties to come, the great Caucasian race will cease to be the foremost in the world, and will be squeezed out of existence by the races to whom wheaten bread is not the staff of life.

As far back as 1892, Crookes performed, in the presence of the Royal Society, an experiment on the flame of burning nitrogen, which consisted in passing a pow-

erful induction current between terminals, the nitrogen of the air burning to produce oxides which interacted with water to form nitric and nitrous acids. This soon led to an important process for the production of nitric acid and nitrates.



Courtesy, United States Department of Agriculture

FIGURE 12

Synthetic Ammonia by the Haber Process

Nitrogen is being fixed by several processes, the most important of which is the production of synthetic ammonia. This process was perfected before the late war by the German chemist Haber, as stated in Chapter XI. A mixture of nitrogen and hydrogen, under high pressure and at a temperature of about 500° C., is passed over a suitable catalyst, such as some form of

iron. The reaction is a reversible one and is accompanied by the evolution of heat:

$$\underset{\text{Nitrogen}}{N_2} + \underset{\text{Hydrogen}}{3H_2} \rightleftarrows \underset{\text{Ammonia}}{2NH_3} + \text{Heat}$$

The ammonia may be condensed to a liquid or dissolved in water (Figure 12). The nitrogen is obtained from liquid air. Over 300,000 tons of nitrogen were fixed by this method in 1921, most of which was done in Europe.

Much nitrogen is also fixed by the cyanamide process. Calcium cyanamide is produced by passing nitrogen over calcium carbide (CaC_2) at a temperature of about 1000° C. When calcium cyanamide is treated with superheated steam, it yields ammonia. The great cyanamide plant at Muscle Shoals has a rated annual capacity of 40,000 tons of fixed nitrogen. The chemical changes are as follows:

$$\underset{\text{Calcium carbide}}{CaC_2} + \underset{\text{Calcium cyanamide}}{CaCN_2} = \underset{\text{Calcium carbonate}}{CaCO_3} + \underset{\text{Ammonia}}{2NH_3} + \underset{\text{Carbon}}{C}$$

Large quantities of nitrogen have been fixed by the arc process, which is somewhat similar to lightning discharge. This process was developed on a large scale years ago in Scandinavia, where abundant water-power means cheap electricity. In the Birkeland-Eyde process, the electric arc is spread between the poles of an electromagnet, the nitrogen burning to form nitric oxide (NO):

$$\underset{\text{Nitrogen}}{N_2} + \underset{\text{Oxygen}}{O_2} + \text{Heat} \rightleftarrows \underset{\text{Nitric oxide}}{2NO}$$

A very high temperature favors the formation of the oxide. The action is reversible, heat being absorbed in forming the oxide. When the nitric oxide is cooled, it unites with oxygen to form nitrogen dioxide (NO_2), which may be transformed into nitric acid or into nitrates.

During the year 1924-25 the production of fixed nitrogen was over 500,000 metric tons (1 metric ton equals 1000 kilograms, or 2205 pounds), about 325,000 tons (65 per cent) being by the Haber process, 140,000 tons by the cyanamide process, and 36,000 tons by the arc process.

3 Soil Bacteria; Nitrogenous Fertilizers

Certain bacteria living in the nodules on the roots of certain plants, particularly the Leguminosæ,—peas, beans, clover, etc.,—are able in their obscure way to convert free atmospheric nitrogen into complex substances which, in their turn, are able to supply food for animals. This fact is of great importance in agriculture. Nitrogen undergoes a never-ceasing cycle in nature. Every particle of nitrogen in plants, animals, and fertilizers was once atmospheric nitrogen. Free nitrogen may be fixed—*i.e.,* brought into chemical union—by electrical discharge or by bacteria, and thus rendered available as plant food. Plants serve as food for animals; and when plants and animals die and decay, ammonia, nitrates, nitrogen, and other substances are formed. The nitrogen compounds enrich the soil for living plants, and the nitrogen returned to the air repeats the cycle over and over throughout countless ages.

Not only does nitrogen keep up an endless cycle in nature, but matter in general undergoes an eternal circulation. This idea was well expressed by the ancient Greek philosopher Heraclitus as follows: "Change is everywhere; everything is and is not. There is no stability. Even in the same river one cannot bathe twice, nor even once." And Hamlet's familiar words are suggestive:

> Imperious Cæsar, dead and turn'd to clay,
> Might stop a hole to keep the wind away:
> O! that that earth, which kept the world in awe,
> Should patch a wall to expel the winter's flaw!

In 1913, the year before the war, Germany imported over 600,000 tons of Chilean nitrates; but in 1925 only a little more than 24,000 tons were purchased, which means that Germany has developed an enormous air-nitrogen fixation industry. In 1924 the total exports of nitrates from Chile was over 2,300,000 tons; and in 1925 the United States imported 1,112,000 tons of nitrates, virtually all from Chile, and valued at over $52,500,000.

An immense quantity of ammonium sulphate, also extensively utilized as a fertilizer, is produced from the ammonia obtained as a by-product from coke- and gas-plants. It is reported that Germany produced over 300,000 tons of ammonium sulphate from her coke ovens in 1917. For several years our exports of ammonium sulphate have averaged over 125,000 tons annually, the value of which is much greater than that of our exported phosphate rock and superphosphates. At present the fertilizer industry is the largest

heavy chemical industry in America. About three fourths of the mixed fertilizers produced contain some form of nitrogen compounds.

It is estimated that by the year 1930 the output of fertilizers will have reached over 15,000,000 tons, for the production of which 315,000 tons of nitrogen will be required.

About half of the nitrogen for fertilizer mixtures is derived from inorganic sources, the chief of which are Chile saltpeter and the air.

4 Explosives

Certain nitrogen compounds are very explosive. For instance, when a warm solution of ammonium chloride or sal ammoniac is treated with an excess of chlorine, drops of an oily liquid, nitrogen trichloride (NCl_3), are obtained. This compound was first prepared by Dulong, in 1811, who lost an eye and three fingers in experimenting with it, but continued his investigations in spite of the accident. Faraday and Davy were also injured as the result of an explosion of the compound. The following is from Gladstone's Life of Faraday:

Knowing that the liquid would go off on the slightest provocation, the experimenters wore masks of glass, but this did not save them from injury. In one case Faraday was holding a small tube containing a few grains of it between his fingers and thumb, and brought a piece of warm cement near it, when he was suddenly stunned, and on returning to consciousness found himself standing with his hand in the same position but torn by the shattered

tube, and the glass of the mask even cut by the projected fragments. Nor was it easy to say when the compound could be relied on, for it seemed very capricious; for instance, one day it rose quickly in vapor in a tube exhausted by the air-pump, but on the next day, when subjected to the same treatment, it exploded with a fearful noise and injuring Sir Humphry Davy.

This is a good illustration of the fact that science has had many men of heroic mold enlisted in her service.

Another extremely explosive compound is nitrogen iodide. This substance may be obtained in the form of a brown precipitate by dissolving iodine in an aqueous solution of potassium iodide, followed by the addition of strong ammonia. The compound may be handled while wet; but when dry it explodes with great violence, liberating nitrogen and iodine. The gentle touch of a feather, or possibly the tread of a fly, is sufficient to explode it.

While these halogen compounds of nitrogen are most interesting, they are far too unstable to be utilized as military and industrial explosives.

Black gunpowder, which consists of a mixture of saltpeter, charcoal (carbon), and sulphur, was invented by the Chinese, who employed it hundreds of years ago in firecrackers. It was first used in cannon about the middle of the fourteenth century, the English having so employed it in the Battle of Crécy, in 1346; and it was stated by a historian of that period that "The English guns made noise like thunder and caused much loss in men and horses." It appears to have been many years before gunpowder was employed in blasting. In gunpowder there is an

oxidizing agent, namely, potassium nitrate, mixed with combustible materials—carbon and sulphur. Therefore, when the powder is ignited, combustion is supported by oxygen liberated from potassium nitrate and is not dependent upon the oxygen of the air. When employed in guns, large volumes of gases, such as carbon dioxide and sulphur dioxide, are formed at very high temperatures; consequently a ball is projected with great velocity. Black powder is now used largely in blasting, in blank-fire charges, in base charges for shrapnel shells, in primers and fuses, and as a sporting powder.

Guncotton and nitroglycerine are the two basic substances employed in modern smokeless powder and in dynamite. Trinitrotoluene (TNT), picric acid, and ammonium nitrate are also utilized as explosives. It is interesting to know that all these compounds contain either the nitrate ($—NO_3$) or the nitro ($—NO_2$) group, and are therefore either nitrate or nitro bodies. None of them can be produced without nitric acid. Under ordinary conditions they are relatively stable bodies, but are capable of breaking down or exploding when subjected to slightly changed conditions, such as mechanical shock. When a high explosive, such as guncotton or nitroglycerine, breaks down, the explosion or detonation is primarily the result of internal combustion. Thus, the nitroglycerine molecule, $(C_3H_5(NO_3)_3$ $(C_3H_5N_3O_9)$, contains nine atoms of oxygen, which are sufficient to oxidize all the carbon to carbon dioxide and the hydrogen to water.

Guncotton, or nitrocellulose, was discovered by Schoenbein in 1845. It is manufactured by treating

cellulose fiber, or cotton, with a mixture of concentrated nitric and sulphuric acids. Guncotton has the appearance of cotton. It is exploded by a detonating cap, being employed in torpedoes and mines, and as the basis of certain smokeless powders.

It should be noted in this connection that mercuric fulminate is the chief detonator for gunpowder and high explosives. It was discovered by Howard, in 1799, and is prepared by treating mercury with strong nitric acid and alcohol. Its discovery led to the invention of the percussion cap, which displaced the old flintlock.

When cellulose is less thoroughly nitrated, pyroxylin, or collodion-cotton, is obtained. It dissolves in a mixture of alcohol and ether, forming collodion. Pyroxylin is used very extensively in the manufacture of collodion, artificial leather and silk, celluloid, smokeless powder, blasting gelatin, photographic film, etc. Celluloid is produced on a large scale by mixing pyroxylin with camphor and a little alcohol and passing the material between rollers.

Nitroglycerine was discovered by the Italian chemist Sobrero, in 1846, and in 1864 Nobel began its manufacture on a large scale. In 1866, Nobel invented dynamite by absorbing liquid nitroglycerine in diatomaceous earth, or kieselguhr. Nitroglycerine is produced by slowly injecting glycerine into a well-cooled mixture of nitric and sulphuric acids:

$$\underset{\text{Glycerine}}{C_3H_5(OH)_3} + \underset{\substack{\text{Nitric}\\\text{acid}}}{3HNO_3} = \underset{\text{Nitroglycerine}}{C_3H_5(NO_3)_3} + \underset{\text{Water}}{3H_2O}$$

Strictly speaking, nitroglycerine should be called glyceryl nitrate, for it is not a nitro-body. A true nitro-

body contains the nitro group, NO_2, which consists of one atom of nitrogen combined with two atoms of oxygen.

Dynamite is too sensitive and violent for use in guns and shells. It is employed on a large scale for blasting and wrecking purposes.

Blasting gelatin is prepared by dissolving one part of pyroxylin in nine parts of nitroglycerine. It is used for blasting and for the manufacture of smokeless powders.

Cordite is a smokeless powder produced by incorporating guncotton with nitroglycerine, and dissolving in acetone. A little vaseline is added to prevent corrosion of the guns. When the acetone is evaporated, solid cordite is left.

Trinitrotoluene (TNT) is manufactured by treating toluene, or toluol, with a mixture of nitric and sulphuric acids. Toluene is a colorless liquid obtained from coal-tar, being very similar to the hydrocarbon, benzene (C_6H_6). Trinitrotoluene is a solid, which melts at 81.5° C. It is used for filling high-explosive shells. The compound is not easily exploded by shock during transportation, but can be exploded readily by a detonator. Before the close of the World War, large quantities of ammonium nitrate were being mixed with the more expensive TNT. The mixture is an excellent explosive. Amatol contains 80 per cent of ammonium nitrate.

Picric acid was discovered by J. A. Glauber, in the seventeenth century. He obtained it by treating wood with concentrated nitric acid. It was perhaps the first chemical body known to be explosive, and long ago

was employed as a yellow dye. In 1871, Sprengel discovered that picric acid may be detonated by fulminate of mercury. The compound is produced by nitrating carbolic acid, or phenol, another very useful coal-tar product. Picric acid is a yellow, crystalline compound, which can be melted and poured into shells. The British call it lyddite, while the French call it melinite. The latter used great quantities of it during the recent war.

According to C. L. Reese, of the DuPont Company, smokeless powders for rifled arms may be divided into two classes—nitroglycerine powders, consisting of nitroglycerine and nitrocellulose, and nitrocellulose powders, consisting of nitrocellulose only. Virtually all smokeless powders when burned are transformed into gases, principally carbon monoxide, carbon dioxide, and nitrogen, all of which are colorless and hence invisible.

High explosives did not come into general use until after the close of the Civil War. It is known to all that they played a great part in the World War. According to Reese, if the war had continued, the United States could have manufactured 1,000,000,000 pounds of smokeless powder during the year 1919. While war calls for a greatly increased supply of explosives, these are used in tremendous quantities in times of peace, the normal domestic consumption amounting to more than 500,000,000 pounds per annum, while during the late war our annual production of all military explosives was perhaps from 2,000,000,000 to 3,000,000,000 pounds.

There have been some very disastrous explosions. In

1921, for instance, the great Oppau plant, in Germany, which was engaged in the manufacture of ammonia and other nitrogen compounds, was totally wrecked by a terrific explosion, the cause of which is not known. Four hundred and thirty lives were lost and the property destroyed was worth about $50,000,000. A hole 250 feet in diameter and over 50 feet deep was formed in the earth. The potential energy stored up in high explosives is stupendous.

CHAPTER XIV

PHOSPHORUS AND RELATED ELEMENTS

There used to be a tradition to the effect that phosphorus was food for the mind, because there is a slight amount of it found in the brain. It was held that a diet of fish was especially to be recommended because phosphorus is also found in fish, and therefore that the aspirant after intellectual life should address himself to codfish, shad, and even bullheads and suckers. The element is indeed found in fish, but chiefly as calcium phosphate in their bones.—ELLWOOD HENDRICK in "Everyman's Chemistry."

1 PHOSPHORUS AND ITS EXTRAORDINARY PROPERTIES

PHOSPHORUS is a member of the nitrogen family. The other members of this family are arsenic, antimony, and bismuth.

The story of phosphorus, the "light-bearer," is an interesting one. It is generally supposed that the element was accidentally discovered by Brand, a Hamburg alchemist and merchant, in 1669. He was searching for the philosopher's stone, hoping to be able to transmute silver into gold. Brand heated to a high temperature, in a retort, white sand and the residue from evaporated urine and observed that a vapor was formed, which condensed to a white, translucent solid having the marvelous properties of glowing in the dark and igniting spontaneously in the air. Moreover, it left a luminous trail when drawn along a wall or

board. Brand called the newly discovered substance cold fire, owing to the fact that it was able to produce light without fire. The discovery of such a remarkable substance attracted a great deal of attention. Krafft, Kunckel, and Robert Boyle learned the secret of its production, but on account of the difficulty of preparation the element was almost as expensive as gold. Phosphorus was regarded as one of the wonders of nature, and Krafft made a tour of Europe, exhibiting the glowing substance before crowned heads, including Charles II of England.

The price of phosphorus remained extremely high until 1771, when Scheele, the great Swedish chemist, discovered a method for producing it from calcium phosphate, or bone-ash, which proved to be a commercial success and was employed for over a century.

Since phosphorus is so readily combustible, it does not occur in the free state; but in the combined state it is widely disseminated, usually as phosphates, or salts of phosphoric acid; it makes up about 0.12 per cent of the earth's crust. The most abundant compound of phosphorus is calcium phosphate, $Ca_3(PO_4)_2$ ($Ca_3P_2O_8$), which is the chief mineral matter found in bones, and is therefore left as ash when bones are burned. Large deposits of phosphate rock are found in the United States. In 1918, Florida, the leading State in the production of phosphate, marketed over 2,000,000 long tons, valued at more than $6,000,000, which was 83 per cent of all the phosphate rock sold that year in the United States. There are also great deposits of phosphate rock in North Africa, Tunis exporting large quantities to southern Europe. Impor-

tant deposits of phosphate rock also occur in other parts of the world. The deposits are probably of animal origin, being filled with fossil remains.

Phosphorus also occurs in complex organic compounds found in living matter. For instance, it is an essential constituent of protoplasm and of brain and nerve material. There is a wide-spread popular notion that brain-activity depends to a large extent upon phosphorus. In the sixties the materialists of Germany said, *Ohne Phosphor, kein Gedanke* [without phosphorus, no thought]; and in America there has been a popular notion, attributed to Louis Agassiz, that "fishermen are more intelligent than farmers, because they eat so much fish, which contains so much phosphorus." The fact of the matter is that the brain contains many chemical elements and it is impossible to say that phosphorus is more important in the brain than such elements as carbon, nitrogen, and hydrogen.

Phosphorus is needed to build up vegetable matter, especially the fruit and seeds of plants; consequently it is an essential constituent of certain compounds in all fruitful soils. Animals depend upon plants for phosphorus very much as they do for nitrogen; and when animals die and decay, phosphorus compounds are returned to Mother Earth. Some of the phosphorus now in our own bodies may once have "formed part of huge reptiles, living millions upon millions of years ago, which tore and fought and died along shores vanished ages ago."

Certain compounds of phosphorus are utilized as stimulants or tonics. Thus, acid phosphates, representing phosphates similar to those in wheat, are pre-

scribed as a nutrient tonic in nervous and wasting diseases.

When farm products are sold, phosphorus is gradually removed from the soil; to make good the loss it is necessary to supply fertilizer in the form of phosphates. According to an English writer, the pasture lands of England became greatly impoverished a century ago, on account of the removal of phosphorus; but the fertility of the soil was restored by manuring it with bones gathered from the battle-fields of Europe. In this connection it is of interest to note that the growth of the indigo-plant is largely dependent upon phosphates.

Phosphoric acid is supplied to plants in the form of soluble phosphates. Since normal calcium phosphate—bones and rock phosphate—is almost insoluble in water, it is treated with sulphuric acid in order to secure soluble superphosphate, which is employed on an enormous scale as a fertilizer. About 45 per cent of the output of sulphuric acid is used in the manufacture of fertilizers, including superphosphate of lime and ammonium sulphate.

In the year preceding the begining of the war, our sale of phosphates abroad amounted to nearly $11,000,000; but since the war our export trade has been subject to wide fluctuation. While our exports of phosphate fertilizer were higher in 1925 than for several previous years, most classes of phosphates are still below pre-war figures. Germany is our best customer for high-grade phosphate rock, and most of our surplus of acid phosphate goes to Canada and to Cuba.

Other important sources of phosphorus for use in

agriculture are barnyard manure and guano, the latter coming from islands of the Pacific Ocean.

The electric-furnace process has displaced the older method for the production of phosphorus. In the manufacture of phosphorus a mixture of calcium phosphate, carbon, and silica, or quartz sand, is heated to a high temperature in an electric-furnace, electricity being transformed into heat. The phosphorus is liberated as a vapor and is distilled out of the furnace and condensed, air being excluded. The sand serves as a flux, uniting with the lime of the phosphate to form a liquid slag (calcium silicate), which is tapped off at the bottom of the furnace. The crude phosphorus which is first obtained is purified and finally cast in the form of "sticks" by pouring the molten substance into glass or tin tubes surrounded by cold water.

Phosphorus is an extraordinary substance. Like carbon and sulphur, it may be prepared in different forms, the two common varieties being white (or yellow) phosphorus and red phosphorus. White phosphorus is the ordinary form of the element. When phosphorus vapor or the liquid is quickly cooled, it gives a translucent, wax-like solid, which may be easily cut with a knife. This form of the element melts at 44° C., is insoluble in water, but soluble in carbon disulphide. It is very poisonous, less than 0.15 gram usually being a fatal quantity. Years ago, particularly in Europe, phosphorus was frequently used by homicides and suicides. Being a component of the head of the old-fashioned match, it was widely distributed. Children were sometimes poisoned because they sucked the heads of matches. The phosphorus of three match-heads has

been known to cause death; and since there is phosphorus enough in the average adult body to produce about eight hundred thousand old-fashioned phosphorus matches, it is sufficient to kill over a quarter of a million people. It is one of the mysteries of chemistry that a free substance which is so poisonous is an essential constituent of the body.

When white phosphorus is exposed to the air it glows or phosphoresces, due to slow oxidation. But the luminescence of the firefly and of the glow-worm has nothing to do with phosphorus; neither has the so-called phosphorescence of the sea.

Interesting experiments may be performed with the carbon disulphide solution of phosphorus. To illustrate, when a pointed glass rod is dipped into the solution, and characters traced on a sheet of paper, the carbon disulphide evaporates quickly, leaving a layer of finely divided phosphorus, which catches fire and burns, producing a charred tracing on the paper. Phosphorus burns brilliantly in air or oxygen, forming a white smoke of phosphorus pentoxide. Phosphorus airplane drop-bombs have been employed in naval warfare, the white cloud of the oxide, produced by the burning phosphorus, completely enveloping the ship over which it is dropped. When phosphorus is melted in water and oxygen passed in through a glass tube, the element burns vigorously under water, which seems almost a paradox. When white phosphorus is heated to about 250° C., air being excluded, it passes into the red variety. Red phosphorus does not melt when heated, is insoluble in carbon disulphide, is not poisonous, and does not catch fire in the air below 240° C. When

heated, however, it forms a vapor which is identical with that of white phosphorus. Since this variety of the element may be safely handled, it is often substituted for the more active form.

The greater part of phosphorus is used in the manufacture of matches. It is also used as a poison for vermin, in the laboratory, and in the hardening of metals. The addition of phosphorus to bronze yields phosphor-bronze, which is characterized by great hardness, elasticity, and toughness. During the late war phosphorus was employed in incendiary bombs or grenades and was burned to make smoke screens.

2 Friction Matches

Friction matches were invented by John Walker of England in 1827. The head of the first match contained potassium chlorate (an oxidizing agent), antimony trisulphide, and starch, and it was ignited by being drawn between two layers of sandpaper. The first friction matches were not very satisfactory, for it required much pressure to ignite them. In the course of a few years white phosphorus, which has a low temperature of ignition, was substituted for antimony trisulphide. Sulphur was used for coating the matches, but paraffin was found to be more agreeable, owing to the sharp odor produced by burning sulphur. In general, the head of a match contains an oxidizing agent, such as potassium chlorate or nitrate, and a combustible material, such as some form of phosphorus. When rubbed on a rough surface, heat is generated by friction, the combustible material being raised to its kindling tempera-

ture. On account of the poisonous nature of white phosphorus, workers in match factories were often afflicted with a disease called necrosis or "phossy jaw," which was due to continued exposure to the vapor of phosphorus. This terrible and mysterious disease starts with toothache, and in the course of time the teeth decay and drop out, and the jawbones become affected. Not only is the disease exceedingly painful but in many cases it proved to be fatal. One civilized country after another has legislated against the use of white phosphorus in match-making. In 1913, the United States Government placed a tax of two cents per hundred on the manufacture of matches by the old process, which led to its abandonment. In 1898, it was discovered that phosphorus sesquisulphide, P_4S_3, or Schenck's scarlet phosphorus, is a good substitute for white phosphorus, and all the strike-anywhere matches produced in the United States contain this substance in the composition of the heads.

The safety-match, or strike-on-the-box-only match, was invented by Böttger in 1848. Neither phosphorus nor a compound of phosphorus is used in the head of the safety-match, but it consists of potassium chlorate (or other oxidizing agent), antimony trisulphide, powdered glass, and a binder, such as glue or dextrine. These matches are ignited by rubbing on a surface consisting of antimony trisulphide, red phosphorus, and glue. If the so-called safety-match be dry and drawn rapidly over slate or glass, it can be ignited.

The manufacture of matches is an interesting process. Blocks of white pine are fed into a machine and cut into sticks, which are forced into holes of

metal plates. The plates are then fastened together in the form of an endless chain, followed by treatment with appropriate materials for completing the matches. The manufacture of matches, from wood to finished product, is all done by machinery.

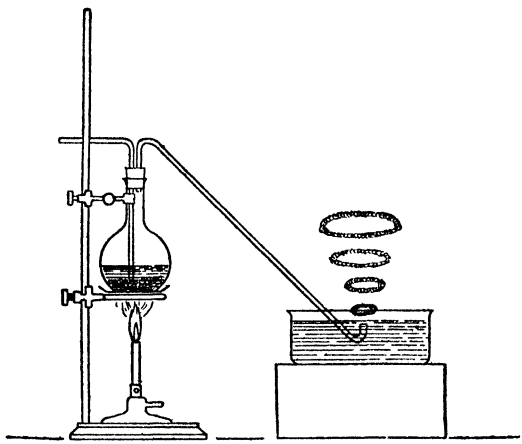


FIGURE 13
Phosphine (PH_3)

3 PHOSPHINE

When white phosphorus is treated with a hot, concentrated solution of potassium hydroxide, phosphine (PH_3) is formed. This compound is a colorless, poisonous gas with an odor similar to that of decaying fish The gas thus prepared is not pure, and therefore ignites spontaneously on exposure to air. When the gas is allowed to escape into the air in the form of bubbles (Figure 13), it burns, forming vortex rings of phosphoric acid, which are most interesting:

$$\underset{\text{Phosphine}}{PH_3} + \underset{\text{Oxygen}}{2O_2} = \underset{\text{Phosphoric acid}}{H_3PO_4}$$

Phosphine is analogous to ammonia gas (NH_3). Indeed, nitrogen and phosphorus form many other analogously constituted compounds, showing that the two elements are members of the same family.

As phosphine is poisonous and forms an explosive mixture with air, only experienced chemists should experiment with the gas.

4 Arsenic, Antimony, and Bismuth

Arsenic, As, was known to the Greek alchemists, the word being derived from a Greek word meaning *masculine* or *potent*. The ancients were also acquainted with certain compounds of arsenic, particularly with its sulphides, and with its oxide (As_2O_3). Arsenic occurs quite widely distributed in nature, most commonly in combination with sulphur or a metal or both. The most important of its ores is arsenopyrite or mispickel (FeSAs). Arsenic may be prepared by heating this ore, air being excluded.

Arsenic is a brittle, steel-gray, crystalline solid having the appearance of a metal. Allotropic forms of arsenic are known, so its properties are somewhat variable. While arsenic possesses some metallic properties, it is far from being a typical metal: *e.g.*, it is brittle. Arsenic is both basic and acidic in character, and is therefore called a metalloid, or an amphoteric element. Thus, in arsenic trichloride ($AsCl_3$), the element functions as a metal, as does sodium in common salt (NaCl); while in arsenic acid (H_3AsO_4) arsenic plays

the part of an acid-forming element, as does phosphorus in phosphoric acid (H_3PO_4). Nitrogen and phosphorus have no metallic or basic properties; *i.e.*, they only play the part of acid-forming elements.

Arsenic forms many compounds which are analogous to those of phosphorus. One of its most interesting compounds is arsine (AsH_3), which is the analogue of phosphine. Arsine may be produced by placing an arsenic compound in a hydrogen generator in which zinc is interacting with hydrochloric acid. It is a colorless gas with a peculiar and disagreeable odor and is exceedingly poisonous. The chemist Gehlen, in 1815, lost his life by breathing only a bubble or two of the gas. Arsine is of great importance in the detection of arsenic by what is known as Marsh's test. The material suspected of containing arsenic is put in a hydrogen generator, and in case arsenic is present, it is converted into arsine, which may be burned at the exit, giving a lilac-colored flame. By holding a clean porcelain dish in the flame, a metallic-appearing deposit of arsenic is obtained; and by heating the tube in front of a constriction, arsenic deposits in the constricted portion. Marsh's test is exceedingly delicate.

As a rule, compounds of arsenic are poisonous. Its most important compound is arsenic trioxide or white arsenic (As_2O_3), which is produced by heating mispickel in air; it is also a by-product of many metallurgical operations. Owing to its abundance and wide distribution, it has often been employed by homicides and by suicides, and cases of accidental poisoning with this compound have not been uncommon. Arsenic trioxide dissolves in water to form arsenious acid

(H_3AsO_3), which is a powerful poison. Two to four grains of white arsenic are usually a fatal dose. Freshly precipitated ferric hydroxide or magnesium hydroxide is a good antidote. A person can accustom himself to sustain the action of quantities of arsenic that would ordinarily prove fatal. It is said on good authority that arsenic-eating occurs especially in Styria. "A woodcutter was seen by a medical man to eat a piece of pure arsenious oxide weighing 4.5 grains, and the next day he crushed and swallowed another piece weighing 5.5 grains, living on the following day in his usual state of health." Arsenic-eaters claim that the substance enables them to carry heavy loads to great elevations with ease.

Arsenic trioxide finds extensive use as an insecticide and weed-killer, and for preserving skins and furs. Lead arsenate is employed on a large scale in spraying fruit-trees; calcium arsenate, for fighting the boll-weevil; and Paris green, a complex compound of arsenic, as a pigment and insecticide. Metallic arsenic—*i.e.*, the elemental form of the substance—is used for hardening shot, which is manufactured by allowing molten lead, alloyed with arsenic, to fall from a tower, through openings in colanders, into water. The addition of arsenic renders the lead more fluid in the liquid state, increases the tendency to assume the spherical form, and makes the shot harder.

Chemicals, such as metals and sulphuric acid, frequently contain arsenic as an impurity. According to Sir H. E. Roscoe:

> In 1900 a serious outbreak of arsenical poisoning occurred chiefly in the neighborhood of Manchester, due to the con-

tamination of beer with arsenious acid, and a number of fatalities occurred. The presence of this arsenic in beer was traced to the impure sulphuric acid in the manufacture of glucose employed in the brewing, which was found to contain considerable quantities of arsenious acid.

Antimony (stibium, Sb) occurs in nature chiefly as the mineral stibnite (Sb_2S_3), which is abundant in China, in Japan, in Mexico, and in South America. Antimony trisulphide, or stibnite, was used in very early times by Oriental women for painting the eyebrows; indeed, it is still so used. The medical chemists of the long ago were acquainted with many preparations containing antimony.

Antimony may be prepared by heating stibnite with iron in graphite crucibles, the iron robbing the ore of its sulphur, and the antimony separating from the slag of iron sulphide. Antimony, like phosphorus and arsenic, has allotropic forms, the most peculiar and interesting of which is explosive antimony, which may be obtained by the electrolysis of a solution of antimony trichloride. When this form of antimony is heated to 200° C., it explodes sharply, forming a fine powder; it also breaks down when scratched with a metallic point or when touched with a red-hot wire.

Antimony is similar to arsenic in many respects, but is more metallic. It has the useful property of forming alloys with most heavy metals, which are harder than the pure metals; and on solidifying, most of these alloys slightly expand. The alloys of antimony are excellent for making sharp castings. Type metal is an alloy of antimony, lead, and tin; Britannia metal, used in making cheap tableware, etc. is an alloy of anti-

mony, tin, copper, and zinc; Babbitt (antifriction) metal is usually an alloy of antimony, tin, and copper.

The red sulphides of antimony are employed as paint pigments and in vulcanizing and coloring red rubber.

The compounds of antimony correspond, in general, to those of arsenic, which resemble phosphorus compounds. Arsenic and antimony exhibit some of the properties of metals.

The trichloride, or butter of antimony, and tartar emetic are both important salts. The former is used for giving a brown stain to iron and steel wares (*e.g.*, gun-barrels), and the latter in medicine and as a mordant in dyeing.

Bismuth, Bi, is a shining, brittle, silvery, crystalline metal with a ruddy tint. It is not an abundant element, but occurs rather widely distributed. The metal is produced chiefly in certain South American countries, in Saxony, in Bohemia, and in the United States. In 1918, we imported 135,700 pounds of the metal. Bismuth is used in the manufacture of fusible alloys: *e.g.*, Wood's metal and Rose's metal. Wood's metal contains four parts of bismuth, two of lead, one of tin, and one of cadmium and melts at 50.5° C. Rose's metal contains two parts of bismuth, one of lead, and one of tin; it melts at 93.8° C. These fusible alloys are used in the manufacture of safety-plugs in boilers, automatic fire-curtains, water-sprinklers, etc.

Bismuth subnitrate, $Bi(OH)_2NO_3$, is used in medicine as an internal remedy in the case of certain intestinal and stomach disorders and in cosmetics.

CHAPTER XV

THE WONDERS OF RADIUM

It is the glory of God to conceal a thing: but the honour of kings is to search out a matter.—Proverbs xxv 2.

1 Discovery and Sources of Radium

The discovery of radium is one of the most important and brilliant in the history of the world, for it has created a new science, namely, radioactivity.

One discovery leads either directly or indirectly to another. Let us briefly tell the story of the discoveries leading up to the discovery of radioactive elements and radioactivity.

When a glass tube containing air or other gas is exhausted by means of an air-pump until the pressure is only a very small fraction of a millimeter, the tube is known as a vacuum tube. When a high-voltage electric current is passed through such a tube, very small negative particles—*electrons*—emanate from the cathode at high velocity. These are known as cathode rays, and were discovered by W. Crookes in 1878. The negative electrons constituting the cathode rays move in straight lines and when they strike the surface of the tube or the surface of another body placed athwart their path, a fluorescence is produced (Figure 14). With lead glass, for example, the glow is bluish. The

discovery of electrons has had a great deal to do with discoveries pertaining to radium and radioactivity.

In 1895 W. C. Röntgen discovered that the radiation produced outside an ordinary cathode tube has great penetrative power. These Röntgen rays, or X-rays, were found to produce photographic action similar to light; but X-ray photographs may be taken without removing the cover of the plate-holder. By means of X-rays it is possible to peer into our very flesh and bones, wholly opaque bodies becoming trans-

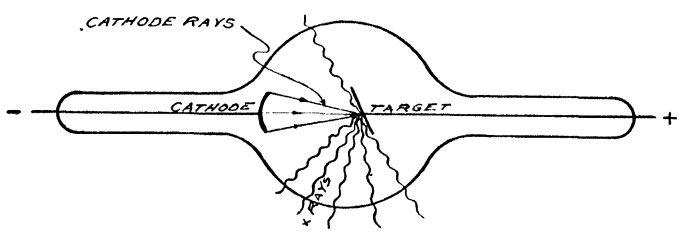


FIGURE 14
X-Ray or Rontgen Tube

parent. These rays are produced when the anode of a vacuum tube is employed as a target for the cathode discharge, that is, when bombarded with electrons.

In 1896 the French physicist H. Becquerel discovered that minerals containing uranium gave off rays which were capable of (1) penetrating black paper and affecting the photographic plate; (2) producing fluorescence in certain substances, such as zinc sulphide; (3) discharging an electroscope (Figure 15); and (4) passing through plates of metal. These rays were called Becquerel rays; they are similar to X-rays in many of their properties.

The discovery of this new sort of radiation soon led to the discovery of radium. It should be noted that the phenomenon of radioactivity is associated with a mineral containing uranium.

Anatole France once said, "France has two geniuses —Rodin and Madame Curie." The momentous and far-reaching discovery of radium belongs primarily to Madame Curie, who to-day stands crowned as the

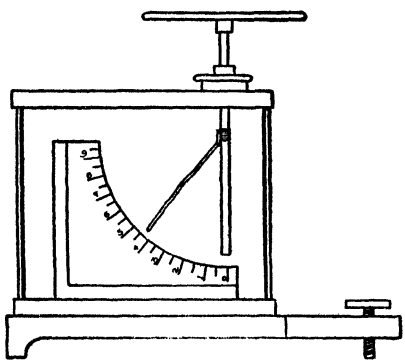


FIGURE 15
Electroscope under the Influence of an Electric Charge

greatest woman scientist in history. Marie Sklodowska was born in Warsaw, Poland, in 1867, where she received her early education under her father, Dr. Sklodowski, who was a teacher of science in a gymnasium. The young girl had a great bent for science and was naturally drawn to her father's laboratory. The part of Poland in which she lived belonged to Russia. Being dissatisfied with political conditions under the czar's régime and desiring a wider field for her activities, Miss Sklodowska decided to go to Paris.

Having virtually no money and but few acquaintances, she was thrown upon her own resources, and her hard struggles to complete her education command the admiration of the world. To quote Benjamin Harrow:

> Miss Sklodowska did not arrive in Paris as a conquering hero. Far from it. Her pockets were empty and her acquaintances few. She established herself in the "east side" section of the town, in a small back room, four flights high, to which she carried her own coal. Her diet consisted of bread and milk for so long that, as she herself said, she had to acquire anew the taste for wine and meat. Ten cents were her daily expenses, and this she made largely by private tutoring, and later, by preparing the furnace and washing bottles at the Sorbonne.

In the course of time she became a pupil of Pierre Curie, Professor of Physics at the Sorbonne, which led to a romance; the two were married in 1895, "both poor in life's necessities, but rich in sympathy toward, and understanding of, one another." This happy marriage had a very tragic ending early in 1906, when Professor Curie was knocked down and instantly killed by a dray in Paris.

Soon after the discovery of the radioactive properties of uranium by Becquerel in 1896, it was noticed that certain uranium-bearing minerals, such as pitchblende, discharged a gold-leaf electroscope more rapidly than the element itself, so the presence of an unknown substance or substances was suspected. Monsieur and Madame Curie subjected Bohemian pitchblende from which the uranium had been removed, to a laborious process of fractional crystalliza-

tion, which led to the discovery, in 1898, of two new elements, polonium and radium. Polonium was found associated in small quantity with bismuth, and was named in honor of Madame Curie's native country.

Something like a ton of the pitchblende residues was separated into different components, and it was discovered that the barium sulphate obtained was radioactive. By treating the barium sulphate, a small quantity of a new compound was prepared, which was at least a million times as active as uranium. The compound was radium bromide, and the new element was named radium. The spectrum, general chemical relations, and atomic weight of the element showed it to be a member of the alkaline earth family, its properties being very similar to those of barium or calcium.

After discovering the marvelous properties of radium, the Curies made the following generalization: "Radioactivity is a property of the atom. It is not affected at all by the nature of the chemical combination in which the atom exists, nor by the conditions." This means that man has no control over the process of radioactivity. It is a natural process which occurs in spite of all we are able to do.

As to the sources of radium, uranium is the parent element from which radium is produced. Radium is found, therefore, in all ores of uranium, and in no others. Furthermore, the ratio between the radium present and the uranium is constant, amounting to about one part of radium to three million parts of uranium. This means that after uranium has been producing radium for a sufficient time, the system comes to radioactive equilibrium, with about three million

times as much uranium as radium. This shows why the quantity of radium in existence is so small, and why its preparation from uranium minerals is so expensive. To illustrate, there are about three tons of uranium per gram of radium. According to Soddy, ten tons of pitchblende contain only one gram of pure radium.

On May 25, 1921, Madame Curie was presented with a gram of radium bromide ($RaBr_2$) at the National Museum in Washington. To secure this amount of the substance it was necessary to treat 500 tons of Colorado carnotite ore, containing two per cent of uranium. The women of America raised the money to pay for the gram of radium bromide. In 1 ton of pitchblende containing 0.2 per cent of uranium, there is approximately 0.2 gram of radium.

The price of radium has usually varied from $100,000 to $125,000 per gram, but in 1924 the price was about $70,000, due to the new source of the metal and to the fact that the new high-powered X-ray machines are displacing it, thus enabling the physician to treat many cases at low cost.

In Europe radium is produced from pitchblende or uranium oxide (U_3O_8). There are a number of impurities in the mineral, and the preparation of the bromide or chloride from it is a complicated process.

Considerable radium has been produced in the United States from carnotite, a light canary-yellow mineral, occurring in Colorado and in Utah. This is a valuable ore, for it has been worked for uranium and vanadium as well as radium. The total domestic production of radium up to 1921 was approximately 115 grams.

Valuable deposits of radium ore, much richer in radium than the ores hitherto known, have recently been discovered in the Belgian Congo. The ore is refined in Belgium. At present this is the commercial source of radium. It is reported that the primary mineral is pitchblende, from which several secondary minerals have been formed.

Madame Curie succeeded in preparing pure radium chloride in 1902 and in isolating radium in 1910. Radium chloride was subjected to electrolysis, a mercury cathode being employed. The radium amalgam was placed in an iron boat, and the latter heated in a silica tube while a current of hydrogen under reduced pressure was being passed through. The mercury volatilized, leaving the radium behind as a white shining metal. Radium melts at 700° C., loses its luster in air, and, like calcium, interacts vigorously with water to form hydrogen.

2 Radioactivity; the Cathode-Ray Tube

All uranium and radium compounds emit three types of radiation: namely, the *alpha* (α), the *beta* (β), and the *gamma* (γ). The three types of rays affect the photographic plate, cause certain fluorescent substances to glow, and "ionize" the air and other gases—*i.e.*, make them conductors. These effects are used in the detection and measurement of the different types of radiation.

The alpha rays are positively charged atoms of helium (He^{++}), some of which move with approxi-

mately one fifteenth of the velocity of light, or about 12,000 miles per second. Before the discovery of radioactivity, the fastest known moving material thing was the meteor, which may attain a speed of 40 miles per second. The speed of an alpha particle may therefore be three hundred times as fast as that of a meteor. Alpha rays can be detected by means of the Crookes spinthariscope (Greek: spark + to view) as illustrated by Figure 16. A minute quantity of a radium compound is placed in front of a screen covered with zinc sulphide. When the helium particles strike the zinc sulphide, flashes of light are produced, and these are

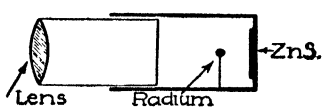
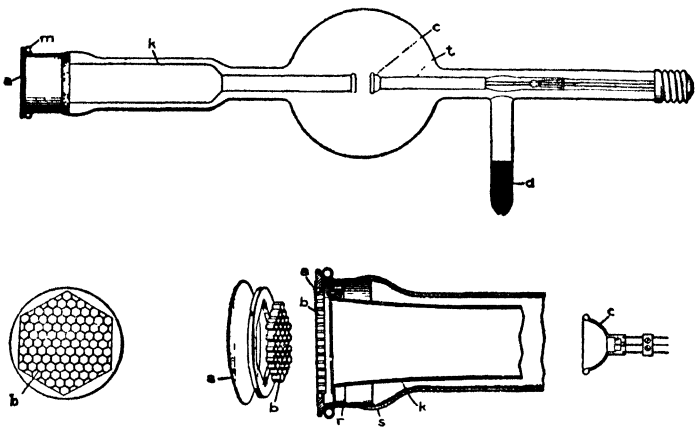


FIGURE 16
The Spinthariscope

magnified by means of a lens. By resting the eye in a dark room for fifteen to twenty minutes, one may see the flashes. The alpha rays are feebly penetrating, nearly all being stopped by a sheet of paper, or by a sheet of aluminium one millimeter thick. The alpha rays, being positively charged, are affected by a magnetic field.

The beta rays are identical with cathode rays; that is, they are electrons, or free atoms of negative electricity. The velocity of beta particles varies in different cases, the maximum (178,000 miles per second) being nearly as great as that of light, which is 186,000 miles

per second. They have greater penetrating power than alpha particles, but are virtually stopped by a sheet of aluminium one centimeter thick. These rays are greatly deviated by a magnetic field.



EXPLANATION OF CATHODE-RAY TUBE

Upper: Diagram of tube.
Lower left. Construction of window.
Lower center: Details of window, shield and seal. Right: Section of cathode.

a Anode window, a very thin piece of nickel foil through which the electrons pass into the air.
b Window-support, a molybdenum hexagonal grid, to reinforce the window against the pressure of the atmosphere.
c Hemispherical cathode cup, focusing the electrons released by the tungsten filament within the cup.
d Charcoal trap for residual gases. When immersed in liquid air, the charcoal removes all traces of gas within tube.
k Copper shield, preventing the electrons from striking the glass tube.
m Water-cooling tube, to prevent the window from becoming heated.
r Sleeve of invar, an alloy with about the same expansion as glass upon being heated. To this sleeve the anode is soldered.
s Glass-to-invar seal.
t Cathode shield.

FIGURE 17

Cathode-Ray Tube

In this connection it is interesting to note that, under the direction of Dr. W. D. Coolidge, the General Electric Company has recently invented a cathode-ray tube which produces as many electrons per second as a ton of radium—and it is estimated

that there is only a pound of that rare metal in the whole world. A ton of radium is worth about $100,000,000,000.

At one end of the cathode-ray tube (Figure 17) there is an anode "window" three inches in diameter, of nickel foil the thickness of which is measured in thousandths of an inch. A heated tungsten filament, originally employed by Dr. Coolidge in the X-ray tube and now known to all as an essential part of radio tubes, supplies the electrons. The glass tube is shielded by a copper tube so that the stream of electrons from the filament cannot strike the glass and cause punctures, thereby permitting operation of the tube at voltages far higher than heretofore.

Electrons are released by the heated tungsten filament at the relatively slow speed of one or two miles per second. Between the cathode and the anode—the window and the copper tube which serves as a shield—there is impressed upward to 350,000 volts of direct current. This accelerates the speed of the electrons to the average speed of 150,000 miles per second, depending upon the voltage, within the short space of about one inch between the cathode and the copper-tube shield. The electrons now coast the rest of the way through the highly evacuated tube and pass through the anode window, out into the air with but a slight diminution in speed. While the nickel window appears to be solid, it is really very porous, and the electrons in passing through it rarely hit a nickel atom in spite of the fact that there are about 500,000 layers of the nickel atoms. It is thus seen that the electrons fired off from radium move with greater speeds than those so

far produced with the cathode-ray tube, but otherwise the two are alike.

The rays from the new cathode tube are so concentrated that many startling effects have been observed. When the tube is operated in a darkened room, a hum is heard and the window of the tube is surrounded by a ball of purplish light, about two feet in diameter, with 350,000 volts. This glow results from the molecules of the gases of the air being ionized. Crystals of calcite or sticks of lime appear to become red-hot coals when exposed momentarily to the rays, but they are glowing with cold light; feldspar glows with a variety of rich colors; acetylene gas is transformed into a yellowish, insoluble solid; and a rabbit's gray hair has been destroyed, to be replaced later by a profuse growth of longer, snow-white hair. The rays induce chemical change, and they will cause the death of small animals, such as mice. While the emanation has been referred to as a "death-ray," it could never be employed for an army at a distance, for the electrons do not travel far through air.

The new cathode-ray tube will probably be a valuable instrument for scientific research, and it may be of importance in medicine.

The gamma rays appear to be similar to X-rays, but with shorter wave-lengths. They have great penetrating power, being able to penetrate relatively thick layers of metals. Gamma rays are not deviated by a magnetic field.

There are thirty odd radioactive elements known, all of which are derived from minerals containing either uranium or thorium, the two elements with the

highest atomic weights. E. Rutherford and F. Soddy not only showed by their researches that radioactive substances give out three distinct types of radiation but advanced the theory (1902-03) that the process of radioactive change is the result of a spontaneous disintegration on the part of the radioactive elements, in consequence of which new elements are produced. Some of these new elements are quite unstable, and therefore decompose, other elements being born, the process continuing through many stages until a final, stable disintegration product is produced, which appears to be lead. Polonium is one of the transformation products of radium. The elements which come into existence as the result of spontaneous disintegration of other atoms possess lower atomic weights than the parent elements. Radioactivity is, then, a property of the atom; it has, indeed, opened up a new world, and has given us the first insight into the nature and structure of the atom. These marvelous discoveries impress upon us the meagerness of our knowledge and the limitations of our intellects. As expressed by an anonymous writer:

> For even the things which be in our hands—
> These, knowing, we know not—so far from us,
> In doubtful dimness, gleams the star of truth.

These radioactive changes may be divided into two types:

(1) The alpha-ray change. In this type of change the atom of the element, say uranium, loses a helium atom of mass 4, thereby reducing the atomic weight of the parent element by 4.

(2) The beta-ray change. In this case the particle shot off is an electron. Its mass is negligible, since it requires 1845 electrons to possess the mass of one hydrogen atom, the lightest known atom.

What is known about the length of life of radioactive elements? As a result of calculations based upon experimental data, it has been possible to determine the rate of change or period of *average life* of such elements as uranium and radium. According to F. Soddy, the period of average life is the sum of the separate periods of future existence of all the individual atoms divided by the number in existence at the starting-point. The following illustration is given by Cameron:

> If a church, at a fixed time, contains a number of people of different ages, then, given the number of years each person will live after leaving the church, the average life of the congregation is reckoned from the time fixed by the church attendance.

The periods of the average life of the radio-elements vary greatly. The average life of radium is found to be about 2500 years. This means that if a mass of radium, say one gram, were set aside, at the end of one year 1/2500th of the radium would have changed. The average life of helium is very long; namely, 8×10^9 years, or 8,000,000,000 years.

The time-period of a radioactive element is usually taken as the time required for the element to be *half transformed.* For radium this period is about 1700 years, which means that if one gram of radium were set aside, half of it would be unchanged 1700 years from now. To put it another way, if a gram of radium

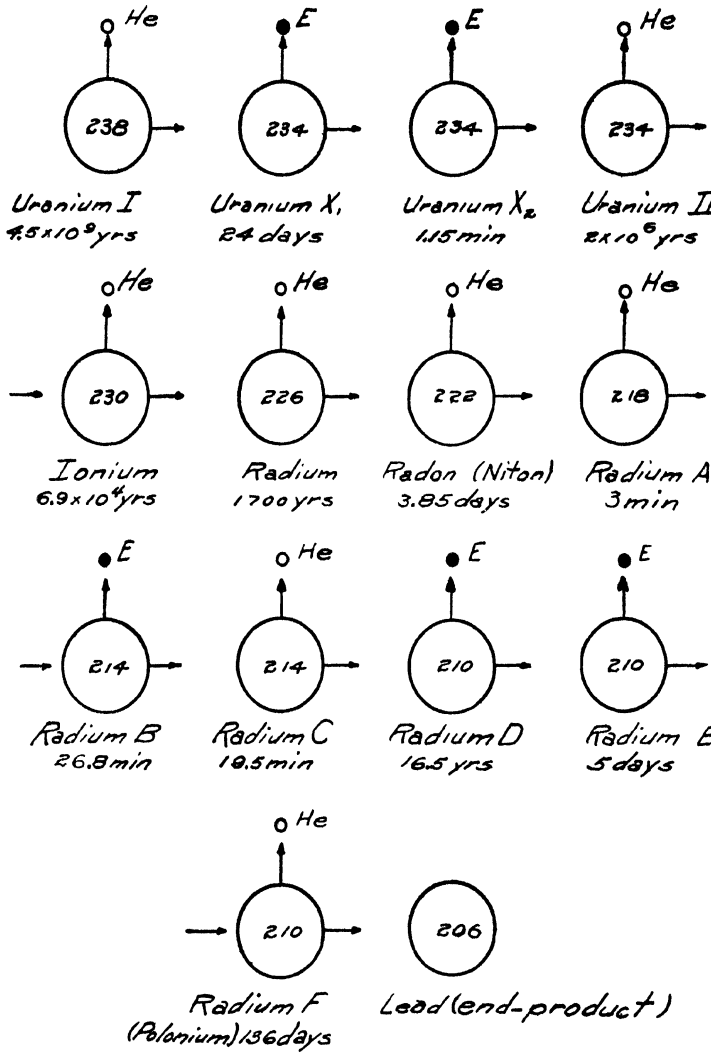


FIGURE 18

Diagram Showing the Disintegration of the Uranium-Radium Series of Elements

had been set aside at the beginning of the Christian era, nearly half of it would still be in existence. The half-period of uranium is about 4,500,000,000 years.

Starting with uranium (atomic weight 238.2), the preceding diagram shows the different elements produced as the result of successive spontaneous disintegrations in the uranium-lead series. When an alpha (helium) particle is expelled, the fact is indicated by the symbol He, and when an electron is lost, the symbol E is employed.

In the transformation from radium to lead, there is a loss of 5 helium atoms ($5 \times 4 = 20$), which means that the atomic weight of the lead of the uranium-radium series should be 206 ($226 - 20$). Ordinary lead, from non-radioactive sources, has an atomic weight of 207.2. In 1913, F. Soddy suggested that lead derived from minerals containing uranium might have a lower atomic weight. T. W. Richards of Harvard University determined the atomic weight of lead in a very pure specimen of uranio-lead from Norwegian clevite and found it to be 206.08, a number in striking agreement with the theory of Soddy and Rutherford. According to Richards, ordinary lead has a density of 11.337, while that of uranio-lead is 11.273—a difference of 0.56 per cent.

We see, therefore, that there are forms of lead which differ in mass or atomic weight. Forms of an element which have slightly different atomic weights but identical chemical properties are called isotopes (Greek: equal + place). They occupy the same place in the periodic table (page 245) and have the same atomic number.

3 Radon (Niton)

An examination of the uranium-lead disintegration series shows that radium gives off an emanation which is called niton (Latin: *nitens,* shining) or radon. It is a heavy, colorless gas belonging to the family of rare gases, being a homologue of argon and helium. It can be condensed to a phosphorescent liquid.

Ramsay and Gray, with only a small fraction of a cubic millimeter of the gas at their disposal at any one time, found its atomic weight to be 223. According to the radium-disintegration theory, the radium atom loses an atom of helium with an atomic weight of 4, leaving behind an atom of radon. Subtracting 4 from 226 (the atomic weight of radium), we obtain 222, the atomic weight of radon, a number in close agreement with the number found by Ramsay and Gray.

In determining the atomic weight of radon, Ramsay and Gray employed a micro-balance which is far more sensitive than the most delicate assay or analytical balance. According to H. E. Roscoe, "with this instrument a difference in weight as small as 1/500,000 milligram can be detected. In experiments on radium emanation the total volume available was less than 0.1 cubic millimeter, and its weight lesss than 1/100 milligram." One tenth of a cubic millimeter is a tiny bubble which can scarcely be seen. There are over 28,000 milligrams in one ounce; so 1/100 of a milligram is about 1/2,800,000 of an ounce. Sir William Ramsay was a chemical manipulator of extraordinary skill, having been appropriately called "the great

wizard of the chemical laboratory." Indeed, Ramsay was a many-sided genius.

4 The Effects of Radium

The effects produced by radium are most interesting and unusual. Radium (or a salt of radium) decomposes water. It is therefore dangerous to seal up radium or other highly radioactive substances, either in solution or in an imperfectly dried condition, for indefinite periods, for the gases formed might burst the containing vessel. The radiations also have a coloring action on common glass and on many gems and minerals. Ordinary glass is usually colored violet or purple, but sometimes brown. The rays produce fluorescence in many substances, such as zinc sulphide or the diamond. Again, they sterilize seeds and destroy micro-organisms.

Radium is used in treating cancer, but the results have not been so successful as was at first anticipated. In certain cases, however, its effects have been very beneficial in the arrest or amelioration of the disease. Early rodent cancer can be cured. In the application of radium it must be borne in mind that its rays may produce sores, for they have a tendency to kill the cells of the skin. Radium is continually producing emanation, which may be used instead of radium itself in the treatment of disease. The emanation is pumped off from time to time, collected in tiny glass tubes, and then inserted in the flesh near the cancer or similar growth. The emanation breaks down, producing the "rays" which act on the diseased tissue. Radium

has been applied with success to chronic infected wounds, and has aided in the treatment of scars, birthmarks, certain conditions of the eyelids, and some cutaneous non-malignant tumors.

Well-endowed establishments, such as the Crocker Research Institute of New York and the Radium Institute in Paris, are thoroughly investigating the value of radioactive substances in medicine. Mme. Curie is at the head of the Radium Institute.

The alpha rays are feebly penetrating, and are but little used. Beta radiation is always employed in conjunction with gamma radiation. Beta radiation is used for superficial conditions, and the gamma radiation in this case may probably be ignored. Gamma radiation is employed when deep penetration is required. One of the chief objects in the employment of radium is to get the effect of the deeply penetrating gamma rays.

The use of radium in the production of luminous paint is interesting. Radium paint can be prepared by mixing a little radium bromide with a relatively large quantity of phosphorescent zinc sulphide. The principle involved in the luminescence of paint is the same as in the spinthariscope, that is, zinc sulphide is bombarded by helium or alpha particles, light being produced. In the course of time the zinc sulphide is worn out, but the radium may be recovered and used again.

5 The Significance of Radium

When the salts of radium disintegrate, an immense quantity of energy is liberated which continually appears as heat. The radium salt is from three to five degrees warmer than the surrounding atmosphere.

One gram of radium evolves about one hundred and twenty calories per hour, which is more than enough to raise its own weight of water from the freezing-point to the boiling-point. In ten years the energy set free by one gram of radium equals that developed in the burning of over a thousand grams of carbon. It is indeed marvelous that radium keeps pouring out this enormous quantity of energy year after year without sign of abatement. Man has no control over the process. He can only look on and wonder. "There is no way of turning the steam on and off as it is wanted."

Professor Joly has calculated that if there are two parts of radioactive material for every million million parts of other matter throughout the whole of the earth, and this is considerably less than he has found on the average in the earth crust, then this earth, instead of cooling off, is actually heating up.

Frederick Soddy says:

> The primary sources of natural energy, by virtue of which the universe keeps going over immense periods of time, are to be sought not in the great masses of glowing matter dotted about the heavens, nor in their motions under the action of gravity, nor in any of the grosser relations between energy and matter in bulk, but in the individual atoms out of which it is made up. . . . Only a beginning has so far been made into the study of these new unsuspected forms of energy, but enough is known to make it clear that, whether it be so or not, radioactivity alone, including in that term processes involving atomic transformations, is competent to be regarded as the mainspring of the universe.

Radioactive changes appear to offer a means of estimating certain periods of time. A mineral is examined to determine the amount of uranium, lead, and helium present. Thus, one gram of uranium gives off helium at the rate of one cubic centimeter in 16,000,000 years. Samples of the mineral fergusonite contain twenty-six cubic centimeters of accumulated helium gas per gram of uranium; hence it is concluded that the samples of this mineral are at least 416,000,000 years old. Some of the helium may leak out, since it is a gas. There are also other complications.

Scientists estimate that the age of our planet is between two and eight billion years. The earth is believed to be less than eight billion years old, for studies in radioactivity indicate that the known radioactive minerals could not radiate more than eight billion years. On the other hand, it is calculated that it must have required at least two billion years for radioactive materials to produce some of the changes which have been observed in connection with minerals.

The discovery of radioactivity has thrown a great deal of light upon the structure of matter. We no longer regard atoms and molecules as imaginary particles. In fact, we are now able to see the flash of light produced on a zinc sulphide screen when it is struck by a single charged helium atom. It is estimated that one gram of radium is continually shooting off helium particles at the rate of 145,000 billion per second, with speeds which reach 12,000 miles per second. These atoms are now being employed in the bombardment of other atoms, and this has led to artificial transmu-

tation. Scientists have also reached the conclusion that an atom is largely a vacuum, for the diameter of the nucleus is exceedingly small as compared with the dimensions of the atom as a whole.

CHAPTER XVI

CLASSIFICATION OF THE ELEMENTS

STRUCTURE OF MATTER AND THE NEW ALCHEMY

For the world was built in order
And the atoms march in tune.
—EMERSON.

1 EARLY ATTEMPTS TO CLASSIFY THE ELEMENTS

THERE are about ninety known elements, many of which differ widely in physical and chemical properties; and in order to simplify their study chemists have given much attention to their classification. Attention has been called already to the division of the elements into metals, or base-forming elements, and non-metals, or acid-forming elements. (See Chapter IV.)

The metals are often called electropositive elements, while the non-metals are termed electronegative. These terms are more or less relative, however, for an element may be electropositive toward one element and electronegative toward another element. Potassium and sodium are the most electropositive of the common elements and fluorine is the most electronegative element known. Atoms of potassium and fluorine therefore unite with great energy to form potassium fluoride. The electrochemical theories of Sir Humphry Davy and J. J. Berzelius were intro-

duced in the beginning of the nineteenth century. According to the dualistic system of Berzelius, electric polarity was a property of the atoms of substances, and every compound consisted of two parts, which were electrically different. For instance, calcium oxide might be represented by the formula $Ca^{+}O^{-}$.

Between the years 1816 and 1829, J. W. Döbereiner noticed that certain closely related elements possessed atomic weights which exhibited an almost constant difference when arranged in sets of three; *i.e.*, the atomic weight of the middle element is approximately the mean of the other two. The following sets will illustrate Döbereiner's triads:

	At. wts.		*At. wts.*
Chlorine	35.5	Calcium	40.0
Bromine	79.9 (81.2)	Strontium	87.6 (88.7)
Iodine	126.9	Barium	137.4

The numbers in parentheses are the mean values of the two extremes. Döbereiner's observations did not lead far, but they were an attempt to arrange the elements according to their atomic weights.

J. A. R. Newlands of England, in 1863-64, arranged a number of the elements according to the magnitudes of their atomic weights, and observed that after the lapse of a certain period the properties of the elements succeeding one another were similar to those of the previous group. To be more specific, he noticed that every eighth succeeding element was "a kind of repetition of the first"; that is, "members of the same group of elements stand to each other in the same relation as the extremities of one or more

octaves in music." Newlands termed this striking relationship "the law of octaves."

The following periods of elements illustrate the law:

Lithium	Li	7	Sodium	Na	23
Beryllium	Be	9	Magnesium	Mg	24.3
Boron	B	11	Aluminium	Al	27
Carbon	C	12	Silicon	Si	28
Nitrogen	N	14	Phosphorus	P	31
Oxygen	O	16	Sulphur	S	32
Fluorine	F	19	Chlorine	Cl	35.5

According to this arrangement of the elements, sodium is the seventh element after lithium, and these metals have similar properties. In the same way magnesium is the seventh after beryllium, aluminium after boron, silicon after carbon, etc. These pairs of elements have similar properties.

2 The Periodic System

Soon after the publication of the classical papers by Newlands enunciating the law of octaves, D. I. Mendeléeff of Russia and Lothar Meyer of Germany independently made similar observations. In 1871 Mendeléeff published his first periodic table, in which the elements were divided into eight groups. In arranging the elements in groups, the atomic weight was considered to be the most fundamental property of the atom. When Mendeléeff arranged the elements in groups according to their atomic weights, a repetition of properties was observed in the periods of the elements.

From 1894 to 1898, several new elements were discovered in the atmosphere. These are known as the

inert gases, or the Helium Family. In modern tables of the periodic system these elements are placed in Group 0; therefore, including the eight groups in the earlier periodic tables, there are nine groups in all, running from Group 0 to Group VIII, the last including closely related elements arranged in triads and having atomic weights of nearly the same value. Hydrogen does not fit into the periodic system.

Omitting hydrogen, the elements are arranged, according to their atomic weights, in nine groups, as shown in the table given below. The first short period contains eight elements (helium to fluorine*). The next element is neon, which is similar to helium, the one above it in the vertical column. Also, sodium resembles lithium, etc. The second short period ends with chlorine, which is in the same family as fluorine. We now come to the first long period, which contains eighteen elements (argon to bromine). Three of these elements—iron, cobalt, and nickel—have similar properties and atomic weights, which are nearly of the same value, so they are placed in the last vertical column.

The groups of the elements from I to VII are divided into two sub-groups or families. Thus, in Group I we find the family of alkali metals and the copper family, or the coinage metals:

Alkali Family	*Copper Family (The Coinage Metals)*
Lithium, Li	Copper, Cu
Sodium, Na	Silver, Ag
Potassium, K	Gold, Au
Rubidium, Rb	
Cesium, Cs	

* The names, symbols, and atomic weights of the elements are given in the Appendix.

Likewise, the halogen elements constitute a natural family. (See Chapter VIII.)

The atomic weight of an element, according to Mendeléeff, conditions its properties. This is expressed by the periodic law: *The properties of the elements are periodic functions of their atomic weights.*

It is important to observe that the valence of the atom of the element—*i.e.*, its capacity to combine with an atom of another element—corresponds to the number of the group in which the element falls. Thus, helium has a valence of zero, sodium is univalent, calcium bivalent, etc. Some elements, however, are multivalent: *e.g.*, chlorine has a minimum valence of —1 (HCl) and a maximum valence of +7 (Cl_2O_7). One valence, however, of the element corresponds to the group in which it falls.

The valence of the element with respect to hydrogen increases regularly from Group I to Group IV, then decreases to Group VII. (See table.)

With respect to oxygen the valence increases regularly from Group I to Group VIII.

The periodic system has important applications. Before its development there was no comprehensive plan for the classification of the elements. By arranging them in groups and families the study of their physical and chemical properties is much simplified, and the memory is greatly aided. Moreover, the system has led to the prediction and discovery of new elements. In arranging the elements in groups and families Mendeléeff considered it necessary to leave gaps for missing elements; in 1869 he boldly prophesied the discovery of yet unknown elements, and in 1871 he

actually predicted the properties of three new elements, which he called eka-aluminium, eka-boron, and eka-silicon. The confirmation of these bold predictions was complete. Eka-aluminium was discovered by Lecoq de Boisbaudran of France, in 1875, and named gallium (Ga = 69.7); eka-boron was discovered by Nilson, a Scandinavian chemist, in 1879, and named scandium (Sc = 45.1) in honor of his country; eka-silicon was discovered by the German chemist, C. Winkler, in 1888, and appropriately called Germanium (Ge = 72.4).

As expressed by H. C. Bolton, "The periodic law has given to chemistry that prophetic power long regarded as the peculiar dignity of the sister science, astronomy."

The prediction and discovery of these new elements call to mind the discovery of the planet Neptune, which Professor C. A. Young says "is justly reckoned as the greatest triumph of mathematical astronomy." It had been observed by astronomers that the planet Uranus failed to move precisely in the path which had been predicted for it. These small discrepancies, which were caused by the hitherto unknown planet Neptune, enabled Leverrier of Paris and Adams of Cambridge University independently to calculate the position of the unknown planet which was causing the perturbation of Uranus. Leverrier wrote to Galle, the German astronomer, substantially as follows: "Direct your telescope to a point on the ecliptic in the constellation of Aquarius, in longitude 326 degrees, and you will find within a degree of that place a new planet, looking like a star of about the ninth magni-

ure 14). When different elements are employed as targets, X-rays of slightly different wave-lengths are obtained and X-ray spectra are produced. Moseley, a brilliant British physicist, only twenty-seven years of age, who was shot and killed instantly in the trenches in Gallipoli in 1915, employed as targets most of the elements from aluminium to gold, and measured the wave-lengths of the X-rays produced. He observed that the higher the atomic weight of the element the shorter the wave-length of the X-rays. Furthermore, the shift was of the same magnitude in passing from one element to the element next to it in atomic weight, say from copper (atomic weight, 63.6) to zinc (atomic weight, 65.4). The atomic number of zinc is one greater than that of copper. Numbers have been assigned to all the elements. Starting with hydrogen, which has the lightest atom, the atomic numbers run from 1 to 92, which is the atomic number of uranium, the heaviest atom known (U = 238.2). The atomic weights and numbers of a few of the elements are as follows:

Element	*Symbol*	*At. Wt.*	*At. No.*
Hydrogen	H	1.008	1
Helium	He	4.00	2
Lithium	Li	6.94	3
Beryllium	Be	9.02	4
Boron	B	10.82	5
Carbon	C	12.00	6
Nitrogen	N	14.01	7
Oxygen	O	16.00	8
Fluorine	F	19.00	9
Neon	Ne	20.20	10
Sodium	Na	23 00	11
Magnesium	Mg	24.32	12

When Moseley prepared the first chart of atomic numbers, there were several gaps, which indicated that

new elements would be discovered. The missing elements corresponded to numbers 43, 61, 72, 75, 85, and 87; but all of these have been discovered with the exception of numbers 85 and 87.

The most recently discovered elements are:

Number	*Name*	*Discoverer*	*Country*	*Year*
72	Hafnium	Coster and Hevesey	Denmark	1923
43	Masurium	Noddack	Germany	1925
75	Rhenium	Noddack		
	Bohemium	Heyrovsky and Dobysek	Czecho-Slovakia	1925
61	Illinium	Hopkins	United States	1926

Recent experiments at the Platinum Institute of the Russian Academy have failed to confirm the discovery of elements 43 and 75. Number 85 is an unknown halogen, and Number 87 is believed to be related to the alkali metals, being called ekacesium.

The atomic numbers are of great value, for it appears that they are indicative of all the physical and chemical properties of the elements, and they are more fundamental than the atomic weights.

As stated previously (in Chapter III), the atom is no longer considered to be an indivisible particle, but a system consisting of smaller units—protons (positive) and electrons (negative). According to a theory propounded by Sir Ernest Rutherford, now of Cambridge University, the nucleus of an atom is positive, is exceedingly minute, and contains nearly the whole mass of the atom. Outside the nucleus there are a number of electrons corresponding to the atomic number of the atom. This number of electrons is exactly equal to the excess of protons in the nucleus. In general, a nucleus contains some electrons, and it is the number of positive charges (protons) of a nucleus in excess

of the number of negative charges (electrons) which determines the atomic number of the element. An atomic system, therefore, consists of a nucleus and associated planetary electrons—*i.e.*, electrons situated outside the nucleus. The electrons which encircle the nucleus are relatively far from it and from one another. The dimensions of atomic nuclei are approximately one billionth of those of the smallest object

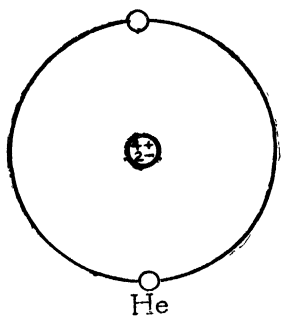


FIGURE 19
The Helium Atom

which has ever been viewed and measured in our most powerful microscope. One may obtain a rough picture of an atomic system by comparing it with our solar system, if one imagines the sun to be very small. The sun corresponds to the nucleus of an atom, and the planets to electrons outside the nucleus.

The ordinary chemical and physical properties of an atom are ascribed mainly to the configuration and motion of the outer electrons, while the mass and the radioactivity depend upon the structure of the nucleus. To illustrate, the hydrogen atom—the simplest atom—consists of one proton and one planetary elec-

tron, which revolves around the positive nucleus (Figure 2). The atomic number of hydrogen is 1. The helium atom, according to this theory, may be pictured as consisting of four protons, two nuclear electrons, and two planetary electrons (Figure 19). The atomic number of helium is therefore 2. Such an arrangement of protons and electrons would appear to be very stable, and it is well known that helium is an inactive gas, having a valence of zero.

Atomic numbers may be accepted as well-established facts, but the grouping or circulation of electrons around the nucleus is still in the hypothetical stage.

The circulation of electrons, as just described, is not in harmony with all the facts. A theory propounded by Professor N. Bohr of Copenhagen has met with much favor. Bohr saw that if the simple structure of the hydrogen atom as explained in the previous section be adopted, it is impossible to account for the complicated optical spectrum of the atom, together with its chemical and physical properties. Under ordinary conditions Bohr assumes that the electron of the hydrogen atom rotates rapidly in a circular orbit relatively close to the nucleus; he also assumes that the single electron can move in any one of a number of stable orbits, which are controlled by the attractive force of the nucleus. Now, in case the hydrogen atom is excited, the electron may be displaced to another stable orbit where it circulates. It is furthermore assumed that the atom radiates only when the electron is transferred from one stable orbit to another of lower energy—*i.e.*, to an orbit closer to the nucleus.

It is also assumed that the atom absorbs light when the electron passes in the other direction.

Free * attempts to make this clear by the following rough analogy:

> Imagine a series of race tracks one inside the other like the concentric grooves of that once familiar game called "Pigs in Clover." Imagine these tracks are separated by high board fences. Now put a race horse in the outermost track and instruct him to run around it until, when he happens to feel like it, he is to jump the inside fence into the next track, run around it for a while, and then jump the next fence, and so on until he reaches the innermost track of all. If, then, you watch this procedure from the field outside the outermost fence, you will not see the horse at all as long as he is running in a single track. The fences hide him. But whenever he jumps from one track into the next, you will see him for an instant as he goes over.

In the Bohr atom it is assumed that the orbits of the electrons lie in different planes. The theory affords a satisfactory explanation of complex optical spectra, and is also helpful in explaining X-ray spectra. With increase in atomic weights, the Bohr atom becomes much more complicated.

G. N. Lewis of the University of California proposed, in 1916, the theory of the cubical atom, or the octet theory, which was subsequently extended and applied by Irving Langmuir. According to this theory, it was held that the electrons are either stationary or vibrate or oscillate about certain fixed positions so

* *Ind. and Eng. Chem.*, Vol. 16, No. 2, p. 192.

that the system of planetary electrons of any particular atom constitutes a symmetrical arrangement. It is assumed in case of the lighter atoms that these electrons arrange themselves in a series of concentric shells, the first containing two electrons, while all others tend to hold eight, these eight being placed symmetrically at the corners of a cube or in pairs at the corners of a regular tetrahedron. As expressed by John Mills, we may imagine that the electrons are arranged about the positive nucleus as if they lay in the shells of one of those Chinese toys which consist of a concentric series of wooden egg-shaped shells. The innermost shell would represent the nucleus. In the next or first shell there may be one or two electrons, one in the case of hydrogen and two in that of helium. In the case of helium, the arrangement would be particularly stable, for the electrons are assumed to be on diametrically opposite sides of the nucleus. With the exception of the hydrogen system, all atomic structures are assumed to have two electrons in the first shell.

The next outer shell is twice as far from the nucleus, and therefore has four times the superficial area, and may contain as many as eight electrons. To illustrate, lithium (Li) has one electron in this shell (Figure 20). In the figure, lithium is represented as having an excess of three protons in the nucleus; *i.e.*, its atomic number is 3. There is one electron in the second shell, and we may imagine that it is placed at one corner of a cube. Lithium has a positive valence of one; its atom has a great tendency to lose one electron.

In a similar way, we may represent the fluorine atom (F), which has an atomic number of 9. This atomic

system is assumed to have seven electrons in the second shell. Fluorine has a positive valence of seven or a negative valence of one; its atom has a great tendency to capture one electron, which would fill up the second shell; *i.e.*, there would be a total of eight electrons in the shell.

When lithium and fluorine combine to form lithium fluoride (LiF), we may picture the lithium atom as giving up an electron to an atom of fluorine.

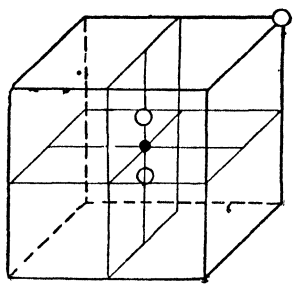


FIGURE 20
The Lithium Atom

The Lewis-Langmuir theory accounts very satisfactorily for valence in case of the elements having lower atomic weights. Thus, the elements of the alkali metals have a positive valence of one, for their atoms have one electron in the outside layer; the metals of the alkaline earth family have a positive valence of two, for their atoms have two external electrons; the elements of the chlorine family have a negative valence of one, for their atoms require one electron to complete a shell of eight. The positive valence of an element is determined by the number of electrons its

atom can give up, and the negative valence by the number of electrons an atom can take up.

The views of the physicists Rutherford and Bohr are not in entire accord with those entertained by the chemists Lewis and Langmuir. It is likely that, with increasing knowledge, all known theories will be considerably modified.

Moseley's atomic numbers indicate that all the chemical elements constitute one family, each member of which is simply related to every other member. It appears that there is one primordial element out of which all substances are made. This was suggested by certain of the early Greek philosophers (Chapter I); and in 1815-16, W. Prout, an English physician, published papers in which he propounded the hypothesis that the atomic weights of the elements—taking that of hydrogen as unity—were multiples of hydrogen, the lightest element. This meant that all the atomic weights of elements were whole numbers, and that hydrogen was the primary form of matter, of which atoms of other elements were different aggregates. According to Prout, hydrogen corresponded to the protyle of the ancients. The hypothesis of Prout was found, apparently, to be untenable, for careful determinations of atomic weights proved that some of the atomic weights were not even approximate multiples of that of hydrogen; *e.g.*, that of chlorine is about 35.5. This theory of Prout was abandoned until recently; but careful investigation has shown that elements having fractional atomic weights, such as chlorine, neon, and lithium, are mixtures of simple substances, having atomic weights expressable in whole numbers, the mix-

tures being known as isotopes (Greek: equal + place), because they occupy the same place in the periodic system. Two or more elementary substances having the same atomic number and different atomic masses, but occupying the same place in the periodic table of the chemical elements, are termed isotopes.

F. W. Aston has shown that neon is composed of 90 per cent of atoms of atomic weight 20 and about 10 per cent of atoms of atomic weight 22. Chlorine consists of atoms having weights of 35 and 37 so mixed as to give the atomic weight 35.46.

PARTIAL TABLE OF ELEMENTS AND ISOTOPES (ASTON)

Element	*Atomic number*	*Chemical at. wt.*	*Minimum no. of isotopes*	*At wt. of isotopes in order of intensity*
Li	3	6 94	2	7, 6
B	5	10 8	2	11, 10
Ne	10	20 2	2	20, 22
Cl	17	35 46	2	35, 37
Br	35	79.92	2	79, 81

The spectra of the components of an isotopic mixture are almost identical, and their chemical behavior appears to be the same.

No isotopes of hydrogen, helium, carbon, nitrogen, oxygen, phosphorus, and of certain other elements are known. This indicates that these are pure elements; *i.e.*, only one atomic species is known.

It is clear now that Prout's hypothesis has some foundation, for the hydrogen nucleus or ion (H^+) appears to be one of the two fundamental units which have to do with the building up of more complex nuclei or atoms, the other unit being the light negative electron. Since the helium nucleus has a mass of

4, it may be regarded as consisting of four hydrogen nuclei and two electrons closely packed together. The hehum atom contains, in addition, two exterior electrons. But if the helium atom contains four hydrogen nuclei, why is not its mass 4.032, when that of the hydrogen atom is 1.008 ($4 \times 1.008 = 4.032$)? There is a loss in mass of 0.032 in the assumed transformation. In answering this question we must know that at present there is no real distinction made between matter and energy: matter is potential energy; and energy is potential matter. Therefore, when four hydrogen atoms are assumed to come together to form an atom of helium, the excess of matter, namely, 0.032, should appear as energy. It has been computed that the transformation of one gram of hydrogen to helium would liberate energy equivalent to 166,000,000,000 calories! The conversion of hydrogen to helium would yield, therefore, immense quantities of energy, such as is found in the sun; and it may be that this change accounts, at least in part, for the tremendous heat of the sun. It is very interesting to know that both hydrogen and helium are conspicuous in the sun; indeed, helium was discovered in the sun many years before it was found in terrestrial matter.

It should be stated that the experiments of F. W. Aston show that the average mass of the hydrogen nucleus, or proton, is very nearly 1.000 when packed in the nuclei of other atoms, which compares with its value of 1.008 in the free state. The helium nucleus of mass 4 is probably a *secondary unit* of great importance in the building of atoms. It has been suggested by W. D. Harkins and by Rutherford that hydrogen

and helium are the fundamental "bricks" out of which all other elements have been built.

4 The New Alchemy

Since the atoms of different elements seem to be fundamentally the same, the question of artificial transmutation is again confronting us. The following passages are taken from R. A. Millikan's excellent book entitled "The Electron":

But what a fascinating picture of the ultimate structure of matter has been presented by this voyage to the land of the infinitely small! Only two ultimate entities have we been able to see there, namely, positive and negative electrons; alike in the magnitude of their charge but differing fundamentally in mass; the positive being eighteen hundred and forty-five times heavier than the negative; both being so vanishingly small that hundreds of them can somehow get inside a volume which is still a pin point after all dimensions have been swelled ten billion times: the ninety-two different elements of the world determined simply by the difference between the number of positives and negatives which have been somehow packed into the nucleus; all these elements transmutable, ideally at least, into one another by a simple change in this difference. Has Nature a way of making these transmutations in her laboratories? She is doing it under our eyes in the radioactive process—a process which we have very recently found is not at all confined to the so-called radioactive elements but is possessed in very much more minute degree by many, if not all, of the elements. Does the process go on in both directions, heavier atoms being continually formed as well as continually disintegrating into lighter ones? Not on the

earth so far as we can see. Perhaps in God's laboratories, the stars. Some day we shall be finding out. Can we on earth artificially control the process? To a very slight degree we know already how to disintegrate artificially, but not as yet how to build up.

Rutherford and Chadwick of Cambridge University have bombarded atoms of various elements with alpha-rays (a stream of helium ions, He^{++}, spontaneously expelled from the nucleus of a radioactive element), and have succeeded in expelling hydrogen nuclei from a number of different atoms, such as those of nitrogen, sodium, aluminium, and phosphorus. This means that artificial transmutation has been accomplished in these cases, but only on an exceedingly small scale. Rutherford has shown that the lighter atoms are the less stable; and most of the light atoms which he has decomposed have odd atomic numbers. With the exception of nitrogen, all these elements have atomic weights which are multiples of that of helium ($He = 4$) plus three units; and none of these elements, except boron, exhibits isotopy.

Recent attempts have been made to transmute certain of the metals into other metals. Miethe and Stammreich of Germany announced in 1924 that they had been able to change mercury into gold by passing a current of high voltage through a quartz-mercury vapor lamp containing pure mercury. Also, in May, 1925, the Japanese scientist Nagaoka reported that he had effected the transmutation of mercury into gold by passing an electric discharge between terminals of tungsten and pure mercury. The atomic number of mercury is 80, while that of gold is 79. Mercury is an

isotopic element, one of its atoms having a mass of 198, which is very close to the atomic weight of gold. If, therefore, the atomic number of mercury could be reduced to 79, a form of gold should result. If a proton, or hydrogen nucleus, could be ejected from the nucleus of a mercury atom, gold should be formed. It is also conceivable that gold might be formed by knocking or firing an electron into the nucleus of a mercury atom, thereby reducing its atomic number from 80 to 79.

All this work is receiving a great deal of hostile criticism. It is possible that the mercury employed was not perfectly pure, or it may be that it became contaminated with gold from an outside source. According to "Nature," Professor Haber of Germany relates that one of his young collaborators found traces of gold in a material he was analyzing, but no other experimenter could confirm the observation on other samples of the material. It is possible that the trace of gold detected by the young chemist came from his gold spectacles, which he was in the habit of removing.

In January, 1926, A. Smits of Holland reported the transmutation of lead into mercury and thallium by means of a quartz-lead vapor lamp, but his results are not generally accepted.

Paneth and Peters of the University of Berlin recently claimed to have transmuted hydrogen into helium. They adsorb hydrogen on palladium and burn it off with slight excess of oxygen, water being produced. The water is then condensed out by means of liquid air, the excess of oxygen removed with charcoal cooled in liquid air, and the residual gas brought into a

small capillary tube, and the electrical discharge from it examined for helium lines, external electrodes being employed to insure that the element does not come from the electrodes. They report that 10^{-7} cubic centimeter of helium was thus prepared, and that they can detect as small an amount as 10^{-9} cubic centimeter of the gas. This problem is being further investigated.

The new alchemy is indeed a fascinating subject. As yet we cannot tell how much farther it will be possible to go in artificial transmutation.

As Henry D. Hubbard says: "When its magic is more widely known the atom will become as fascinating for study and experiment as radio has become. Indeed, the varied properties and individuality of the atoms already form a subject of surpassing interest."

CHAPTER XVII

MINERALS AND METALS

The primitive metallurgist could only make use of such metals as he found free in nature, that is, such as had not been attacked and corroded by the ubiquitous oxygen. These were primarily gold or copper, though possibly some original genius may have happened upon a bit of meteoric iron and pounded it out into a sword. But when man found that the red ocher he had hitherto used only as a cosmetic could be made to yield iron by melting it with charcoal he opened a new era in civilization.—EDWIN E. SLOSSON.

1 THE MINERAL WORLD: ROCKS, CLAY, AND SOIL

THERE is an important and interesting science called mineralogy, which treats of the substances occurring in and upon the earth in a state of nature. These natural substances may be either uncombined elements or chemical compounds, and are known as minerals. A mineral is usually defined as "an inorganic species or substance occurring in nature, having a definite chemical composition and usually a crystalline form."

Incidentally, mineralogy may refer to meteorites, which come from extra-terrestrial space, as well as to substances, such as salts and gems, which are produced by artificial means.

In general, things are divided into three kingdoms —animal, vegetable, and mineral. The mineral king-

dom includes the inorganic substances, such as quartz, feldspar, mica, and the ores. Animal and vegetable organisms contain organic substances which may change by decomposition or distillation, yielding such materials as coal, mineral oils, asphalts, fossil resins, and gases. These also constitute part of our natural mineral resources.

While there are about ninety well-defined elements, only a few occur in quantity in the uncombined or native state, among which may be mentioned copper, gold, platinum, nitrogen, and oxygen. The mineral species which have been identified, exclusive of the organic or carbon compounds, number about one thousand, though by artificial means innumerable compounds can be prepared. In the chemistry of the earth's crust, therefore, the range of possibility appears to be very much limited.

Rocks, which make up such a large part of the earth's crust, are either simple minerals or aggregations of minerals, and they are the fundamental units of geology. Limestone, for example, is substantially a single mineral,—calcium carbonate ($CaCO_3$),—while granite is a mixture of the minerals quartz, feldspar, and mica. As rocks are usually mixtures, they are widely variable in composition. The minerals which most commonly take part in rock formation are the very stable ones of the abundant elements: *e.g.*, quartz or silica (SiO_2). The rocks are the outcome of relatively simple reactions.

As stated previously (in Chapter IV), twenty elements constitute 99.5 per cent of the earth's crust, the most abundant being oxygen, silicon, aluminium, iron,

calcium, magnesium, sodium, and potassium, all of which may be present in an eruptive rock.

For convenience of study F. W. Clarke divides the crust of the earth into three shells or layers:

(1) The innermost shell, which consists of plutonic or igneous rocks of crystalline structure, having unknown thickness. The compositions of these rocks are the nearest approach to the original materials.
(2) Sedimentary and fragmentary rocks. This shell overlies the innermost shell, being rather thin.
(3) Soils, clays, gravels, etc. This also is a thin layer.

The material of the second and third layers is derived chiefly from the first, due to the weathering and disintegration of the rock.

Quartz and the silicates—*i.e.*, salts of the acids of silicon—are the most important and abundant minerals constituting the earth's crust.

The specific gravity or density of the earth is about 5.5, while rocks have a mean specific gravity of only 2.6. This fact leads to the conclusion that the inner portion of the earth must have a specific gravity greater than 5.5; and long ago it was suggested that the center of the earth might be composed principally of heavy metals in the molten state, largely iron. This view seems to be a logical one, for the spectroscope indicates that iron is probably the most important element in the sun, and it is the most abundant metal in the earth's crust, with the exception of aluminium. Moreover, meteorites are composed principally of iron.

It is believed that the central mass of the earth

constitutes more than half of its entire mass. Overlying this central mass there is a lighter mass of silicates, the composition of which appears to correspond to that of igneous rocks. The heavier silicates of iron, aluminium, and magnesium probably form the lower layers, while the lighter silicates of calcium, potassium, and sodium are above. Quartz or silica is still higher up. It is possible that all these silicates, except the uppermost, are in the molten state, and they correspond to the magmas erupted by active volcanoes. The temperature of liquid lava is high; that of the uppermost layers of Kilauea was found to be 1000° C. Magmas solidified to form igneous rocks. Volcanic rock is sometimes formed on the earth's surface in great quantities, due to the solidification of magma or lava, which is poured out. The pouring out of magma may be accompanied by immense volumes of gaseous substances, such as water vapor, sulphur dioxide, hydrogen sulphide, hydrogen, and carbon dioxide. Sometimes so much gas is inclosed in a natural rock that it explodes when struck by a hammer, as does the red quartz of Branchville, Connecticut.

Rocks are gradually broken down by exposure to natural agencies, the change being partly mechanical and partly chemical. Water, carbon dioxide, and animal and vegetable life all play an important part in this disintegration which has been going on for countless ages. The most abundant minerals occurring in igneous rocks are the feldspars. Potash feldspar is called orthoclase ($KAlSi_3O_8$), and soda feldspar, albite ($NaAlSi_3O_8$). Now, by the weathering of feldspar, kao-

lin or clay, silica or quartz, and potassium carbonate are formed:

$$\underset{\text{Potash feldspar}}{2KAlSi_3O_8} + \underset{\text{Water}}{2H_2O} + \underset{\text{Carbon dioxide}}{CO_2} =$$

$$\underset{\text{Kaolin}}{H_4Al_2Si_2O_9} + \underset{\text{Quartz}}{4SiO_2} + \underset{\text{Potassium carbonate}}{K_2CO_3}$$

This change explains, in part, the formation of soil together with the potash contained therein, as well as the formation of clay, which is so abundant and widely distributed. Kaolin is a very pure form of clay which is sometimes found deposited extensively in beds. More frequently, however, the kaolin is carried away by running water and deposited along with other substances, such as sand and compounds of iron, calcium, and magnesium, forming what is known as common clay. Clays which have not been transported by natural waters from the place where they were formed are called primary. Some sedimentary beds, however, are very pure clay.

Kaolin burns white when heated, forming the basis of fine pottery and porcelain. The impure varieties of clay are utilized in the manufacture of tile, drain-pipes, bricks, etc.

The disintegration of igneous rocks is of prime importance in the development and maintenance of life upon the earth, for it is by this process that soils or loose surface layers have been formed.

The formation of limestone is due almost entirely to the action of organisms. This may be witnessed on coral reefs, where the coral animals die, their dead

sections being ground to a sand by the action of the waves. This sand is cemented together, forming solid limestone. It is of interest to know that a hard block of limestone was formed by W. Spring, who subjected powdered limestone to a pressure of six to seven thousand atmospheres for a period of seventeen years. According to Arrhenius, heat and pressure are the agents which have produced the greatest changes in the original earth-deposits. Water also has played a great part in changing the surface of the earth, a fact well expressed by Tennyson in the following familiar lines:

> There rolls the deep where grew the tree;
> O Earth, what changes hast thou seen!
> There where the long street roars hath been
> The stillness of the central sea.

2 Minerals and Ores

As oxygen is an active element, very abundant and widely distributed, many oxides occur in nature: for example, the oxides of such metals as iron, copper, zinc, tin, and aluminium. Oxides of non-metals are also abundant, being represented by quartz, water, and carbon dioxide. Also, many minerals occur in the form of sulphides, which are analogous to oxides, as well as in the form of carbonates, sulphates, or silicates.

The metals which have the greatest tendency to undergo oxidation are the more active ones. The least active metals—gold, platinum, silver, copper, etc.—are the ones which occur free in nature. A majority of the metals occur in combination with another element or elements. Some of the natural oxides are ores,

for they are minerals from which useful metals may be profitably extracted. Many sulphides and carbonates of metals are also valuable ores.

The most abundant of our iron ores is ferric oxide, or hematite (Greek: meaning blood-like), Fe_2O_3. This is the red oxide of iron. Enormous quantities of the mineral occur in the Lake Superior region, where it is mined in large open quarries, since the ore lies near the surface. Ferric oxide is employed in red paint and in jeweler's rouge.

While large masses of native copper are found in Michigan, the metal has a tendency to unite with other elements such as oxygen and sulphur. One important ore of copper is cuprite, or the red oxide of copper (Cu_2O), sometimes called ruby copper. This ore is found in connection with all copper ores. Some specimens of cuprite are more or less transparent and possess a beautiful red color.

Corundum or alumina is the oxide of aluminium (Al_2O_3). Corundum ranks next to the diamond in hardness, so it is a very important abrasive. Emery is a compact or granular form of corundum, which contains a large proportion of oxides of iron. The precious stones ruby and sapphire are varieties of corundum. The ruby owes its color to small quantities of chromium. When of the dark pigeon-blood red of the right transparency, it is the most expensive of gems. The color of sapphire is due to titanium or iron.

Alumina is a white solid which fuses at about 2000° C., and on cooling crystallizes. One form of alumina is an electric-furnace product which is sold under the name of alundum. It has many uses, such as for cut-

ting glass, for grinding steel, as crucibles, combustion boats, etc. Without such abrasives as alundum and carborundum (SiC), it would be impracticable to produce modern automobiles or aircraft engines.

Artificial gems are now produced from molten alumina. The white sapphire is pure alumina, but is changed into the ruby by the addition of a trace of chromic oxide. Blue sapphires are produced by adding traces of titanium oxide. The artificial sapphires and rubies are quite the equal of the natural gems. In the manufacture of gems, the pulverized oxides are melted in the oxyhydrogen flame and the droplets are caught on a disk in the flame and built up in the shape of an inverted chestnut. The oxide may be produced by sprinkling ammonium alum in the flame.

The sulphide ores are represented by galena, or lead sulphide (PbS), which crystallizes in cubes, and is the most important lead ore.

Stibnite, or antimony sulphide (Sb_2S_3), occurs as very beautiful, lustrous crystals, the Japanese specimens being particularly lovely.

Quartz or silica (SiO_2) is a very common mineral, of which rock-crystal is a clear, colorless form. It is perhaps the most prized, the most beautiful, and the most varied of minerals. Amethyst is a purplish or bluish-violet quartz, which is used for making ornamental objects. Other forms of quartz are: agate, jasper, chalcedony, flint, and opal. Silica also occurs abundantly as sea-sand, gravel, pebbles, and sandstone. The grains of the last substance are cemented together with a foreign substance.

Silica is also found abundantly as diatomaceous

earth, or kieselguhr. This is an opal-like silica secreted by organisms. It is used as an absorbent for nitroglycerine, as a wood-filler, a polishing powder, etc.

Silica occurs in the hard parts of straw and bamboo, and as "petrified wood."

The colored varieties of silica owe their color to small quantities of impurities. Thus, the color of amethyst is due to manganese and iron, and that of smoky quartz to organic matter.

Quartz, or rock-crystal, crystallizes in six-sided prisms capped with pyramids, and the mineral is hard enough to cut glass. Clear crystals of quartz are used in the manufacture of optical instruments and spectacles. The melting-point of quartz is 1600° C.; therefore, it fuses in the oxyacetylene flame and in the electric furnace. "Silica ware" is now manufactured by fusing quartz. Quartz has the lowest coefficient of expansion of any known substance (one seventeenth of that of platinum); therefore, quartz vessels may be heated to redness and suddenly chilled without cracking. This may be strikingly shown by heating a quartz dish or tube to redness and then plunging it into ice-water. By employing special methods the General Electric Company is now able to produce comparatively large masses of perfectly clear quartz which resembles rock-crystal in appearance; and objects such as tubes, rods, and lenses are fashioned out of it.

According to Elihu Thomson, this beautiful material is probably the most transparent solid in existence. It is remarkable for its wonderful transparency to rays of the visible spectrum, to low heat or ultra-red rays, as well as to the ultra-violet invisible rays. Rods

of the material are employed to convey ultra-violet rays to the cavities of the body in order to treat diseased areas, such as the ear, the nasal cavity, and the throat. A rod or tube of fused quartz as much as twenty-six feet in length will convey, by internal reflection, the light of a match from one end to the other with little apparent loss. Even bent rods convey heat- and light-rays for considerable distances. Fused quartz is the ideal glass, for not only is it remarkably transparent but its coefficient of expansion with temperature change is almost negligible. Blocks of the material are now produced for use in the construction of prisms and lenses, etc.

3 The Arrangement of Atoms in Crystals

Minerals usually possess a crystalline form: *i.e.*, they are bounded by planes so as to make symmetrical solids. While crystals appear to assume an almost infinite variety of forms, they may be classified in six systems, which are readily defined by referring each to fundamental axes. Each crystal has three or more axial directions, and these retain to one another an invariable relation: *e.g.*, the first system of crystals is called the regular or isometric system. Crystals belonging to this system have three equal and interchangeable axes at right angles, as has the cube. Common salt, for instance, crystallizes in cubes. Iron pyrites, galena, alum, and most metals belong to this system.

The branch of mineralogy which has to do with the study of crystals is called crystallography. What is known about the arrangement of the atoms in crystals? We are certain that they are arranged according to a

definite pattern. We have learned much about crystal structure by means of X-ray analysis. When a beam of X-rays is passed through a thin section of the crystal and then allowed to strike a photographic plate, a diffraction pattern of the crystal lattice is produced. Laue of Zurich, for example, made photographs of sodium nitrate. From the position of the crystal, its distance from the photographic plate, and

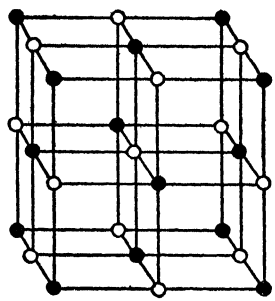


FIGURE 21
Structure of Crystal of Sodium Chloride

its crystallographic measurements, mathematicians are able to construct a model of the space-lattice of the crystal.

Bragg and Bragg employed an X-ray spectrometer and mounted the crystal so as to use it as a reflection grating, its various faces being successively employed. From the X-ray spectra thus obtained they were able to determine the relative positions of the atoms in the space-lattice of the crystal. In other words, they were able to measure the distances between the rows of particles in crystals.

Hull has devised a method in which the substance is employed in the form of fine powder consisting of tiny crystals. A beam of X-rays is passed through the powdered substance, the rays being diffracted to a photographic plate, where a line is produced for each kind of crystal face. The crystal structure can be calculated from the positions and intensities of these lines.

The arrangement of atoms in a crystal of sodium chloride is shown in Figure 21. The structure of the crystal depends upon the arrangement of the constituent atoms and not upon that of the molecules. The atoms, therefore, are the units that give the crystallographic pattern. When the diamond is examined by means of X-rays it is found to consist of atoms arranged in the form of tetrahedra, with four atoms at each corner of a tetrahedron, and a fifth atom at the mass-center.

4 Metals and Their Properties

The metals known to the ancients were either those that occur in nature or those that may be obtained readily by reducing their ores. They are: gold, silver, copper, lead, tin, iron, and mercury. The use of gold and copper dates from prehistoric times, and it is probable that these were the first metals used by man. Both metals occur in the free state. As a rule ancient gold is alloyed with silver, the latter metal having been known since at least 2000 B.C. Gold coins nearly twenty-five hundred years old have recently been found in the ruins of Sardis, the ancient capital of

Lydia. They were coined during the reign of Crœsus. The manufacture of bronze, an alloy of copper and tin, dates from about 3000 B.C. Copper and tin ores were reduced together to form the alloy, which is harder than copper. A ring of tin has been discovered which dates from 1450 B.C. Brass, an alloy of copper and zinc, was known to Aristotle. The word was used indiscriminately in the Old Testament, both for copper and its alloys.

The use of iron was no doubt later than that of gold and copper, for very little of the metal occurs in the native state. The Assyrians and the Egyptians, however, employed iron implements many centuries before the Christian era. The word iron is mentioned in the Pentateuch, together with the furnaces in which it was prepared. Owing to its high melting-point, iron is more difficult to work than copper. Lead is mentioned in the Book of Job and in the Book of Numbers. Pliny points out a distinction between lead and tin. Lead was used by the ancient Romans for water-pipes. Mercury was first described by Greek writers. Its ability to dissolve other metals was known before our era. Nickel, cobalt, manganese, and platinum were discovered during the eighteenth century, but most of the remaining metals were first prepared during the nineteenth century.

Typical metals not only have a characteristic luster but are malleable and ductile. Gold is the most malleable and ductile of the metals, followed by silver, copper, tin, and platinum. Gold has been hammered out into sheets so thin that it requires 280,000 leaves placed one upon another to occupy the thickness of an

inch, and one ounce can be hammered out so as to cover 189 square feet. The thickness of the layer of the precious metal on gold lace is about 0.000002 millimeter. Gold is so ductile that one ounce can be drawn into a wire about 50 miles long.

The fusing- or melting-points of the metals are generally higher than those of non-metals, but they vary within very wide limits, ranging from —39° C. in the case of mercury to 3400° C. in the case of tungsten (see Appendix). Gold melts at 1063°, pure iron at 1530°, and platinum at 1755°. The high melting-point of tungsten is of great value in the manufacture of filaments for incandescent lamps. All the metals can be vaporized in the electric arc.

In general, metals are good conductors of electricity, although they vary much in this respect, silver conducting more than sixty times as well as mercury. Of the cheaper metals, copper is the best conductor, being nearly as good a conductor as silver. Aluminium has about two thirds the conductivity of copper for equal diameter of wire. The electrical conductivity of metals increases with fall in temperature.

There are about fifty well-known non-ferrous metals, the most important of which is copper. Tin, zinc, lead, aluminium, and nickel are also very common. A mixture of two or more metals is known as an alloy. According to H. W. Gillett, there are over sixteen hundred alloys of the more common non-ferrous metals, which are used more or less commercially. It is fairly common for a non-ferrous alloy to contain three or four metals.

Copper is used extensively in all electrical apparatus, over a billion pounds having been used in the United States for this purpose in 1923. It is also employed in the manufacture of vessels of various types, and is an essential constituent of valuable alloys, such as bronze and brass. The world's annual production of copper is normally about a million tons, more than half of which is furnished by the United States.

Tin is employed in the manufacture of tin-plate, which is accomplished by dipping cleaned sheets of low-carbon steel into molten tin. As the metal does not tarnish appreciably when exposed to moist air or to organic acids of food, it is of much importance, for modern life is greatly dependent upon the tin can. Tin is produced largely by the Federated Malay States, by the island of Banca in the Dutch East Indies, and by Bolivia. After Julius Cæsar's conquest of the British islands, the tin of the Cornish mines was carried to Italy. It is reported that the familiar mines of tin are showing signs of depletion. The chief ore of tin is tinstone or cassiterite (SnO_2).

Zinc finds use for coating iron to prevent rust (galvanizing), in alloys, and in dry cells, such as are employed for ringing door-bells and in flash-lights. The United States is the leading producer of zinc, followed by Germany and Belgium. One of its most important ores is zinc blende (ZnS).

Lead is employed in the storage-battery, for conveying water, and in the manufacture of linings, alloys, paints, and shot. Articles made of lead have been found in Egyptian tombs of great antiquity. The United

States stands first in the production of lead. Much of this metal is also produced by Spain, Germany, and Australia.

Aluminium is a light, strong metal, a good conductor, and tarnishes but slowly, so it is used extensively in the manufacture of aircraft, automobiles, cooking utensils, food-wrappers, and alloys. Mixed with oil or other liquid, it is utilized as a paint for metallic objects. In 1918, the world's consumption of aluminium was about 500,000,000 pounds, on account of the increased use in the war, of which the United States produced almost half. Aluminium is an essential constituent of clay.

Nickel is very valuable for plating articles and for alloys, such as German silver, monel metal, and coins. The most important nickel-bearing ores are found in the Sudbury district, Ontario, and in New Caledonia. The metal usually occurs associated with cobalt.

The uses of the precious metals—gold, silver, and platinum—are well known to all. Gold, silver, and copper are the metals universally used in coinage. They all occur native, and are the three best conductors of electricity. Africa, the United States, Australia, and Mexico are the leading producers of gold. The world's production in 1913 was valued at over $460,000,000, and in 1920 at $337,000,000. There was a decline, therefore, in the production of gold. This metal is the basis of international credit, the price remaining stationary, namely, $20.67 per ounce. The cyanide process has increased the production of gold enormously since its introduction in 1890; it is applicable to very low-grade ores and tailings.

Silver is largely a product of the New World. In 1913 the world's production of silver was 225,400,000 fine ounces, while in 1918 it was 197,395,000. In 1913, silver was worth $0.604 per troy ounce, and in 1918, $0.98. The price of silver therefore varies within rather wide limits. The United States and Mexico produce about 50 per cent of the world's supply. The greater part of our silver is obtained as a by-product in the refining of copper and lead.

From 1911 to 1914, the estimated world's production of crude platinum averaged annually approximately 290,000 troy ounces, of which Russia produced over 94 per cent and Colombia nearly 5 per cent. Pure platinum is used extensively as a catalyst in the manufacture of sulphuric acid by the contact process. Platinum gauze is employed as a catalyst in the manufacture of nitric acid. Platinum dishes, crucibles, tongs, foil, wire, etc., are required in the chemical laboratory.

Platinum is so scarce and is such a necessary metal, in time of peace as well as in war, that its use in jewelry should be discontinued. Before the war the average consumption of the platinum metals in the United States was about 165,000 ounces, of which it was estimated that the jewelry and dental industries used 75 per cent, the electrical industry 20 per cent, and the chemical industry 5 per cent. This makes it clear why the stocks of the larger producers of platinum were requisitioned by the Government in February, 1918. Platinum is much more valuable than gold, the present (1927) price being about $110 per troy ounce.

Mercury, commonly called quicksilver, is produced in Spain, Italy, Austria, and the United States. It is

utilized in the manufacture of thermometers, scientific instruments, drugs and chemicals, and mercury vapor lamps. When mercury is boiled, the heat of its vapor can be utilized to drive a turbine, and the heat of the turbine exhaust can be used to generate steam. The mercury vapor boiler is more efficient than the usual steam distillation. The ore of mercury is cinnabar (HgS).

Magnesium is used in the production of flash-light powders, in fireworks and flares, as a high-explosive ingredient, and as an alloy with aluminium in airplane and frame castings. The alloys of magnesium possess both lightness and strength. Magnesium is the lightest material available for gas-engine pistons and connecting-rods.

Chromium, manganese, and tungsten are employed in the manufacture of special steels. Chrome steel is extremely hard and tough, being excellent for cutting-tools, armor-plate, crushers, and automobiles. Stainless steel contains from 12 per cent to 15 per cent of the metal. Chromium is now being used for coating more corrosive metals. Chromium occurs chiefly in British South Africa, New Caledonia, Russia, and Asia Minor.

Manganese increases the toughness of steel: *e.g.*, it is a constituent of the jaws of crushers and of burglar-proof safes. The chief ore of manganese is the dioxide, or pyrolusite (MnO_2). High-grade pyrolusite is used on a large scale in the manufacture of dry batteries. It oxidizes the hydrogen which would otherwise collect on the carbon pole. From 1910 to 1913, Russia, India,

and Brazil supplied about 95 per cent of the world's production. Before the war the United States imported most of the manganese ore and manganese alloys required in our industries. The war showed that domestic ores could supply about 35 per cent of the nation's needs. The signing of the armistice brought a sudden collapse to the mining of manganese ores in the United States.

The ores of tungsten are found principally along, or comparatively near, the shores of the Pacific Ocean, the Asiatic shore being richer than the American. Southeastern Asia is the greatest producer of tungsten ores, followed by the United States and Mexico. Until the year 1912, the leading tungsten-producing country was the United States. The average domestic production was about 1400 tons, and the average production from 1916 to 1918 was over 5000 tons, the great increase in production being due to the stimulus of the war. After the signing of the armistice, prices fell rapidly. On account of the abundance of ore and cheap labor, the Chino-Malayan Province is in a favorable position to supply the greater part of the metal. Tungsten is used extensively in the manufacture of high-speed tool steel. As the tools can be heated to redness without losing their temper, the efficiency of the workmen is greatly increased. The metal is also used largely in the manufacture of filaments for incandescent lamps. The bulbs are either exhausted or filled with argon. This lamp is far more efficient than the one containing the ordinary carbon filament, 1.30 watts per candle-power being required for the former,

while 3.25 watts are required for the latter. Tungsten is also used for targets and cathodes of X-ray tubes, for electric contacts in explosion engines, etc.

5 Metallurgy

Metallurgy may be defined as the science and art of preparing metals for use, from their ores, by separating them from mechanical mixture and chemical combination.

It is often necessary to prepare an ore for metallurgical treatment, especially a low-grade ore, by subjecting it to some process by which a large part of the gangue, or earthy matter, may be removed mechanically so as to lessen the cost of the subsequent metallurgical treatment. Such treatment is generally termed concentration, and the products of the concentration process are termed concentrates and tailings. Concentrates are subsequently treated, as before stated, by a metallurgical process and the tailings, as a rule, go to waste.

Preparatory to concentrating an ore it is generally first crushed to a suitable size, screened and sized, and then passed over or through some form of apparatus, called a concentrator. This removes the major portion of the gangue material from the valuable metallic portions of the ore. This separation is usually effected by reason of the difference in specific gravity of the gangue and of the valuable portion of the ore. The process is known as the wet gravity concentration process, due to the fact that separation is effected in water; the laws governing falling bodies in water are

taken advantage of in order to increase the efficiency of the process and effect the desired separation.

In recent years, the oil process of ore concentration-flotation has been used on a large scale, particularly for the concentration of low-grade sulphide ores such as those of copper. It is said that over sixty million tons of ore are treated annually by this process in the United States. Finely ground ores or tailings—*e.g.*, tailings of copper ores—are agitated with water and a little oil. Metallic particles contained in the material treated, together with whatever gangue particles have not been liberated from them by crushing, rise to the top of the oil, and the gangue sinks in the water. The sulphide is preferentially wetted by the oil and the gangue by the water. The froth can be scraped or shoveled off. This is just the reverse of what happens in the gravity concentration process; that is, heavy metallic particles rise instead of sinking. For this reason some one has spoken of the oil-flotation process as being "gravity concentration upside down."

It is of interest to note that only a small quantity of oil is required. Not all oils are suitable. In America the so-called pine-oil has been used extensively with or without admixtures of mineral oils. Eucalyptus oil has been used with success in Australia.

The ore must be of a metallic or semi-metallic character. In addition to the "oiling reagent," a "gangue modifying reagent" (usually alkalis or mineral acids) is employed. Air is introduced under such conditions that a stiff and lasting froth is produced, the oiled mineral particles adhering to the air-bubbles. The froth is then mechanically separated.

Metals are most generally obtained from their ores by a process known as pyrometallurgy; *i.e.*, fire-smelting. It was through the writings of Georg Agricola (1490-1555) of Germany that this process became known to us.

In fire-smelting it may be stated, in general, that the ore, containing more or less earthy matter known as matrix or gangue, is heated with a flux, which unites with the earthy matter to form a fusible slag. Thus, when hematite (Fe_2O_3) occurs mixed with silica (an acidic matrix), the latter is removed by heating the ore with limestone or lime (flux), the fusible slag, calcium silicate, being formed:

$$\underset{\text{Silica}}{SiO_2} + \underset{\text{Lime}}{CaO} = \underset{\text{Calcium silicate (slag)}}{CaSiO_3}$$

In case the ore is an oxide, the oxygen is separated from the metal by heating the ore in an appropriate furnace or crucible with some form of carbon, such as coke or charcoal. The carbon is oxidized at the expense of the oxygen of the ore: *e.g.*, when zinc oxide (ZnO) is heated with carbon, zinc and carbon monoxide are obtained:

$$ZnO + C = Zn + CO$$

This process is called reduction.

Immense quantities of coke are used in winning iron from its ores. Carbon is our greatest reducing agent.

When the ore is a carbonate or a basic carbonate—*i.e.*, part carbonate and part hydroxide—it is first heated to obtain the oxide. To illustrate, malachite is one of the important copper ores. When it is heated,

water and carbon dioxide are expelled, leaving copper oxide:

$$\underset{\text{Malachite}}{CuCO_3.Cu(OH)_2} \text{ (heated)} = 2CuO + H_2O + CO_2$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\quad \underset{\text{oxide}}{\text{Copper}}$$

The oxide may then be reduced, as before, by means of coke.

Sulphide ores are first roasted—*i.e.*, heated in air—in order to get rid of sulphur, which is a nuisance in metallurgy. The sulphur is oxidized to sulphur dioxide, leaving the metal in the form of an oxide, which may be reduced by means of coke.

Large quantities of sulphur dioxide are obtained as a by-product in the smelting of sulphide ores; it is used in the manufacture of sulphuric acid, sulphites, etc.

Powdered coal is being used in smelting. It is blown into the furnace, and burns with a flame similar to that of a jet of gas.

Certain metals may be obtained by using aluminium as a reducing agent.

Finely divided aluminium, at high temperatures, has great affinity for oxygen; it reduces oxides of most of the metals. In recent years this method has been employed to prepare such metals as chromium and manganese. Once the process is started, the reaction is exothermic. As a great quantity of heat is liberated, the procedure is called aluminothermy, and the mixture of oxide and aluminium is called thermite. This method was first employed by the German chemist Goldschmidt. It can be readily illustrated by reducing

an oxide of iron, manganese, or chromium in a fire-clay crucible. A mixture of the oxide and aluminium is introduced into a dry crucible, which is surrounded by sand. A small amount of a starting mixture—*e.g.*, barium peroxide and magnesium powder—is placed on top of the thermite, and this is ignited by means of a burning magnesium ribbon (Figure 22). As the re-

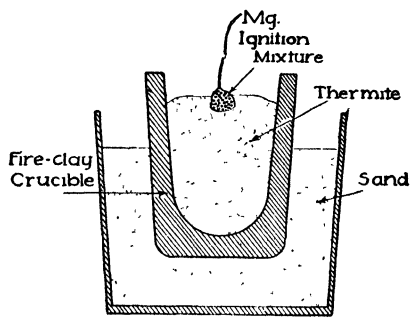


FIGURE 22
The Thermite Process

duction proceeds, more thermite may be added. The metal forms a regulus in the bottom of the crucible, the slag (Al_2O_3) collecting at the top:

$$\underset{\text{Iron oxide}}{Fe_2O_3} + 2Al = \underset{\text{Iron}}{2Fe} + \underset{\text{Alumina}}{Al_2O_3}$$

Owing to the great production of heat, the Goldschmidt process is used in welding metals. For example, thermite is employed for welding the frames of locomotives, steel rails, and the broken sternposts of boats.

Electrometallurgy is the department of metallurgy

in which the electric current is employed not only for electrolytic separation or deposition of metals from solutions but as a source of heat (the electro-thermal process) in smelting, refining, annealing, and welding. The use of the electric current is increasing: *e.g.*, sodium is manufactured by the electrolysis of fused sodium hydroxide (NaOH). Electrolytic zinc can be produced by leaching the ore and then passing an electric current through the solution of the salt.

The electrolytic refining of metals is becoming more and more important. For many purposes copper must be relatively pure; therefore, crude copper, or blister copper, must be refined. Blister copper is cast into ingots each of which weighs several hundred pounds. These are arranged as anodes in electrolytic tanks, while the cathodes are thin sheets of pure copper, each anode being arranged opposite a cathode. The electrolyte is a solution of cupric sulphate and sulphuric acid. A properly regulated current is passed through, and copper is carried from the anode to the cathode, where it is deposited. Certain impurities pass into solution, while others, such as silver and gold, collect on the bottom of the tank as a mud (slime), which is worked over for the precious metals. Selenium, tellurium, and other by-products are sometimes obtained in the refining of copper. A representative electrolytic copper contains from 99.94 to 99.98 per cent of the metal.

The production of industrial aluminium is a great triumph in the field of metallurgy. In the year 1883 the total production of the metal was only eighty-five pounds, and the metal was as costly as silver. In 1886, C. M. Hall, a student in Oberlin College, invented a

process which may be described as follows: Alumina (Al_2O_3) is dissolved in a bath of molten cryolite, and an electric current passed through the solution. The operation is conducted in cells lined with carbon, which constitute the cathodes. Carbon bars form the anodes, which combine with the oxygen. The heavier metal sinks to the bottom and is withdrawn from time to time. In 1889 Hall organized a company for the commercial production of aluminium. By 1914 the domestic production of the metal was valued at more than ten million dollars, and the price had fallen to about eighteen cents per pound.

Bauxite is the source of aluminium oxide used in the production of aluminium. This ore usually contains ferric oxide as an impurity. France possesses high-grade bauxite deposits, but the American company which is the sole manufacturer of aluminium in the United States has recently secured control of a very large deposit in British Guiana, which is said to be of higher grade than the French ore.

Hall borrowed from his professor most of the apparatus which he employed for his first experiments. He had to make by hand the zinc plates needed for his batteries. In spite of his many handicaps, he perfected a process for the production of a metal which had been as costly as silver and for half a century had received the attention of some of the world's leading chemists.

CHAPTER XVIII

THE MARVELOUS STORY OF IRON AND STEEL

Iron, the most abundant and the cheapest of the heavy metals, the strongest and most magnetic of known substances, is perhaps also the most indispensable of all save the air we breathe and the water we drink. . . . The coincidence that so indispensable a thing should also be so abundant, that an iron-needing man should be set on an iron-cored globe, certainly suggests design. The indispensableness of such abundant things as air, water and light is readily explained by saying that their very abundance has evolved a creature dependent on them. But the indispensable qualities of iron did not shape man's evolution, because its great usefulness did not arise until historic times, or even, as in the case of magnetism, until modern times.

—HENRY M. HOWE, in *The Encyclopædia Britannica.*

1 THE STONE, BRONZE, AND IRON AGES

ARCHÆOLOGISTS divide prehistoric time into three periods, namely, the Stone, Bronze, and Iron ages. The Bronze Age began in Greece about five thousand years ago, and the Iron Age began about eight hundred years later, or about 2300 B.C. In Egypt, Chaldea, Assyria, and China the age of iron perhaps reaches as far back as four thousand years before the Christian era. Pieces of iron of great antiquity have been found, an iron implement having been discovered in an Egyptian pyramid. It is certain, then, that iron implements were employed in the ancient world; indeed, the old symbol

for the metal was that representing the spear and shield of Mars, the god of war—♂.

In the fourth chapter of Genesis, the twenty-second verse, mention is made of Tubal-cain as an instructor of workers in iron and "brass," that is, copper. It is probably from Africa that iron first came into use. Great skill in metallurgy was attained at an early period by the Hindus, iron being one of the six metals which are mentioned in their ancient literature. Their great skill in the metallurgy of iron is well illustrated in the celebrated iron pillar near Delhi, which was manufactured about fifteen hundred years ago. This pillar weighs fifty-five tons and is still standing. It is marvelous to find that after exposure to the elements for fifteen centuries it is unrusted, and the inscription on it is as clear and sharp now as it was when the pillar was erected. Chemical analysis has shown that the pillar is pure malleable iron without any alloy. Even now it is exceptional that forged masses of iron of such size are produced.

2 The Occurrence and Manufacture of Iron

Iron occurs very abundantly and widely distributed, constituting 4.5 per cent of the earth's crust, which places it next to aluminium amongst the metals. Iron in the free state has been found in considerable masses in Greenland. The occurrence of the metal in large lumps may have been due to the firing of coal-pits; or it may possibly have been of meteoric origin.

Iron in the combined state is found in many minerals and in most rocks and the soil. Hematite (Fe_2O_3) is

by far the most important iron ore in the United States. In 1918 it constituted nearly 95 per cent of our iron mined. The number of gross tons of ore shipped from our mines in 1918 was 72,000,000, valued at $244,000,000. Of the total, Minnesota furnished 43,260,000 tons, Michigan 17,580,000 tons, and Alabama 6,120,000 tons. By modern methods, 12,000 tons of ore can be loaded into a steamer in less than twenty minutes, and the vessel may be unloaded in not more than four hours.

It is interesting to note that hematite imparts a red color to certain soils and rocks: for example, the Grand Cañon in Arizona and Red Rock Cañon in California. Finely divided hematite is used very extensively as a pigment.

Brown hematite, or limonite, another very important iron ore, consists of ferric oxide in chemical union with water ($2Fe_2O_3.3H_2O$). This oxide imparts a brown color to soil. It is present in many ordinary clays; and when they are used in the manufacture of brick and earthenware, the material turns red when it is fired, due to the loss of water. Limonite is abundant in Alabama and Tennessee and in France and Germany.

Various pigments are produced by heating the naturally occurring hydrates of iron: *e.g.*, red, yellow, and brown ochers. They are used for decorative purposes.

Magnetite (Fe_3O_4) is another important iron ore, particularly in Norway and Sweden; it is the richest of the iron ores (72.4 per cent iron). This mineral is attracted by a magnet, which is sometimes used in separating the oxide from crushed earthy matter.

Lodestone, a natural magnet showing polarity, is a variety of magnetite. It is thought that the unknown people of the Southwest, who lived before the American Indian, used lodestone as a magnet in orienting their temples, for these are all placed parallel to the magnetic meridian.

Another important ore is siderite, or spathic iron ore (ferrous carbonate, $FeCO_3$). It is the chief iron ore of England, being known as clay ironstone, because it occurs associated with clays and shales of the coal-measures. The blackband ironstone contains from 20 per cent to 25 per cent of carbonaceous matter.

The only ores of iron which are applicable to smelting are the oxides and carbonate; for they must be ores that can be readily reduced and must be low in sulphur. Iron pyrites (FeS_2), for example, is abundant, but is not a commercial source of iron; it is used, however, as a source of sulphuric acid and sulphites. Iron is assimilated by plants and animals. It is an essential constituent of hemoglobin and therefore plays a very important part in life-processes. Without sufficient iron in the soil a plant becomes pale, while a deficiency of iron in the blood is indicated by the pallor of the cheeks. When the portion of iron in the blood is reduced too low, our bodies are attacked by disease-producing germs, which multiply until death may follow. It is now customary to have laboratories where the number of iron-bearing corpuscles in the blood may be counted. As expressed by Slosson:

The reason why iron is able to serve this unique purpose of conveying life-giving air to all parts of the body is because it rusts so readily. Oxidation and deoxidation proceed

so quietly that the tenderest cells are fed without injury. The blood changes from red to blue and *vice versa* with greater ease and rapidity than in the corresponding alternations of social status in a democracy. It is because iron is so rustable that it is so useful.

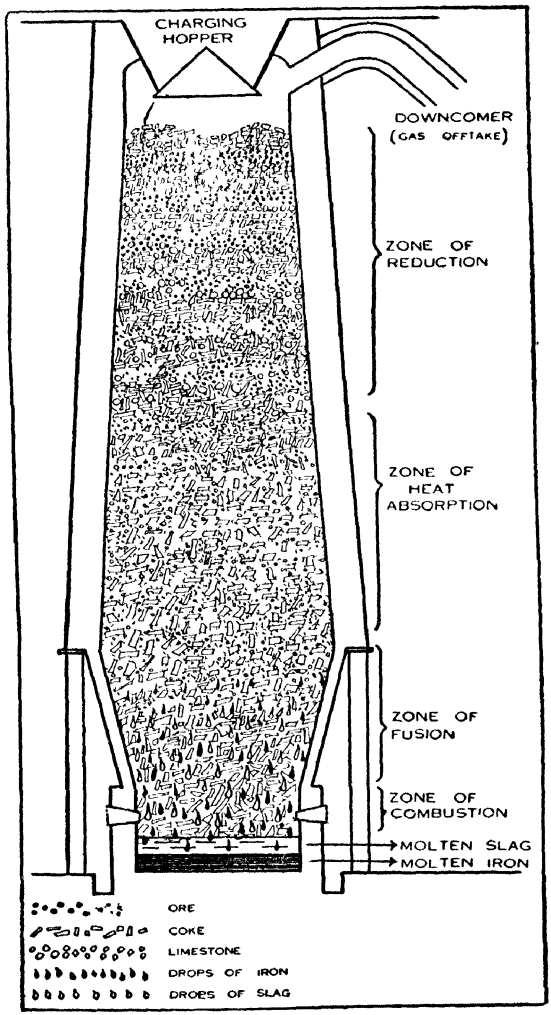
It is important that a large portion of the articles of diet contain iron. Preparations of iron have an astringent taste and blacken the tongue and teeth, owing to the formation of iron sulphide. It is therefore wise to administer iron preparations through a tube or a quill. The salts of iron have a powerful astringent action, because they bring about the coagulation of albuminous fluids of the tissues. They are also very effective in stopping flow of blood, as hemorrhage of the nose, for they cause the blood to clot, thus plugging the bleeding vessels. In certain forms of anemia the administration of preparations of iron causes rapid improvement in the condition of the blood.

It may be assumed that the first iron was produced by accident. Possibly lumps of iron ore were employed instead of stones in making fires for cooking, perhaps in connection with some feast. When the fires burned long enough, metallic iron was formed, due to the action of charcoal, which is a good reducing agent. By experience it was learned that higher temperatures were produced when the wind was blowing, and a better product was obtained. Hearths were therefore located on hilltops where the wind had full sway, or in valleys where advantage was taken of the topography in securing the needed wind currents. Since wind is variable, in the course of time this crude beginning was followed by the invention of devices for the arti-

ficial production of a blast, the first of which was probably the goatskin. By means of two appropriately shaped skins it was learned that a more constant blast could be produced, the operator throwing his weight first on one skin and then on the other. This method of operation is still employed in parts of India, and in Europe the two-part bellows still employed by the country blacksmith is a natural development of the two goatskins.

Iron on the commercial scale is now produced by first calcining the ore, if necessary, and then subjecting it to the operation of smelting in a huge blast-furnace, limestone ordinarily being employed as the flux and coke as the reducing agent. Furnaces are usually located so as to secure as cheap a supply as possible of the three great raw materials required in the manufacture of pig-iron. In the calcination of the ore, carbonates yield oxide of iron and carbon dioxide, hydrated oxides give up water, and sulphides are oxidized. The oxides of iron, limestone, and coke are raised to the top of the furnace by means of a hoist. The furnace is usually about 90 feet in height, but furnaces 125 feet in height have been constructed. A furnace 90 feet in height and from 12 to 14 feet in diameter usually produces from 500 to 600 tons of pig-iron in twenty-four hours.

The Trumbull-Cliffs Furnace of Warren, Ohio, produced 23,364 gross tons of iron during the month of January, 1923. This is an average of 754 tons per day. For each ton of iron, 1986 pounds of coke were used. To produce 400 tons of pig-iron in twenty-four hours, it is necessary to feed a furnace about 800 tons of ore,



Courtesy, Iron Trade Review

FIGURE 23

Blast-Furnace Showing Sequence of Principal Reactions

400 tons of coke, 100 tons of limestone, and about 2500 tons of air. According to J. J. Porter, "the modern blast furnace is not only the most tremendous and spectacular of machines, but it is representative of the most important of all manufacturing operations."

The furnace is constructed of heavy steel plates lined with fire-brick (Figure 23). The raw materials are introduced into a hopper at the top of the furnace, and by lowering a bell they are dropped into the furnace. The bell-shaped devices are so manipulated as to prevent the escape of furnace gases. Great volumes of dry preheated air are blown in through pipes called tuyeres, near the bottom of the furnace. In ascending, the hot air acts chemically on the charge, the excess of gas (furnace gases) escaping through a large pipe called the downcomer. The furnace gases usually contain over 20 per cent of carbon monoxide by volume, and are utilized in preheating the blast and to drive the gas-engines.

Some of the oxygen of the ascending air combines with coke in the lower part of the furnace, forming carbon dioxide, which is partially reduced to carbon monoxide by the hot coke higher up in the furnace. The oxides of iron are reduced by carbon and carbon monoxide, the latter being very effective for the reason that it is a gas, thus coming into very intimate contact with the ore and burning to form carbon dioxide.

The upper zone of reduction is not hot enough to melt the iron, so the spongy metal and any remaining oxide descends to the lower zone, where further reduction occurs, the metal then descending to the very hot zone of fusion, through which the melting

charge trickles down. The molten iron collects on the bottom of the furnace, the lighter slag forming a layer above. The iron is tapped off every six hours or so, while the slag is removed more frequently through a small cinder-notch. The iron is run into molds of sand or iron, the product being known as pig-iron or cast-iron; or the molten metal is carried in large ladles to be converted into steel by the direct process—*i.e.*, without allowing the crude iron to solidify.

The slag is a complex silicate of calcium and aluminium. It may be granulated by pouring into water; it is utilized as ballast for railroads and in the manufacture of Portland cement. For the latter purpose, it is burned with more lime and then ground.

A blast-furnace is kept in continuous operation; it must be interrupted now and then in order to renew the linings.

The efficiency of the furnace is greatly increased by removing the moisture of the air before it goes to the stoves. This is accomplished by means of the Gayley process, the moisture being removed by artificial refrigeration.

3 Pig-Iron and Wrought-Iron

The United States of America produces more than half of the world's pig-iron. In the year 1918, over 38,000,000 tons were produced from our blast-furnaces, the value being over $1,180,000,000. Our iron has a greater value than any other manufactured product; indeed, greater than that of all other metals combined. In sixty years the output of pig-iron in the United

States has increased from about 700,000 tons to approximately 40,000,000 tons annually. The rate of growth of the iron industry is one of the marvels of the age. At one time, however, iron was regarded as a precious metal, as it was so scarce. During the early part of the fourteenth century, in the reign of Edward III, the iron utensils of the royal household were classed among the jewels.

Pig-iron, the product of the blast-furnace, varies in composition and properties with the character of the ore and the operation of the furnace. In general, it may be stated that a pig-iron contains about 93 per cent of iron, 4 per cent of carbon, from 0.4 per cent to 4 per cent of silicon, from 0.5 per cent to 1 per cent of manganese, and less than 0.1 per cent each of sulphur and phosphorus. The presence of the impurities affects the properties of iron greatly. Thus, pure iron melts at 1530° C., whereas cast-iron melts from 1150° to 1250°. Moreover, cast iron is hard and brittle. Carbon and silicon increase the hardness and strength; phosphorus, the fluidity, causing it to make better castings. Iron and steel which contain phosphorus are "cold short,"—*i.e.*, brittle while cold,—while those containing sulphur are "red short," or brittle while hot. Furthermore, sulphur in iron tends to produce unsound castings.

There are two commercial grades of pig-iron—gray iron and white iron. The gray pig-iron is obtained by allowing the molten metal to cool slowly, thus affording time for the carbon to crystallize in large flakes of graphite. The iron is coarse-grained, and has a gray

fracture. When it is dissolved in acids, graphitic carbon is left as a residue.

White pig-iron is produced by rapid cooling. The iron combines to a certain extent with carbon, forming an iron carbide, or cementite (Fe_3C). This grade of iron is hard and brittle, and the color is much lighter than that of gray iron. The cementite is in solid solution in the metal.

The gray iron is high in silicon as well as graphitic carbon. It melts to a thinner liquid and is better adapted for fine castings than is white iron.

Pig-iron is melted in foundries and cast into various useful objects, such as stoves and radiators. The larger part of pig-iron is converted into steel, and a relatively small quantity into wrought-iron.

Wrought-iron is manufactured by heating pig-iron on the bed of a furnace of the reverberatory type. In a furnace of this type the fuel does not come into direct contact with the material being treated. The furnace, called a puddling furnace, is lined with hematite or magnetite, which furnishes oxygen to burn out the carbon, silicon, manganese, phosphorus, and sulphur in the pig-iron. The oxygen of the air also assists in removing the impurities. Heat is reflected and radiated from the dome of the furnace down upon the charge. The pig-iron melts, but as the impurities are burned out the melting point of the metal is raised, until a pasty mass is finally formed. The metal is worked by a puddler who, by means of an iron rod, finally gathers the iron into balls or blooms, each weighing about one hundred pounds. The pasty metal is worked under

a steam-hammer or in a mechanical squeezer in order to remove as much of the slag as possible. The product is soft and fibrous, and is called wrought-iron. It often contains only 0.1 per cent to 0.2 per cent of carbon, but there is more or less slag between the fibers of iron. Being very malleable and having great toughness and tensile strength, it is used in the manufacture of horse-shoes, anchors, etc.; also as a corrosion-resisting metal. In recent years wrought-iron has been largely displaced by low-carbon steel, which is soft. Wrought-iron resists corrosion better than soft steel, on account of the fact that the fibers are surrounded by ferrous silicate, a sort of slag, which is stable and is not affected by the atmosphere.

4 Steel and Steel Alloys

In the United States, steel is manufactured largely by two processes: (1) the acid Bessemer process and (2) the basic open-hearth process.

The Bessemer process was invented by an Englishman, H. Bessemer, in 1856. An American named Kelly patented, in 1852, a process for purifying pig-iron, which was based on the fact that when a blast of air is forced through molten pig-iron, in a suitable container, the impurities such as silicon, manganese, and carbon are oxidized, at the same time furnishing heat to keep the metal in the molten condition. Bessemer invented a converter suitable for the process, and he bought Kelly's patents. The Bessemer process is extensively employed in the United States and is applicable to pig-irons which are low in phosphorus and

sulphur, for neither of these substances is removed during the operation.

The converter, which is egg-shaped and constructed of steel, is lined with silica or siliceous rock; it is supported by and revolves on trunions. About fifteen tons of molten pig-iron are poured into the converter while it is in a horizontal position, and an air-blast is turned on, which enters the bottom of the converter through tuyeres; the converter is then turned to the vertical position. The air in passing up through the molten metal first oxidizes the silicon and manganese, which greatly increases the temperature of the charge. Before the last of the silicon has been oxidized, the carbon begins to burn. In the course of from ten to twenty minutes the silicon, manganese, and carbon are burned out. Carbon passes off largely as carbon monoxide, which burns at the mouth of the converter, accompanied by a brilliant shower of sparks, while the oxides of silicon and manganese unite with oxidized iron to form slag.

When the character of the flame at the mouth of the converter indicates that virtually all the carbon has been oxidized, the converter is turned down and the requisite amount of high-carbon alloy—*e.g.*, ferromanganese—is added to produce a steel of definite composition. The molten metal is now poured into molds and cast into ingots which are placed in a soaking-pit to be heated to a uniform temperature, and are then rolled or hammered into sheets, rails, bars, or other objects.

When the metal is poured into molds, more or less air is trapped in the mass, so there is danger of weak

places in steel rails or beams unless the gas-bubbles are removed. Deoxidizers, or "scavengers," are used for this purpose. Manganese has been employed extensively, but in recent years aluminium has been in great demand; ferrosilicon and alloys of vanadium and titanium also are used. These substances combine with the absorbed gases, the compounds formed passing into the slag.

The basic Bessemer process has been largely employed in Germany. The ores of that country contain more phosphorus than the ores of this country. The converter is lined with calcined dolomite or limestone cemented with tar. A phosphate slag is obtained, which has some value as a fertilizer.

The basic open-hearth process is employed extensively in the United States. As the furnaces are lined with a basic material, usually magnesite, pig-irons containing phosphorus may be used. The pig-iron, scrap-steel, and iron ore are heated on the hearth of a regenerative, reverberatory furnace, which may hold as much as one hundred tons. Heat is furnished by the combustion of gas or sprayed oil and is reflected and radiated upon the charge from the dome of the furnace. The temperature of the operation is greatly increased by means of the Siemens regenerative process. This means that both the air and the gaseous fuel are preheated by passing through a checkerwork of hot brick. The checkerwork of brick is so placed that the hot products of combustion escaping from the furnace may be conducted through it. While the hot products of combustion are passing through one checkerwork of brick, the air and gas are passing through another.

By frequently reversing the direction of the gases, it is possible to secure great economy in heating.

Ordinarily, a furnace holds from fifty to one hundred tons, eight to twelve hours being required for an operation. The carbon is oxidized to carbon dioxide, which escapes and gives the metal the appearance of boiling. Silicon, phosphorus, and sulphur are oxidized to acid anhydrides, which unite with the lining or flux to form a slag. When chemical tests show the desired amount of carbon to be present, the metal is poured into ladles along with suitable quantities of deoxidizers and alloys, and then run into molds. The oxygen of the rusty scrap-iron or ore is used in burning out the impurities. The steel is of high grade.

The gross tonnage of steel ingots and castings manufactured in the United States for the years 1914 and 1918 was as follows:

	1914	1918
Open-hearth process	17,170,000	34,460,000
Bessemer process	6,220,000	9,380,000
Total production	23,390,000	43,840,000

In 1925 the domestic production of steel ingots was over 44,000,000 tons, and in 1926 it was greater still.

The open-hearth process is rapidly replacing the Bessemer process.

On January 1, 1919, the domestic capacity for manufacturing steel ingots was close to 50,000,000 tons, which was estimated to be about 48 per cent of the world's facilities for producing steel.

Special steels are required for the manufacture of razors, tools, cutlery, files, needles, etc. The production

of these steels is carried out in crucibles of clay, or of clay and graphite. A very pure open-hearth steel or wrought-iron is melted with charcoal and pig-iron, or with an alloy of iron and manganese. Other metals, such as chromium, nickel, and tungsten, may be added if desired. The crucibles are covered and heated for several hours. This is essentially a melting process. Considerable steel of superior quality is now produced by electric heating. Electric-furnace refining produces very high-class steel for special purposes. As the operation is carried out at very high temperatures, the impurities are more completely removed, especially gases. Phosphorus and sulphur are almost completely eliminated, and deoxidation is more complete than that attained by other processes. This method is rapidly replacing the crucible process for producing tool steel. It is somewhat similar to the open-hearth process, but heat is generated by electricity instead of by the combustion of fuel.

In 1908 only 55 tons of electric steel were produced in the United States, but in 1923 the production had risen to nearly 516,000 tons. It may be that in the course of time the electric furnace will replace the open-hearth process, very much as the latter is replacing the Bessemer process. Since some of the modern electric furnaces hold 20 tons and can readily make ten heats in twenty-four hours, the total production would be equal to that of a 100-ton open-hearth furnace making but two heats in twenty-four hours.

Steel may contain from about 0.03 per cent up to about 2 per cent of carbon, less than 0.2 per cent of silicon, and very small amounts of phosphorus and

sulphur. Steel low in carbon is soft. Thus, steel containing 99.85 per cent of iron is manufactured by the open-hearth process; it is very soft. By an increase in the carbon content of a steel, it is made harder and less ductile, and the tenacity increases until the carbon reaches about 1.1 per cent, after which it decreases. Some rail steel contains as much as 0.8 per cent of carbon. Tool steel contains from 0.5 per cent to 1.5 per cent of carbon, but contains almost no phosphorus and silicon. It is not necessary that steel should contain less than 0.2 per cent of silicon. Manganese is an essential constituent of steel.

The hardening and tempering of steel is an operation of the highest importance. While vast improvements have been made in the methods of producing steel, no improvement has been made recently in its quality; the old blades of Toledo and Damascus have never been excelled. A steel containing from 0.5 per cent to 1.5 per cent of carbon becomes very hard and brittle when heated to a high temperature and then suddenly chilled, as when plunged into cold water or oil. This hardness and brittleness may be modified to almost any degree desired, by tempering the hardened product. This consists in gradually heating the steel to a moderately high temperature and then allowing it to cool slowly. By this treatment the steel becomes less hard and less brittle. By regulating the heat treatment and the carbon content, a steel of virtually any desired degree of hardness may be obtained.

Case-hardening of steel may be accomplished by heating a soft steel or wrought-iron in contact with

powdered carbon. The latter is slowly taken up, producing a layer of hard high-carbon steel on a body of softer metal. This process (or a similar one) is employed for hardening the surfaces of automobile gears, etc., and for the manufacture of armor-plate.

The heat-treatment of steel is made easier and better physical properties are developed when certain alloying elements, notably nickel, chromium, vanadium, or molybdenum, or a combination of two or more of these, are present. Heat-treated alloy steels are essential for all present-day automobiles, aircraft, and high-speed machinery in general. The microscope and photography have become very important in the study of the structure of metals and alloys. When the surface of iron or steel is polished and then carefully etched by means of acids, something may be learned about the characteristic crystalline formations. Photomicrographs are made, and the relation of crystalline forms to physical properties may be studied. This branch of science is called metallography.

A large number of steel alloys are manufactured for various purposes. The properties of steel may be greatly modified by addition of relatively small quantities of certain foreign elements, such as manganese, nickel, chromium, tungsten, or titanium.

Manganese increases the toughness of the steel. Nickel increases the tenacity and elasticity. Chromium increases the hardness. Tungsten, molybdenum, and cobalt prevent the loss of the temper of the steel when heated to a high temperature. Silicon forms alloys which are very resistant to acids. Vanadium and titanium are used to remove gases dissolved in the iron:

i.e., they are purifiers. Vanadium is not primarily a purifier; it aids in the production of better physical properties by heat-treatment. Aluminium, silicon, and manganese are also used as purifiers, or scavengers.

Dr. Karl Mueller of Berlin reports that he has been able to produce transparent steel. Iron is deposited electrolytically, the sheets being so thin that they are as transparent as glass, and a film of the metal is possibly not over thirty atoms thick.

5 Rust, Ink, and Blue-prints

Pure iron possesses a silvery-white luster, is strong and magnetic, but loses its magnetism rapidly. Iron, unlike steel, cannot be hardened by sudden cooling. The pure metal is of no practical value.

Chemically, iron is a moderately active metal, standing just below zinc. Thus, it displaces hydrogen readily from dilute acids. Pure iron rusts very slowly in pure water at ordinary temperatures. With water containing carbon dioxide in solution, the corrosion is greatly increased. Corrosion is the worst enemy of iron and steel. The metal may be protected from rusting by coating it with either its trioxide or tetroxide (Fe_2O_3 or Fe_3O_4), the coated metal being known as Russian iron.

Iron forms two series of compounds—ferrous and ferric. In the former the metal has a valence of two, while in the latter its valence is three.

Ferrous sulphate ($FeSO_4.7H_2O$) is often called green vitriol, or copperas. This salt may be obtained by dissolving iron in dilute sulphuric acid, with the

exclusion of air or oxygen, and by concentrating the solution until crystallization occurs. The salt is used in the purification of water, the dyeing industry, as a reagent for killing weeds, and in the manufacture of black inks.

Inks are commonly produced by adding ferrous sulphate to an extract of nut-galls, ferrous tannate (colorless) being formed, which is oxidized, when exposed to the air, to ferric tannate (black). A dye is added to the ink to make it visible from the first.

Ink stains and rusts may be removed by soaking the material in ammonium oxalate solution.

Ferric salts of certain organic acids can be reduced to ferrous salts by exposure to light. The production of blue-prints is based upon this reaction. Thus, ferric oxalate yields ferrous oxalate:

$$\underset{\text{Ferric oxalate}}{Fe_2(C_2O_4)_3} = \underset{\text{Ferrous oxalate}}{2FeC_2O_4} + 2CO_2$$

Paper can be prepared by treating it with a solution of ferric oxalate and then drying. When an ink drawing or a negative is placed over a paper thus prepared, sunlight will reduce only the exposed ferric oxalate to ferrous oxalate. When the paper is now dipped into a solution of potassium ferricyanide (developer), blue ferrous ferricyanide (Turnbull's blue) is formed where the sheet has been exposed to the light. Where the paper has not been exposed to the light, no change occurs, and the ferric salt can be washed away. There is thus left a white pattern or picture on a blue background; that is, a blue-print is obtained.

Commercially, blue-print paper is coated with a

mixture of ammonium ferric citrate and potassium ferricyanide (developer). After exposure to light, the paper is dipped into water and the blue color quickly disappears. The sheet is now washed, giving a permanent print.

When a solution of a ferric salt is mixed with a solution of potassium ferrocyanide, a magnificent blue precipitate of complex composition is obtained, being known as Prussian blue. It is used extensively as a pigment and for the preparation of blueing for the laundry.

CHAPTER XIX

THE A-B-C OF POTTERY AND GLASS

A potter near his modest cot
Was shaping many an urn and pot;
He took the clay for the earthen things
From beggars' feet and heads of kings.
—OMAR KHAYYAM.

1 ANCIENT POTTERY AND GLASS

THE word pottery in its widest meaning includes all objects fashioned from clay and then hardened by means of fire or heat. Nowadays, ceramics (Greek: earthenware) is the term generally employed for the study of the art of pottery. The ceramic industry therefore includes not only the production of pottery and porcelain, but brick, tile, etc. The arts of producing pottery, brick, and glass were practised by the primitive races of mankind. Pottery and glass are perhaps the earliest products of the chemical industry of man. Clay, the fundamental material required in the production of pottery, is formed by the weathering of feldspars or feldspathic rocks, such as granite. (See Chapter XVII.) It is therefore widely distributed over the face of the earth, and wherever deposits of clay were found, whether on the surface of the earth or in river-beds, primitive men became potters just as naturally as they became hunters, herdsmen, and builders.

The earliest pottery, which was produced by prehistoric man, was very rude. The clay was spread out on stones or slabs and kneaded by simple means to make it more pliable. Finally, it was fashioned by hand into the desired objects, and then dried in the sun. Pottery thus produced was soft and porous, as is the nest of the mud-wasp, but was suitable for containing dried grain, etc. In the course of many centuries fire was employed instead of the sun, which yielded pottery of various hues—buff, drab, brown, or red, due to the expulsion of water.

While the introduction of the potter's wheel is very ancient, it is relatively modern, having been invented many centuries after pottery was first made. According to a legend, the potter's wheel was brought down from heaven by one of the gods to a favored race. In a painting in a tomb at Thebes of about 1800 B.C. a potter is shown molding a vessel on a wheel, which consisted of a heavy disk pivoted on a central point, to be worked by hand as the workman squatted on the ground. This simple wheel is still in use in India, in China, and in Japan.

Many wonderful clay tablets covered with interesting inscriptions have been unearthed in Mesopotamia.

Brick, tile, and glass also were produced at a very early date. More than sixty centuries ago great cities in Mesopotamia were built of brick and their streets paved with asphalt.

Babylon, the capital of the Asiatic world, was a wonderful city. It covered an area of about two hundred square miles, and Herodotus says it was surrounded by a brick wall which was about 335 English

feet in height and 85 feet thick. Brick was also the material selected for building the tower of Babel, for there was no stone on the plain of Shinar. In the eleventh chapter of Genesis, the third verse, we read: "Let us make brick, and burn them thoroughly. And they had brick for stone, and slime had they for morter." The mortar employed was bitumen, which was brought down from Hit, about one hundred and forty miles higher up the river.

The Egyptians produced glass thousands of years ago. Egyptian glass perhaps was not perfectly transparent. The Phœnicians manufactured and exported glass. Glass is also mentioned in the Bible.

Geoffrey Martin says:

> In 1700 B.C. we find beautiful blue-and-white glass vases. We know that Sesotis, in the year 1643 B.C., had cast a monument of green glass. In later times the seat of the old glass industry was Alexandria and the towns of Tyre and Sidon. Here, centuries before our era, gleamed and glowed great glass furnaces, while glass merchants grew wealthy and built themselves houses and palaces.

From the Orient, knowledge concerning the arts of producing pottery and glass passed to Greece and Rome, and subsequently spread to all parts of Europe.

2 The Manufacture of Pottery; the Potter's Wheel

It may be of interest to learn more concerning the manufacture of pottery. The purest variety of clay is

kaolin, which is a salt,—aluminium silicate—, the formula for which may be written:

$$Al_2O_3.2SiO_2.2H_2O$$

The melting-point of pure clay is approximately that of platinum, 1755° C., or nearly 2400° F.

Kaolins are divided into two groups, the primary and the secondary kaolins. The primary clays have not been transported by water from the place where they were formed, while the secondary clays have been washed away from their original beds and deposited elsewhere. The latter variety has a much finer grain, is more plastic, though not so pure as the former.

Another variety of clay is called ball clay. The ball clays are secondary clays, are very plastic and strong, and when fired have a creamish or buff color. They impart strength to pottery. The purest form of clay is free from iron, so it fires to a pure white color, being used in the production of china and porcelain. Clay has the property of undergoing progressive hydration in contact with water. Being very finely divided, it settles slowly when suspended in water, and in the solid state it is very plastic. When the clay is heated, it loses water of hydration, forming a hard stone-like mass which has lost its plasticity. These properties of clay are the basis of the ceramic industry.

In preparation for molding, the finely divided materials are mixed thoroughly with water, the suspension being known as slip. This is stored in large containers and pumped to the filter presses as needed, the object of the filtering operation being to squeeze out the

water, leaving the clay in the form of cakes. Finally, the cakes are kneaded and worked up in a machine, the process being called pugging. The material is now ready for molding and shaping. This may be accomplished by three operations—jiggering, pressing, and casting. Jiggering is done by means of the mechanically driven potter's wheel. As previously stated, the potter's wheel is very old, its use being mentioned in the Old Testament. For instance, in the eighteenth chapter of Jeremiah, the third verse: "Then I went down to the potter's house, and, behold, he wrought a work on the wheels." The simple form of potter's wheel already mentioned was the only one known until about the Christian era, when a wheel was invented which could be operated with the foot, leaving both hands free. In the seventeenth century the wheel was spun by a cord working over a pulley, and about the middle of the nineteenth century a steam-driven wheel was introduced. The mechanically driven wheel carries a plaster mold of the desired shape. The lower side of a piece of pottery is formed by revolving the mold, and the upper side by means of a steel profile, which can be raised and lowered.

A large dish may be made by throwing the clay upon a plaster mold, which shapes the inside. The outside is then finished by hand. This process is known as pressing.

All fabricated ware must be carefully dried in fire-clay receptacles, called saggers. These are put into kilns and stacked up in tall columns. The temperature of the kiln, which may be heated by oil, usually varies

from about 1270° to 1400° C., depending upon the object of the firing. Not only does the very high temperature of the kiln expel water, but other changes occur. The product of the first firing is porous and is called bisque. To render it impervious to liquids and gases, the porous ware is covered with a paste of finely divided feldspar and silica (or lead oxide or other suitable material) and fired a second time at a temperature high enough to melt the feldspar, which fills the pores. The articles may be decorated by means of suitable materials, such as the oxides of certain metals, followed by a third firing, which brings about the union and fusion of the oxides with the glaze. The colors are largely silicates. Cobalt oxide gives a blue glaze, chromium oxide yields green, etc.

The Greeks produced pottery of a very high order from the standpoint of form and decoration. Many fine specimens of black-figured and red-figured vases have been discovered. The nature and composition of the superb black glaze on Greek pottery has been a subject of discussion for many years. W. Foster, in 1910, analyzed the black glaze on a fragment of a vase from the American excavations at the Heræum, and obtained evidence that the color is due to ferrous iron (probably as ferrous silicate). S. W. Tonks has confirmed this conclusion by synthesis. He says:

Not to be tedious by enumerating the numbers of trials I made before getting the desired result, I may say that it proved eventually that a combination of eight parts of nitrate of soda to one of clay, fritted together, and then mixed in the proportions of two parts of frit to one of

ferrous oxide, produced a glaze identical with that on Greek vases.

Tonks also succeeded in reproducing the glaze by the use of magnetic oxide of iron in place of pure ferrous oxide. This compound is, of course, found in nature, and contains iron in both the ferrous and the ferric condition, one chemical name for it being ferroso-ferric oxide. Franchet of France, in 1911, reproduced the black luster "in an oxidizing fire at 850° by fluxing 55 parts of quartz sand with 45 parts of sodium carbonate and grinding the frit with an equal weight of magnetite." This method is similar to the one employed by Tonks.

3 China, Porcelain, and Stoneware

China and porcelain are manufactured from pure clay, which must contain no iron. The clay is mixed with a small amount of feldspar, which is more fusible, and is then fashioned into various articles which are fired to expel water. Hard porcelain has a body consisting of kaolin, quartz, and feldspar. It softens only at the very highest temperatures, is harder than glass, and attacked by only a few chemical reagents.

The marvelous white translucent porcelain produced by the Chinese was one of the wonders of the medieval world. In "Kéramos," Longfellow wrote:

> And yonder by Nankin, behold!
> The Tower of Porcelain, strange and old,
> Uplifting to the astonished skies
> Its ninefold painted balconies,

With balustrades of twining leaves,
And roofs of tile, beneath whose eaves
Hang porcelain bells that all the time
Ring with a soft, melodious chime.

The porcelain of China found its way to Europe during the fifteenth and sixteenth centuries, and perhaps was first imitated at Florence by the potters or alchemists about 1575. The Chinese are the greatest race of potters in the history of the world.

The establishment in Europe of the manufacture of true porcelains belongs to Böttger of Germany, who died in 1719. The story of his life reads like a romance, as does that of the subsequent development of the porcelain industry in the German Empire. At one time Böttger and his workmen were kept virtually as state prisoners in a fortress at Meissen in order that their secrets might not become generally known. Great factories were founded in various parts of Europe, the one at Meissen being very famous. The porcelain produced there has been commonly known as Dresden porcelain.

Stoneware is a non-porous body, being made from difficultly fusible material, and burned at a high temperature. The finest quality is the famous Wedgwood ware, which may be had in various colors, and is usually not glazed. Porous ware is produced extensively in all countries, the finest grade being called faïence. Majolica ware has a colored porous body, covered with transparent glaze. Bricks also are porous ware. They are produced from common clay, which contains impurities such as iron oxide and lime. Fire-

bricks are manufactured from fire-clays, which contain silica or free quartz, and are very resistent to heat. Fire-clays are usually found underlying coal-beds.

4 The Manufacture of Glass; Varieties of Glass

Nobody knows when glass was first produced, but the story of glass-making is a romantic one. According to Pliny, Phœnician sailors landed on the shores of the Belus River in Syria, and in order to cook their food they rested their kettles on lumps of natron—ballast taken from their ship. The fire brought about the union of sea-sand and natron (a sodium salt), a glass being produced which was found in the dying embers. While this is a fanciful story, we do know that Egyptians produced glass at a very early date; for glass vessels have been discovered in Egyptian tombs. By cutting and coloring glass the Egyptians imitated precious stones. The Greek writer Aristophanes refers to a glass lens which was employed as a burning-lens; but the Greeks did not contribute a great deal in the way of glass-making. The Romans, on the other hand, achieved great success in the production of glass, particularly under the Cæsars, and their legions carried glass and methods for producing it to various parts of the world.

Glass-making in Venice perhaps dates from the seventh century, but there is no record of the Venetian industry, as such, earlier than the eleventh century. The interior of St. Mark's was covered with glass mosaic in the eleventh and twelfth centuries. In the latter part of the thirteenth century the Venetian glass

industry was carried on almost wholly on the island of Murano, where the glass-houses extended a mile or so and employed eight thousand workers. Venice became a wonderful center of art and wealth, and the fifteenth and sixteenth centuries witnessed the greatest development of art and industry in glass since the time of the Roman Empire. Beautiful glass was also produced in Germany in the fifteenth and sixteenth centuries, but in the eighteenth century the ascendency passed to Bohemia. The Bohemians produced fine crystal glass, and invented the art of engraving on it. Henry Schwanhard invented the engraving of glass with hydrofluoric acid.

Window-glass was not used much in ancient times. A piece of Roman window-glass was found in England, and it is known that window-glass was made for churches as early as the fourth or fifth century. Some of the glass produced for Gothic cathedrals was most lovely: for instance, the "Window of Paradise" was the masterpiece of Rheims; it was a product of the thirteenth century, being an exquisite example of rose-windows.

Most of the specimens of ancient glass are colored. Perfectly transparent colorless glass was unknown to the early makers. Optical glasses were produced at an early date. In 1303, Gui de Chauliac, a French surgeon, recommended the use of spectacles. Optical glass is of the highest importance, but is difficult to make.

Let us now briefly inquire into the chemistry of glass and the methods employed in producing it. Glasses belong to the class of salts called silicates. Silica, or quartz sand, is therefore required in the pro-

duction of glass. In case we fuse silica with sodium carbonate, sodium silicate is formed, which is soluble in water, and is known as soluble glass, or water-glass. The chemical change is represented by the following equation:

SiO_2	+	Na_2CO_3	=	Na_2SiO_3	+	CO_2
Sand		Soda-ash		Sodium silicate, or soluble glass		Carbon dioxide

Sodium silicate is soluble in water, the solution having an alkaline reaction. It is used as a filler for cheap soaps, for fireproofing and waterproofing textiles and timbers, and for preserving eggs. For the preservation of eggs, a solution may be prepared by mixing one volume of the ordinary water-glass of commerce with nine volumes of pure water. When strictly fresh eggs are immersed in a solution of such concentration, they may be preserved for long periods.

Ordinary glasses, or glasses in the proper sense of the term, contain two or more silicates, are hard, brittle, and transparent, and are virtually insoluble in water and in acids, with the exception of hydrofluoric acid. They may be divided into three general classes:

(1) *Window- or Bottle-glass.* This most common variety of glass is produced by fusing a mixture of sodium carbonate, quartz sand, and limestone, or calcium carbonate. It is a silicate of sodium and calcium containing an excess of silica, and its approximate composition may be represented by the following formula:

$$Na_2O.CaO.6SiO_2$$

(2) *Hard or Bohemian Glass.* This is a potash glass, and may be produced by substituting potassium carbonate for sodium carbonate. This variety of glass is difficult to fuse, being used extensively in the manufacture of chemical apparatus. In the production of Jena and "non-sol" glass, boric anhydride (B_2O_3) and zinc oxide are used in addition to silica. Pyrex glass is very resistant to heat and shock. It is a sodium-aluminium borosilicate.

(3) *Flint Glass.* In the production of this variety of glass, lead oxide is substituted for calcium oxide, or lime, which is supplied by limestone. The potash-lead glass has a high specific gravity and great power for refracting light. It has a high luster, and is used in the manufacture of cut glass, the engraving being done by means of a sand-blast. Strass, a variety of glass, is richer in lead than flint glass, and on account of its fine luster it finds use in the making of artificial gems.

Lead-soda glass is employed in the manufacture of electric-light bulbs.

Glass is produced by heating the raw materials to fusion in a furnace. The materials are contained in carefully made clay pots, which must be capable of sustaining a temperature of 2500° to 3000° F. for nearly twenty-four hours. Pot-making for glass is done by hand and foot. The clay is kneaded by the bare feet of the workmen, and the pots are built up by hand, layer by layer, until all air-holes and cracks have been eliminated.

Glass is blown and fashioned into many different objects. For instance, in the production of window-panes the workman takes a mass of soft glass on the

end of a long iron blowpipe and blows it into a large bubble. It is then drawn out into a cylinder, the ends are cut off, and the cylinder split lengthwise, then spread upon a plate. Plate-glass is rolled by means of hot cylinders. The thick, dazzling glass is poured upon water-cooled metal tables, and rolled out by heavy steel rollers very much as a cook rolls out dough. The drawing of window-glass cylinders is now done by machinery. When the cylinders have reached a length of about forty feet, they are lowered, flattened out, and cut into panes. Bottles and electric-light bulbs are also blown by great machines, which are almost lifelike in their performance, one machine doing the work of a very large number of men. Glass-blowing machines are a great boon, for tuberculosis is the scourge of the glass-blower's trade. It is reported that the mortality in this branch of labor has been materially reduced since the introduction of glass-blowing machines. The first fully automatic bottle-machine was invented in 1903 by J. Owens, an American.

Plate-glass is now manufactured by a revolutionary method. The glass is cast in a continuous unbroken sheet. Molten glass flows in a stream onto a revolving drum, and passes under a roller which forms it into a sheet. The sheet then passes to the lehr, or annealing oven. A slowly moving sheet of glass hundreds of feet long is cooled from 1400° F. to a temperature cold enough to handle. At the end of the lehr the long sheet of glass is cut into sections and then ground and polished. Glass-grinding is also a continuous process.

Glass beads are made from glass tubing. The tubes are cut into short segments, which are then filled with

a paste of ashes and sand. These are put into cylinders containing sand, which are heated and rotated. The soft beads become globular and the sand prevents their adhering, while the paste preserves the bore. Venetian beads are noted for their beauty.

Optical glass is of the highest importance and must be made with the greatest care. Before the World War the United States imported from Germany nearly all the glass used in the manufacture of optical instruments. When the foreign supply of optical glass was shut off, our scientists and manufacturers took up the problem of producing this variety of glass, and before the end of the war our supply was in excess of the demand.

5 How Glasses Are Colored; Iridescent Glass

How are glasses colored? This is accomplished by adding small quantities of certain foreign substances. An exceedingly small quantity of cobalt oxide colors glass blue; chromium oxide, green; manganese dioxide, violet; silver or uranium oxide, yellow or amber; selenium (as a selenate with a reducing agent), orange; metallic gold or copper, cuprous oxide or selenium oxide, red. Ferrous iron colors glass green (bottle-glass), while ferric iron colors it yellow or brown. The green color of common glass may be changed to the less objectionable yellowish tint by the addition of manganese dioxide. During the recent war the supply of pyrolusite from Brazil was cut off, owing to the lack of ships; therefore selenium was temporarily substituted for manganese as a decolorizer of

glass. The color of glass is often due to the presence of colored silicates. The ruby-red color of the glasses made by the addition of gold or copper is due to the metal in the form of very fine particles.

Iridescent glass is also of interest. Pieces or objects discovered in excavating are often exquisitely beautiful. Sometimes they resemble the richest and most varied wings of butterflies or remind one of the feathers of the peacock, almost every known shade of color being presented; in other cases, they present the appearance of metals. One piece was found in the palace of the Cæsars which was similar to burnished silver but with a tint like pearl. Iridescent glass is the result of change or decay, due to the action of ammonia. It is not uncommon to observe rainbow-like films on the glass windows of stables, where ammonia is formed as the result of the transformation which occurs in organic matter.

CHAPTER XX

BUBBLES, DROPS, GRAINS, AND FILMS: COLLOID CHEMISTRY

My hair is gray, but not with years,
Nor grew it white
In a single night,
As men's have grown from sudden fears.
—LORD BYRON.

1 MATTER IN THE COLLOIDAL STATE

THOMAS GRAHAM, in 1861, divided substances into two classes—crystalloids and colloids. Under the head of crystalloids he placed substances which may be obtained in crystalline form, such as salt, sugar, and saltpeter. Colloids included substances which do not crystallize, such as gums, starch, silicic acid, and glue. "Colloid" is derived from a Greek word meaning glue-like, glue, according to Graham, being a typical colloid.

Graham observed that a colloidal solution, like a solution of salt or sugar, passed through an ordinary filter, leaving no solid; but when a fine parchment paper or an animal membrane was substituted for the filter paper the colloid was retained by the filter, while the crystalloid passed through. Graham invented an apparatus called a dialyzer, which he employed to separate colloids from crystalloids (Figure 24).

The parchment paper or membrane (C) is stretched

on a tambourine-like frame (A) and the colloidal solution is poured into the dialyzer, which is partially immersed in a larger vessel (B) containing pure water. When a solution containing common salt and glue is poured into the dialyzer, the salt passes through the membrane into the pure water, leaving the glue above the membrane. Again, the sugar contained in tea will pass through the membrane of a dialyzer, while the brown coloring matter of tea will not, for it is a colloid. Colloidal solutions are therefore characterized by the fact that they do not dialyze. If we wish to find out

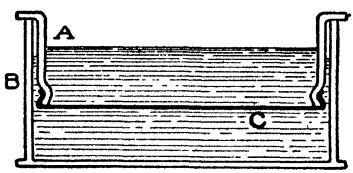


FIGURE 24
Diagram Illustrating Dialysis

whether we have a true or a colloidal solution we put the liquid into a dialyzer and test to see if the dissolved substance will pass into the pure water.

Why do solutions of crystalline substances pass through parchment paper and animal membranes, while colloids do not? The reasons are not fully known. One thing is definitely known, however; particles, such as salt and sugar, in true solution are smaller than particles of starch and glue, which are in colloidal solution. It has been suggested, therefore, that the smaller particles pass through the membrane of the dialyzer while the larger ones are held back, very much as little

fish slip through a net which will not allow larger ones to escape.

Experiments have shown that no very sharp line can be drawn between colloids and crystalloids. It is probable that under suitable conditions all substances can appear as colloids; so it is now customary to speak of a colloidal state instead of a colloidal substance. Common salt, for example, crystallizes in cubes, but it is possible to disperse salt in petroleum ether so that it exhibits the colloidal state. A colloidal substance may therefore be crystalline. According to W. D. Bancroft, "we call any phase (gas, liquid, or solid) colloidal when it is sufficiently finely divided or dispersed." Colloid chemistry is the chemistry of bubbles, drops, grains, filaments, and films, because, in each of these cases, at least one dimension of the phase is very small.

Colloid chemistry is, therefore, primarily a matter of size of particles; it is the chemistry of very small particles.

Since colloid chemistry is the chemistry of bubbles, drops, grains, and films, it is closely connected with everyday life. A knowledge of this branch of chemistry is necessary in order to understand the following as well as innumerable other things: Milk, cream, butter, and cheese; fog and mist; smoke and fine dust; froth and foam; cooking, washing, and dyeing; soap, greases, and oils; photography; living matter; blood serum; the sap of plants; the principal articles of food; rubber and gums; clay, ceramics, and glass-making; asphalt and roads.

What do we know about sizes of particles? We have

seen (in Chapter III) that molecules are exceedingly small, that they belong to the ultramicroscopic world. When a pinch of salt or of sugar is dissolved in a glass of pure water, the solution is perfectly clear and the dissolved matter does not separate out or settle. Moreover, such a solution readily passes through filters and remains dark when a beam of light is passed through it. It is probable that in a true solution the dissolved matter is so finely divided or so thoroughly scattered that the particles are of molecular size. Contrast with the salt or the sugar solution the behavior of muddy water. When a portion of the latter is allowed to stand, the mud gradually settles, leaving a clear liquid above. Muddy water therefore contains particles in true suspension, which settle sooner or later because they are relatively large and are consequently influenced by gravity.

Now, we may assume a state of subdivision which is intermediate between true solution, as in salt water, and ordinary suspension, as in muddy water. Matter in this intermediate state of subdivision is said to be in colloidal solution (or suspension). A colloidal solution passes through an ordinary filter, as previously stated; but when a powerful beam of light in a darkened room is passed through it the presence of the highly scattered colloidal particles is revealed, the visibility being due to the scattering effect on light of the minute particles, which are perhaps aggregates of molecules. This is known as the Tyndall phenomenon. The particles in the colloidal state scatter or diffract the light which falls on them, just as the much larger dust-particles reflect the sunlight, as is so often ob-

served when a beam of light passes through a darkened room.

The diameters of particles vary within wide limits, and may be expressed in microns or in millimicrons,* or submicrons. Particles having a diameter greater than one micron are in coarse suspension and may be filtered out; while particles dispersed or scattered in a liquid and having diameters less than twenty millimicrons do not settle at all.

The best microscope does not reveal particles having a diameter less than about 1/2000 millimeter (0.5 μ). Colloidal particles are still smaller. In 1903, Siedentopf and Zsigmondy invented an instrument known as the ultramicroscope which reveals particles having a diameter of 1/100,000 millimeter (10 μμ). This instrument involves the same principle as the Tyndall phenomenon. In the ultramicroscope a converging beam of intense light in a darkened room is sent horizontally through the liquid under examination and the place where the light is brought to a focus is viewed from above, through an ordinary microscope. In the ultramicroscope, therefore, ultra-illumination is employed.

According to H. Freundlich, with the aid of the ultramicroscope it has been possible to demonstrate in many colloidal solutions particles having a diameter of from ten to five hundred millimicrons. He also states that the diameters of colloidal particles range from one to five hundred millimicrons. In the case of

*The symbol μ is used for a micron and μμ for a millimicron. The micron equals 0.001 millimeter; the millimicron, 0.000001 millimeter.

true solutions it may be assumed in general that the particles have diameters less than one millimicron, which means that the particles are of molecular dimensions.

The sizes of a number of particles are approximately as follows (Figure 25):

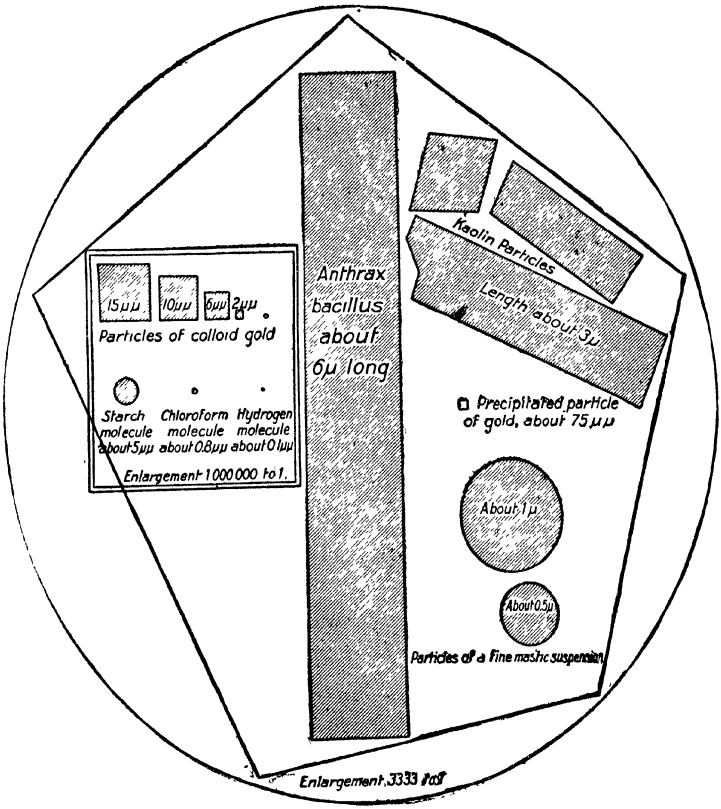
	Diameter	
Hydrogen molecule	0.1	μμ
Water-vapor molecule	0.1	"
Common-salt molecule	0.26	"
Sugar molecule	0.7	"
Particles of colloid gold	2-15	"
Particles of precipitated gold	75	"
Starch molecule	5	"
Red-blood corpuscle	7.5	μ

The length of the anthrax bacillus is about six microns. The sizes of the blood corpuscles and the anthrax bacillus are very large as compared with those of molecules and colloidal particles.

2 Preparation and Properties of Colloids; Emulsions

It is an interesting fact that Michael Faraday prepared violet and purple colloidal solutions of gold in 1857 by treating very dilute solutions of gold chloride with a solution of phosphorus in ether. Some of Faraday's specimens are preserved at the Royal Institution, in London, one or two specimens still retaining a tinge of color, the rest having coagulated. Faraday's gold is an illustration of the preparation of a colloidal solution by chemical means.

Colloidal gold of different colors, such as red, blue,



Courtesy, P. Blakiston's Son & Co., Philadelphia

FIGURE 25

Comparison of Particles of Different Size
(From "Handbook of Colloid Chemistry" by Ostwald-Fischer)

1 Micron (μ)	= 0 001	millimeter
1 Millimicron (μμ)	= 0 000001	millimeter
1 Inch	= 25.4	millimeters

and violet, may be prepared, the color depending more or less upon the size of the particles.

Bredig's arc method is often used to prepare colloidal

solutions of metals. When an electric arc is formed under water between two metal wires such as those of gold, the metal suffers disintegration and assumes the colloidal state. The disintegration occurs chiefly at the cathode, and a current of five to ten amperes at a voltage of 30 to 110 may be employed. A trace of alkali in the water improves the results.

Peptization is the disintegration of a substance or body into colloidal particles by the action of an added agent such as water. It is a peptizing agent, for instance, in dissolving gelatin. As a matter of fact, the gelatin is in colloidal solution. In a similar manner colloidal solutions of glue, starch, and egg albumin may be prepared. Peptization is roughly analogous to digestion, in which pepsin plays a rôle. The cook often adds pectin to fruit-juice to bring about coagulation, or the formation of jelly. This is known as pectization, which is the converse of peptization.

Everybody knows more or less about emulsions, such as Scott's Emulsion of Cod Liver Oil. An emulsion consists of droplets of one liquid suspended in another. Milk is a common illustration of an emulsion, for it consists of droplets of butter-fat (liquid) suspended in water, which constitutes the bulk of the fluid. It is an old saying that water and oil do not mix. If, however, we agitate vigorously a large body of water with a few drops of kerosene, an emulsion is formed. Such mixtures are temporary, however, the emulsions quickly separating into their components. In the case of milk, for example, cream rises. In order to preserve an emulsion, it is necessary to have present a third substance—an emulsifying agent. Mayonnaise dress-

ing, for instance, is an emulsion of olive-oil and vinegar, the yolk of egg being added as an emulsifying agent.

The characteristics or properties of colloids are rather interesting. In the first place, the freezing-points and boiling-points of colloidal solutions differ but little, if any, from those of the dispersing means—say, water. The physical properties of a true solution, such as salt in water, are greatly influenced by the dissolved matter. Moreover, colloids have but little tendency to pass through parchment paper or animal membranes. It is also true that colloidal solutions exhibit the Tyndall phenomenon, while true solutions do not. This optical test is one of the best ways to distinguish between true solutions and colloidal solutions.

Now, why do colloidal particles remain in suspension? In other words, why do they not settle as they do in a true suspension—*e.g.*, as in muddy water? There are at least three reasons, which are as follows:

(1) Colloidal particles carry electrical charges: for instance, particles of colloidal ferric hydroxide are positively charged. Particles carrying the same kind of charge repel one another, thus preventing the matter from settling. If this theory be true, the charged particles should move or migrate when an electric current is passed into a colloidal solution. There are plenty of illustrations of this kind, the phenomenon being known as cataphoresis (Greek: down + bearing). This process may be illustrated by means of milk, in which the fat-globules are negatively charged, and should therefore migrate or travel to the positive electrode, or anode, under the influence of the electric current. The milk is

poured into a U-tube, and a layer of water is carefully introduced above the milk in both limbs of the tube. Platinum electrodes are now immersed in the water and a potential difference of about one hundred volts set up between the electrodes. In the course of time it may be observed that the fat globules are moving toward the anode and away from the cathode.

(2) Colloidal solutions exhibit the Brownian movement, while true solutions do not. The particles of the colloid are suspended in the dispersion means (ordinarily water), and are subjected to lively bombardment by the molecules of the liquid, and are thus kept in a state of perpetual motion. When viewed through the ultramicroscope, this phenomenon is most interesting. The particles are not actually visible, but one sees the light diffracted by them. This phenomenon may be compared to motes dancing in a beam of sunlight.

(3) Settling may be prevented by the presence of protecting films. When Faraday prepared colloidal gold in 1857 he observed that a little jelly kept his preparations from coagulating. The action of gelatin preventing coagulation is of much interest and importance. This fact can be well illustrated by the following experiment: Prepare a colloidal solution of gelatin by adding one gram of the substance to one hundred cubic centimeters of warm water. Cool the solution, add a few drops of concentrated hydrochloric acid, shake, and then add an excess of a solution of silver nitrate. Shake the tube and allow it to stand. The resulting substance is known as colloidal silver chloride. The chloride remains in suspension. But when a solution of silver nitrate is treated with hydrochloric acid, gelatin being absent, a heavy, curdy precipitate of silver chloride is formed at once.

Colloidal silver bromide and iodide may also be prepared. The emulsions of the halides of silver are of great importance in photography.

It is held that the liquid emulsoid particles cover the solid suspensoid particles, thus preventing their coming together to form larger aggregates. Such organic colloids as gelatin and the proteins increase the stability of colloidal metals; hence they are termed protective colloids.

In general, colloids may be coagulated by adding an electrolyte: *e.g.*, hydrochloric acid or a solution of barium chloride will coagulate colloidal arsenic trisulphide. The electric charges (negative) of the sulphide are neutralized by the positive charges of the cations. Again, when a colloidal solution of arsenic trisulphide is mixed with one of ferric hydroxide (positive), precipitation occurs, for the oppositely charged particles neutralize one another. The casein of milk may be coagulated by adding acetic acid.

3 Sols and Gels: "Solidified Alcohol"

The terms sol and gel are frequently used in the study of colloids. A colloidal solution is called a sol when the dispersed substance is sufficiently finely divided and under such conditions that coalescence and agglomeration are prevented. In case water is the dispersing liquid, the colloidal solution is known as a hydrosol. Colloidal gold is a good illustration of a hydrosol. On the other hand, when the colloidal particles agglomerate and precipitate, a gel is obtained. In case water is the dispersing liquid, the precipitate

is called a hydrogel. The term gel includes jelly, such as fruit jelly. Sometimes the cook has difficulty in getting the jelly properly to form, as was stated before, but coalescence and agglomeration can be induced by the addition of pectin, a preparation which may be purchased at any grocery. Pectin is present in ripe fruits, and the jellying of fruit-juices depends upon it. If the fruit is cooked too much, pectin is converted into other substances and the formation of jelly is prevented.

Solidified alcohol, which is so common nowadays, is essentially an alcoholic soap jelly.

A specimen of gel may be readily prepared by pouring ten cubic centimeters of a saturated solution of calcium acetate into ninety cubic centimeters of 95 per cent alcohol. The two liquids should be contained in small beakers, and poured quickly back and forth until the gel forms. Pieces of the gel may be ignited. This preparation was patented by C. Baskerville.

Silica gel is of great commercial significance, being produced by the Silica Gel Corporation of Baltimore. It is known as Patrick's silica gel. This gel is formed when sodium silicate of proper concentration (water-glass) is treated with hydrochloric acid. The gel is broken into small pieces, washed, and dried. Silica gel is a hydrated form of silica (SiO_2). It is a hard, glass-like substance, and has great power for taking up or adsorbing water vapor and certain gases and liquids. Many gels are largely water. They seem to have a regular structure of some kind, and possess a certain amount of rigidity and elasticity.

4 Adsorption and Gas-Masks

In general, all solids have a tendency to condense upon their surfaces any gases or vapors with which they come into contact. This holding of substances on surfaces is called adsorption. Charcoal, for example, is a very porous substance and is therefore capable of adsorbing large volumes of ammonia and other gases. It is well known to all that cocoanut charcoal was employed in gas-masks during the war to adsorb poisonous gases. Silica gel is full of exceedingly fine capillaries and in consequence is able to adsorb enormous quantities of certain gases and liquids. It is a powerful drying agent, removes obnoxious sulphur compounds from crude petroleum, gasoline from casing-head gas, etc. Gas adsorption is now of great industrial importance. Animal charcoal is utilized extensively in the purification of sugar; it adsorbs the brown coloring matter.

A given mass of finely divided substance has a much larger surface than has the same mass in compact form. To illustrate, a cube of gold 1 centimeter on the edge has a surface of 6 square centimeters and weighs 19.32 grams. If the cube could be divided into cubes 10 μμ on the edge (approximately the diameter of colloidal particles of bright-red gold), the total surface would become 6,000,000 square centimeters and the total number of particles 10^{18}. If a cubic centimeter of gold could be divided into cubes having a length of edge of 0.001 μμ (4/100,000,000,000 inch), there would be 1 nonillion (1 followed by 30 ciphers) cubes, having

a total surface of 1482.6 acres, or 2⅓ square miles! These dimensions of the tiny cubes are still a thousand times larger than the theoretical size of the electron. Charcoal, silica gel, and matter in the colloidal form have great adsorptive power, for they all possess very large surfaces in proportion to mass. Solids not only adsorb gases and vapors but they adsorb liquids and other solids. Moreover, liquids may adsorb vapors, liquids, and solids. In fact, adsorption is a very broad term, and it plays a great rôle. Bacteria, for example, are removed from water by means of sand filters; they are small enough to pass between the particles of sand, but are adsorbed by, or held upon the surface of, the sand.

Salts used as fertilizers are adsorbed by the soil and not washed away by the rain. Adsorption also plays an important part in tanning. Skins are colloidal in nature, and they adsorb water to form gels in the processes preliminary to tanning. When the hides are tanned, the positively charged colloidal particles of the hide and the negatively charged particles of the colloid, tannin, mutually attract and coagulate each other, and chemical changes complete the formation of leather.

5 Applications of Colloid Chemistry

There are almost innumerable applications of colloid chemistry, only a few of which will be mentioned. One interesting application is to the precipitation of dust and smoke. F. G. Cottrell, an American chemist, perfected an industrial method which is called the Cottrell process. It is employed, for instance, in smelt-

ing-works, in cement-mills, and in sulphuric acid plants. The colloidal particles are precipitated by means of electrical forces. The dust or smoke is made to pass by a charged point suspended in the center of a chimney or dust-chamber from the end of a high-voltage wire. The particles take on a charge similar to that of the point, whereupon they are attracted to a plate (or to the walls of the chimney or chamber) having the opposite charge, where they are precipitated. The plates or walls of the dust-collector are grounded. It was suggested by Sir Oliver Lodge that a ship might utilize the same principle in clearing its path of fog.

W. D. Bancroft and L. F. Warren scattered electrified sand by an airplane and succeeded in condensing moisture, to fog and clouds, and even producing a slight localized "rain."

As a result of the violent volcanic eruption of Krakatoa, August 26-27, 1883, fine particles were carried around the world and formed a layer from five to fifteen miles above the earth's surface. "After sunset, and by virtue of the diffusion of red light by this layer of particles, the whole western sky, even to the zenith, glared with a lurid red as though lighted up from some great and distant fire."

According to W. D. Bancroft, many new-born babies have very blue eyes probably because in their eyes the suspended particles in front of the iris are exceedingly fine. There is no blue pigment in blue eyes, the blue of the eye is analogous to the blue of the sky or the blue of skimmed milk. With the exception of people who have very black eyes, the pigment

in front of the iris does not develop at birth, but forms later just as do the teeth. Consequently many babies have blue eyes, which change to hazel, brown, or black with increasing age.

Bancroft says:

> The white color of the lily is due to the presence of innumerable air bubbles and the same is true of white hair. In order that hair may turn white in a single night, it is not necessary for the original pigment to disappear and for white pigment to develop. It is only necessary for a mass of minute air bubbles to be formed in the hair as a result of worry. . . . The best explanation of the blue feather is that the horny matter is filled with an enormous number of air bubbles, which scatter blue light and transmit red.

Jerome Alexander suggests that Sodom and Gomorrah were probably destroyed by a colloidal cloud of burning petroleum.

Finely divided or colloidal clay is carried thousands of miles by the water of great rivers, and when it reaches the sea it is deposited as a result of the action of the ions of sea-salts, land being formed. According to geological evidence, this process has added about one thousand miles to the length of the Mississippi River, and is still going on.

Colloidal fuel is now an article of commerce. It consists of finely powdered coal, cheap tars, and similar materials, dispersed in mineral oil and stabilized by means of a protective colloid, such as lime soap. This fuel is stored, piped, and burned, thus taking the place of oil.

The rubber-plant furnishes a milky juice, or latex, which contains very fine particles in colloidal solution. The latex may be coagulated by different processes, yielding a colloidal gel called rubber.

In 1839, Goodyear heated rubber with sulphur and obtained the product known as vulcanized rubber.

As stated before, particles in colloidal solution possess an electric charge, and under the influence of an electric current the particles move toward the electrode of opposite charge. The phenomenon is known as electrophoresis. A new process for the production of rubber goods is based upon an application of this principle.

The colloidal particles of the latex of rubber are negatively charged. When a mold or form is employed as anode in a properly prepared latex electrolytic solution and the circuit closed, the anode becomes rubber-plated. Molds of any form may be plated with rubber of tissue-paper thinness to several inches in thickness. The rubber has great strength and resiliency. Bathing-caps, gloves, hot-water bottles, and many other articles may be manufactured by the new process. It is very promising for insulating electric wires. Indeed, arrangements are being made with wire-manufacturers to employ the process in insulating wires, for the work can be done more speedily and with a stronger coating. This is another triumph of research in the field of chemistry.

Many colored transparent glasses owe their color to colloidal dispersed particles: for example, colloidal particles of gold give a beautiful ruby glass.

An emulsion for killing San José scale and other

parasites can be prepared from heavy mineral oil or lubricating oil. Very small quantities of the colloidal poisons suffice to kill insects.

Colloidal chemistry is just in its infancy, and we may confidently expect great developments in the years to come.

CHAPTER XXI

CARBON, PRODUCER OF ENERGY

In considering carbon one is immediately struck by the protean aspects of its occurrences. To that ubiquitous individual, the man in the automobile, carbon presents itself as a nuisance in his engine cylinders, while, because of carbon in his smoky exhaust, the motorist himself is often regarded as a nuisance by the pedestrian. The householder thinks of carbon in terms of coal, and sees the wood in his fireplace transformed to charcoal. There was no romance in carbon to the London chimney sweep of a century ago, when little boys of five or six were sold for seven years for thirty shillings and forced up chimneys by their masters with slight regard for the danger of burning or suffocation. To these boys carbon became a personal matter, for many went unwashed for years.—ARTHUR D. LITTLE.

1 OCCURRENCE OF CARBON

CARBON and silicon belong to the same family, both being found in Group IV of the periodic system. Carbon may be regarded as the central element of the organic kingdom as silicon is of the inorganic kingdom. Carbon enters into the formation of more compounds than does any other element. Indeed, its compounds are so numerous that it is found convenient to place them in a separate division of chemistry, which is called organic chemistry—*i.e.*, the chemistry of carbon compounds. Carbon is an essential constituent of all plants and animals, many interesting and useful compounds being synthesized in their bodies: for example,

sugars, starch, cellulose, fats, and oils. The element is also a constituent of innumerable hydrocarbons (compounds containing hydrogen and carbon only), which are found in petroleum, natural gas, and among the products obtained by heating coal or wood in closed vessels. Carbon is also a constituent of all alcohols, chloroform, ethers, morphine, and strychnine. Moreover, carbon is a constituent of carbon dioxide, which is present in the air, the earth, and natural waters; also of carbonates such as calcium carbonate, which is exceedingly abundant in the form of limestone, marble, chalk, coral, and shells.

In the free state, carbon is represented by several allotropic forms, namely, the diamond, graphite, and "amorphous" carbon which includes charcoal, coke, lampblack, and carbon-black.

2 The Diamond

The diamond is the purest form of carbon occurring in nature. It has been used for ages as a precious stone. Originally it was obtained solely from alluvial deposits in India. Since the year 1727 the rich diamond-fields of Brazil have been worked. In 1867 diamonds were discovered in South Africa, and the most famous mines in the world are the Kimberley, De Beers, and others. Diamonds are also found in Australia, in the Ural, and in other localities. They have also been found in meteorites. The diamonds of South Africa occur in great pipes extending vertically downward to unknown depths. These pipes are filled with a heterogeneous mixture cemented with a bluish hard mate-

rial, in which "blue earth" the diamonds are imbedded. The "blue earth" consists of decomposed igneous rock. The conical pipes perhaps represent the necks of extinct volcanoes.

The origin of the diamond has always been a riddle, but it must have been formed at vast depths under very great pressure and at high temperature. One theory is that diamonds came to the earth in meteoric showers. While this theory is somewhat fanciful, it is true that black and transparent diamonds have been found in the famous Cañon Diablo meteorite, in Arizona. It seems fairly sure that the diamond has been formed by the slow crystallization of carbon from iron or molten rock. There is some evidence to support this theory; for in 1903, H. Moissan, Professor of Chemistry in the University of Paris, succeeded in preparing very small diamonds. Pure sugar charcoal (carbon) was packed in a graphite crucible with iron, the crucible placed in an electric furnace and a powerful arc formed between carbon electrodes. The temperature rose to about 3500° C., and carbon dissolved in the molten iron. The fiery crucible was then plunged into cold water or molten lead and cooled, and the carbon in the inner part of the vessel was subjected to an enormous pressure. The metal was dissolved in acids, and the residue treated with appropriate reagents and then washed; it consisted chiefly of graphite, but exceedingly small diamonds also were present, some of which were colorless and others black.

The diamond crystallizes in the isometric or cubic system, but the natural form is very different from its shape after it has been cut by a lapidary. A "bril-

liant," for example, has one rather large, flat face, which forms the base of a pyramid of many sides. When the stone has this form, the maximum reflection of light from its interior is produced. The greater part of diamond-cutting is done in Holland. The diamond is the hardest known substance, although different specimens differ in this respect. A diamond of suitable shape will curl shavings off a glass plate very much as a carpenter's tool will plane shavings off a board.

The diamond has a high index of refraction, and its property of scattering light to such a great extent renders it very valuable as a gem. The pure diamond is colorless and transparent, but the stone is frequently colored by small quantities of impurities. Some of the blue, red, yellow, and green diamonds are as valuable as the colorless variety.

The black variety is known as carbonado or bort, but is of no use as a gem. On account of its extreme hardness it is used for boring, cutting, and grinding.

When the diamond is heated in the absence of air above 1000° C., it is transformed into a coke-like mass. When heated in air or oxygen to a high temperature, it burns to form carbon dioxide.

The history of certain large diamonds is very fascinating and romantic. The largest diamond ever found was the celebrated Cullinan; it was discovered in South Africa in 1905, and weighed in the rough state 3,025 carats (1.37 lbs. avoirdupois). It was presented to King Edward VII. This diamond was cut into a number of stones, the largest of which weighed 516.5 carats. The Orloff diamond was stolen by a French

soldier from the eye of an idol in a Brahman temple, and subsequently stolen from him by a ship's captain. Finally, it was bought by Prince Orloff for £90,000, and presented to Empress Catherine II of Russia. It weighs 194¾ carats, and is tinged with yellow. The Pitt or Regent diamond is a magnificent colorless diamond which weighs 136¼ carats. It is in the Louvre, in Paris. This stone was found by an Indian slave, who concealed it in a gash cut in the calf of his leg for the purpose. The poor slave wandered to Madras, where he was murdered on board a ship, and the diamond sold for £1000. In 1710 it was purchased by Thomas Pitt, grandfather of the Earl of Chatham, for £10,000; and in 1717 he sold it to the Duke of Orleans for £130,000.

The Kohinoor diamond, one of the British crown jewels, weighs 106 carats. Its authentic history begins before the birth of Christ. The celebrated Hope diamond weighs 44¼ carats and has an exquisite blue color. The Tiffany diamond weighs 125½ carats and has a magnificent orange-yellow color. The Victoria, a diamond of 180 carats, was cut from a stone weighing 457½ carats and sold to the Nizam of Hyderabad for £400,000, which was at the rate of $20,000,000 per pound troy.

3 Graphite, Charcoal, and Coke

Graphite (Greek: write) is widely distributed in nature, fine deposits being found in Ceylon and in Madagascar. It commonly occurs in old crystalline

rocks, such as granite and gneiss. It was formerly supposed to contain lead; hence the name black-lead, or plumbago.

Graphite is manufactured on a large scale by the Acheson process, chiefly at Niagara Falls, where water-power is transformed into electricity. Anthracite coal or coke is heated in an electric furnace, in the presence of ferric oxide or silica, which acts as a catalyst. A carbon rod (C) is used as a core between the termi-

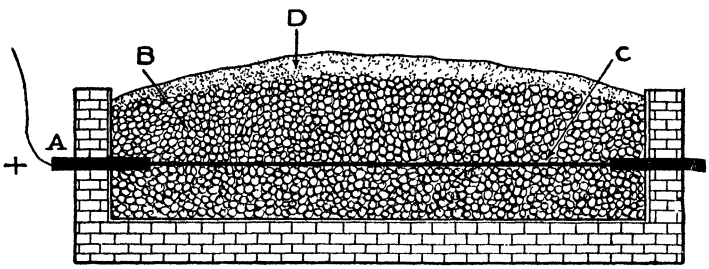


FIGURE 26
Graphite Furnace

nals (Figure 26). Carbides are first formed, but at the very high temperature attained (3,500° C.) these dissociate, yielding graphite, which is deposited as nearly pure carbon. The electrodes (A) are made of graphite. The furnace is nearly filled with coarse grains of anthracite coal or coke (B). The charge is covered with a mixture of sand and carbon (D).

Graphite is a soft, gray-black, shiny substance which feels greasy to the touch. It is a good conductor of heat and electricity.

Graphite, mixed with fire-clay, is used for manufacturing crucibles which are very resistant to heat.

Graphite is also used in the manufacture of "lead" pencils, the hardness being regulated by the addition of clay. It is also employed as a metal polish, for glazing powder, and in many other ways. Artificial graphite can be used for virtually any purpose to which natural graphite is put. It is very well adapted to the manufacture of electrodes.

Charcoal is usually produced by heating wood in retorts, the air being excluded to prevent combustion. The heating of wood or a similar substance in a retort is called destructive distillation. Valuable by-products are obtained, such as wood-alcohol, acetone, and acetic acid.

Bone-black, or animal charcoal, is obtained by heating bones and animal refuse, the air being excluded as in the case of wood charcoal. The residue is calcium phosphate and carbon.

Coke is produced on an enormous scale by subjecting soft coal to destructive distillation, or carbonization. The by-product oven is a brick chamber surrounded by heating-flues and furnished with a pipe through which the volatile products may be led off. When the retort or by-product oven is employed, most valuable by-products are obtained, such as gas, coal-tar, and ammonia. Before the war the greater part of coke in the United States was produced in the wasteful beehive oven; but by 1924 we were producing 70 per cent of it in the by-product oven. The increased use of the by-product oven is an important conservation measure. According to F. W. Sperr, Jr., the following products are obtained from one ton of Pittsburgh coal:

Total coke	1500 pounds
Gas	11,360 cubic feet
Tar	124 gallons
Ammonium sulphate	25 pounds
Light oil (benzenes)	4 gallons

About fifty million tons of coke are produced annually in the United States. It is used largely for removing oxygen from metals and as a source of heat.

Lampblack, a form of soot, is manufactured by the incomplete combustion of organic substances, usually of an oily or resinous character, the carbon depositing as soot in a series of chambers. It often deposits on a lamp chimney when the draft is not properly regulated. It is synonymous with dirt and grime. Lampblack is used in the production of printer's ink. Carbon-black or gas-black is produced by allowing a flame, when the gas is burning in an insufficient supply of air, to impinge upon a cold surface, such as a revolving iron drum. It is used in the manufacture of printer's ink and automobile tires. It adds much to the length of life of tires.

4 Properties of Carbon; Fuels

Carbon is virtually infusible, so it is excellent for electrodes. Sir Humphry Davy, in 1821, first produced the electric arc between charcoal points. Charcoal is very porous and is therefore valuable for adsorbing gases and vapors. According to A. D. Little, specially prepared or activated charcoal may have an internal area as great as twenty thousand square yards, or about four acres, per cubic inch. Bone-black has long been used for refining sugar. Excellent charcoal

for use in gas-masks was produced during the World War from cocoanut-shells and peach-stones. The adsorptive power of charcoal is greatly increased by secondary or so-called activating treatments. Some charcoals are so efficient that very high vacua are obtained by their use. High-grade charcoals may condense within their pores several hundred times their own volume of ammonia gas, as well as large volumes of toxic gases such as were used in chemical warfare. Owing to its porosity, charcoal is a good deodorizer.

X-ray analysis has shown that charcoal is more or less crystalline, the arrangement of the atoms being like that in graphite, which consists of a hexagonal network of carbon atoms. In the diamond, the atoms are arranged in the form of a tetrahedron. At ordinary temperature carbon is not a reactive substance. The cave-man drew pictures on the walls of his cave with soot, and some of these are in a good state of preservation. Printer's ink is much more durable than the paper which bears it. Manuscripts have been discovered at Herculaneum which are written in carbonaceous ink and are unchanged after eighteen centuries. Chlorine bleaches ordinary ink, but not printer's ink. Graphite appears to be the most stable form of carbon, for at very high temperature all other forms of carbon are changed to graphite.

Carbon is a great producer of cheap energy. When twelve grams of the element are burned, 97,000 calories are produced:

Carbon	+ Oxygen	= Carbon dioxide
C	O_2	CO_2
12 grams	32 grams	44 grams

One gram of hydrogen burns to form water, yielding 33,900 calories. Most of the energy for carrying on the work of the world is obtained by burning coal, gas, and petroleum. Coal is largely carbon. It is formed when vegetable matter slowly decays out of contact with air, as under water or when covered by sand or clay. Water, hydrocarbons, and other products escape, leaving a residue richer in carbon. Anthracite coal is the richest in carbon, for it has undergone the greatest change; bituminous coal contains less carbon; and lignite and peat are imperfectly formed coals, being more nearly like wood in composition. This is clearly shown in the table given below:

	Carbon	*Hydrogen*	*Oxygen and Nitrogen*
Wood	51	6	43
Peat	58	6	36
Lignite	70	5	25
Bituminous coal	81	5	..
Anthracite	94	3	..

The wood, peat, and lignite, as given in the table, are free of water and ash. The percentages of carbon in the same variety of coal vary considerably. In 1918 the United States produced 579,385,820 tons of bituminous coal and 98,826,084 tons of Pennsylvania anthracite.

The composition of fuel gases varies. Natural gas is largely a hydrocarbon (methane, CH_4); water-gas is a mixture of hydrogen and carbon monoxide; producer-gas is carbon monoxide diluted with nitrogen; and coal-gas is a mixture of hydrogen, hydrocarbons, and carbon monoxide. Petroleum is principally a mixture of hydrocarbons.

The following table gives the calorific value of a

number of fuels. The heat is expressed in the British thermal units (B.T.U.), which is the amount of heat required to raise one pound of water 1° F. One B.T.U. equals 252 calories, for there are 453.6 grams in one pound, and 1° F. equals 5/9° C.; therefore, 453.6 multiplied by 5/9 equals 252.

CALORIFIC VALUE OF FUELS IN BRITISH THERMAL UNITS

	B.T U. per cubic foot	
Hydrogen	343	
Methane	1064	
Acetylene	1556	
Carbon monoxide	341	
Coal-gas	600	Approximate values
Water-gas	300	
Carburetted water-gas	600	
Producer-gas (from coal or coke)	140	
Blast-furnace gas	100	
	B.T.U. per pound	
Wood	8,000– 9,000	
Peat (theoretically dry)	6,500– 9,500	
Lignite	9,000–14,000	
Bituminous coal	14,600–15,050	
Anthracite	14,500–15,800	
Coke	14,000	
Fuel oil	16,500–20,000	

This table shows that, pound for pound, fuel oil yields much more energy than coal or coke. One ton of good coal, when burned, will raise about 14,000 pounds of water 1° F. According to the International Geological Congress held in 1913, the world's coal-supply down to a depth of 1800 meters amounted to not less than 7,307,553 million tons. The percentages belonging to the chief coal-producing countries were as follows: The United States, 51.8; Canada, 16.4; China, 13.5; Germany, 5.7; Great Britain, 2.6.

In 1920 the world's consumption of coal was 1305 million tons. According to Arrhenius, if we take for the future yearly use an average of 1500 million tons the world's supply cannot last over 5000 years. The United States is a greatly favored nation, for the same authority says:

> The United States even with a production of 2½ times greater than its present production, or a billion tons a year, can peacefully expect a 4000 year period of use, not allowing of course for greatly increased exportation.

Another fact of great economic importance is that, according to data collected and published by the United States Congress in 1910, the estimated iron reserves of three fourths of the world (the polar regions and some comparatively unexplored regions are not included) were 22,408,200,000 tons of iron ore with more than 123,000,000,000 tons of "potential" ore. Of these reserves the United States possessed 4,257,800,000 tons of ore and over 75,000,000,000 tons of "potential" ore. At the present rate of consumption, about 70,000,000 tons annually, the domestic supply, including our potential ores, might be expected to last one thousand years.

5 Carbon Dioxide and the Cycle of Carbon

Carbon forms two important oxides—carbon dioxide and carbon monoxide. Carbon dioxide is formed when carbon or matter containing carbon is burned with free access of air. It is also a product of respiration, fermentation, and decay. For laboratory use it is usually

generated by treating marble, or calcium carbonate, with hydrochloric acid. When a carbonate is treated with an acid, a vigorous effervescence occurs, for bubbles of carbon dioxide escape. This fact is turned to profit in one form of portable fire-extinguisher. The gas is generated by bringing together a solution of sodium bicarbonate (baking-soda) and sulphuric acid. The body of the container is filled with a solution of the bicarbonate, and a bottle of sulphuric acid is placed above. In case of fire the container is inverted, which allows the chemicals to interact. The gas forces the liquid through the hose, and itself escapes at the same time.

The chemical change is shown by the following equation:

$2NaHCO_3$	$+$	H_2SO_4	$=$	Na_2SO_4	$+$	$2H_2O$	$+$	$2CO_2$
Sodium bicarbonate		Sulphuric acid		Sodium sulphate		Water		Carbon dioxide

In the baking of bread and cake, carbon dioxide is generated in the dough, and forces its way through the mass, rendering it light and porous. Carbon dioxide is now produced on a large scale from the flue gases given off during the combustion of fuel such as coke. The gases are scrubbed with a solution in which carbon dioxide is soluble (*e.g.*, sodium carbonate, Na_2CO_3); and on boiling, the gas is obtained. It is compressed into steel cylinders under a pressure of about eleven hundred pounds per square inch, and shipped to manufacturers of carbonated beverages. In the year 1919 nearly sixty million pounds of the gas were used in the United States in soft drinks. Vast

quantities of carbon dioxide are also manufactured by "burning" limestone to quicklime. Carbon dioxide is a by-product of the brewing industry. It is used largely in the manufacture of washing- and baking-soda, this industry in our country requiring over one half million tons of carbon dioxide annually.

Carbon dioxide is a colorless gas with a slightly acid taste and pungent smell. It is more than one and a half times heavier than air, and can be poured, like a liquid, from one vessel into another. It liquefies at 31.35° C. at a pressure of 72 atmospheres, or over 1,000 pounds per square inch. When the stop-cock of a cylinder containing liquid carbon dioxide is opened and the opposite end of the vessel slightly elevated, some of the liquid rushes out. A portion of it evaporates and absorbs so much heat that the remaining portion of the liquid is frozen to a crystalline snow-like solid, called carbonic acid snow. The solid may be collected in quantity by tying a bag of coarse canvas to the nozzle of the tank. Solid carbon dioxide should not be pressed hard upon the skin, for it will produce a blister similar to a burn. When the solid is mixed with ether and allowed to evaporate, a very low temperature is obtained. Thus, mercury may be readily solidified when surrounded by the mixture. Solid carbon dioxide evaporates without melting.

Solid carbon dioxide, or "dry ice," is now an article of commerce. The solid formed by rapid evaporation of the liquid is put in steel molds and pressed into blocks. It is employed as a refrigerant in competition with water ice. Solid carbon dioxide has several advantages: for example, it can be distributed through-

out a car-load of fish to keep it frozen in transit for a period of several days; also, small packages of such foods as butter and ice-cream may be shipped in paper containers by mail or express. "Dry ice" is commercially competitive with water ice at 0.5 cent per pound.

An interesting story is told by oil-prospectors in southern Texas. When a pipe had been driven to considerable depth in search of oil, the gage showed a pressure of over a thousand pounds; and when the pipe was opened up, there was a marvelous shower of carbonic acid snow. The natives rushed up and compressed it into "snowballs," which blistered their hands. If this story be true, carbon dioxide was generated in the earth under such high pressure that it liquefied. The gas cannot be liquefied above 31.35° C. (88.4° F.). It is well known that carbon dioxide escapes through vents and fissures in the earth's crust, as in the Poison Valley in Java and the Grotto del Cane near Naples. The latter is of such construction, says Sir H. E. Roscoe, "that the heavy carbonic acid gas, entering from the fissures in the floor of the cave, at a depth from two to three feet below the mouth of the cave, collects up to this depth, and small animals such as dogs, when thrown into the cave, respiring the impure air, fall down, whilst a man breathing the pure air above this level is unaffected by the gas."

Carbon dioxide unites readily with oxides or hydroxides of the alkali and alkaline earth metals: for example, when the gas is brought into contact with lime-water, or a solution of calcium hydroxide, a white precipitate of calcium carbonate is formed:

$$\underset{\text{Calcium hydroxide}}{Ca(OH)_2} + \underset{\text{Carbon dioxide}}{CO_2} = \underset{\text{Calcium carbonate}}{CaCO_3} + \underset{\text{Water}}{H_2O}$$

The presence of carbon dioxide may be detected by breathing through a glass tube into lime-water; also by attaching a delivery-tube by means of a stopper to a bottle of ginger-ale, from which the gas escapes. An aqueous solution of carbon dioxide under a pressure of from three to four atmospheres is known as soda-water. When such a solution is exposed to the air, it effervesces or sparkles, due to the escape of carbon dioxide under the reduced pressure. Animals soon die of suffocation when brought into an atmosphere of carbon dioxide. Air containing abnormally large quantities of the gas should not be breathed for long periods. Large amounts of the gas in the air exert a narcotic effect; it is not particularly poisonous.

The carbon-carbon dioxide-oxygen cycle is of the highest importance, for these substances are very closely related to life. The oxidation of carbon with the production of heat occurs not only during combustion and decay but in the bodies of animals during respiration. The carbon dioxide of the air is reduced in the green leaves of plants, the carbon being appropriated, along with water, to form cellulose and starch, the oxygen being returned to the air. The generation of oxygen may be readily shown by placing a green plant under water in a jar and then exposing it to sunlight. The radiant energy of the sun is the source of the required energy, and the green coloring matter of leaves (chlorophyll) and the protoplasm take part in the transformation. The radiant energy of the sun

is therefore transformed into the storable form of chemical energy. It is clear now why it is so essential to have as large a portion as possible of the earth's crust covered with green plants. Carbon dioxide is, therefore, an essential food for plants, and the oxygen returned to the air is available for repeating the cycle.

The behavior of limestone in the presence of natural waters containing carbon dioxide makes it easy to understand the formation of caves, such as the Mammoth Cave in Kentucky. On account of the slow action of carbonic acid, soluble calcium bicarbonate is formed, and in the course of time much of the rock is eaten away, leaving a cave. When the solution loses carbon dioxide at the roof of the cave, calcium carbonate is left behind as a sort of stony icicle called stalactite; but when drops of water fall to the bottom of the cave, evaporation occurs with further loss of carbon dioxide, and deposits of calcium carbonate are formed which are known as stalagmites. The stalactites and stalagmites may unite, forming pillars or columns. A limestone cave therefore has a tendency to refill itself.

6 Carbon Monoxide

Carbon monoxide is formed when carbon burns in a limited supply of air, or by passing carbon dioxide over hot coke or charcoal:

$$CO_2 + C = 2CO$$

Carbon reduces carbon dioxide to the monoxide. This reaction explains the formation of carbon monoxide

in an ordinary grate fire, where reduction occurs in the interior of the grate as the dioxide passes over heated carbon. The monoxide, on coming into contact with air at the top of the grate, burns with a blue flame to form the dioxide. Carbon monoxide is formed in

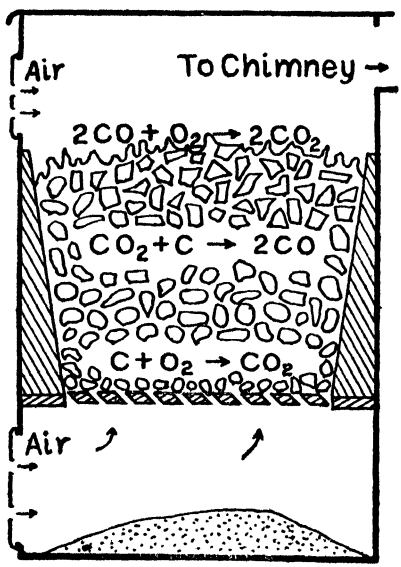


FIGURE 27
Formation of Carbon Monoxide in a Cooking-Stove

ranges, stoves, and furnaces during incomplete combustion and may escape into a room in case of insufficient draft (Figure 27). The gas is also formed in the combustion engine, especially when the "choker" is pulled out, due to the fact that there is an excess of gasoline, and combustion or oxidation is not complete. Producer-gas is formed when air is passed through

heated coke. It contains about 39 per cent of carbon monoxide.

Water-gas is produced on a large scale by passing steam over heated coke or anthracite coal:

$$C + H_2O = \underbrace{H_2 + CO}_{\text{Water-gas}}$$

Water-gas and producer-gas are excellent fuels.

Carbon monoxide is a poisonous, colorless gas which is virtually odorless and tasteless, and therefore especially dangerous to handle. When inspired, it unites with the hemoglobin of the blood corpuscles to form a relatively stable compound, which shuts off the supply of oxygen. One volume of carbon monoxide to about 800 volumes of air will produce death in about thirty minutes, while one volume in 100,000 volumes of air produces symptoms of poisoning. Birds and mice are more sensitive to its action than is man.

Carbon monoxide is a good reducing agent and therefore plays an important part in the blast-furnace in robbing iron oxides of oxygen.

The union of carbon monoxide and chlorine to produce phosgene ($COCl_2$) has already been mentioned. It is one of the chief toxic gases employed in chemical warfare.

CHAPTER XXII

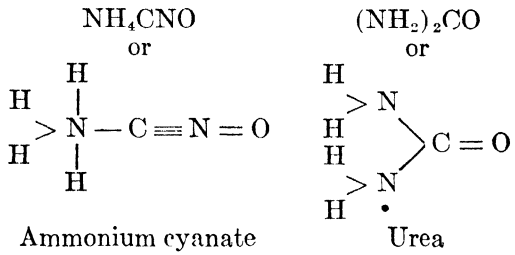
ORGANIC CHEMISTRY

Nearly two thousand different coal-tar dyes are known and among them there are some which cannot be spoken against in any way, as to non-fading qualities, fastness to washing, and in color-tone. One may look upon the preparation of the most valuable and useful dyes in all the colors and shades of the spectrum, from the dirty and ill-smelling coal-tar, as one of the higher triumphs of modern science, for it has given us dyes which are more lovely than the lilies of the field.—SVANTE A. ARRHENIUS

1 ORGANIC CHEMISTRY

ORGANIC chemistry, as stated before, treats of the carbon compounds, which now number over 230,000, whereas the combined number of all other compounds is about 25,000. The laws of organic chemistry do not differ from those of inorganic chemistry. A century ago it was thought that carbon compounds found in organized bodies—plants and animals—were formed only as the result of a "vital force," and could not be synthesized, therefore, by man. This notion was disproved in 1828 by the German chemist, F. Wöhler, who obtained urea, a nitrogenous waste material of the body, by warming ammonium cyanate, a compound capable of synthesis from inorganic substances. Both compounds have the same formula (N_2H_4CO) and identical molecular weight. The transformation of

ammonium cyanate into urea is of great historic interest, for it was the first time an organic compound was prepared independent of life processes. Ammonium cyanate and urea are isomers (Greek: *isos,* equal + *meros,* part), but their properties are different, owing to the different arrangement of the atoms constituting the molecule of each. This may be shown as follows:



Ammonium cyanate Urea

The graphic or structural formulæ show that the architecture of the molecules of the two compounds is different.

Frederick Wöhler, the great teacher and investigator of Göttingen, was at one time a pupil of the world-renowned Berzelius of Stockholm. Before sailing for Stockholm, Wöhler had to spend six weeks at Lübeck, waiting for a small sailing-boat to depart. The last three weeks were spent with an apothecary named Kindt, and in his washing-room Wöhler prepared a specimen of potassium according to the new method of Brenner. When the boat reached Stockholm, Wöhler asked the captain how much he owed him for the passage, whereupon the latter replied that he had too high regard for science and his countryman Berzelius to accept anything.

The name of Wöhler will be forever connected with that of another eminent German chemist, Justus von Liebig, who began life as an apothecary's assistant. Liebig's laboratory at Giessen was famous, and as a teacher Liebig himself stands almost alone. Wöhler and Liebig undertook certain important investigations in common and their mutual friendship is one of the most disinterested in all the pages of science. We are told by Ernst von Meyer:

> Their friendship is beautifully shown by the investigations which they undertook in common, during which each animated the other, while striving at the same time to do his best himself. . . . We are indeed not wrong in asserting that the organic chemistry of today is grounded mainly upon the pioneering labors of Liebig, and of Liebig and Wöhler together. In 1871, at the age of 68, Liebig wrote the following beautiful lines to Wöhler who was three years his senior: "Even after we are dead and our bodies long returned to dust, the ties which united us in life will keep our memory green—not very frequent—of two men who wrought and strove in the same field without envy or ill-feeling, and who continued in the closest friendship throughout."

2 Hydrocarbons: Petroleum and Gasoline

Hydrocarbons, or compounds of carbon and hydrogen only, are very numerous, several hundred being known. These occur as gases, liquids, and solids. Natural gas is chiefly methane (CH_4), and petroleum is composed largely of hydrocarbons. Wood and coal also are sources of hydrocarbons, the most important of

which is benzene (C_6H_6), because from it so many useful compounds can be prepared. Turpentine and rubber are hydrocarbons.

As carbon compounds are exceedingly numerous, it simplifies their study to arrange them in families, the classification being based on composition and properties. Thus, the hydrocarbons, as well as many other carbon compounds, have been divided into families which are called homologous series. Each member of a homologous series differs from the member which precedes or follows it by one atom of carbon and two atoms of hydrogen, or by CH_2. Members of a homologous series have the same general formula and similar chemical properties. The table below contains a few of the members of the methane or paraffin series.

HOMOLOGOUS SERIES OF PARAFFINS

General formula: C_nH_{2n+2}

CH_4,	Methane	Gases
C_2H_6,	Ethane	
C_3H_8,	Propane	
C_4H_{10},	Butane	
C_5H_{12},	Pentane	Liquids
C_6H_{14},	Hexane	

With increasing molecular weights the boiling-points rise and the tendency to assume the solid state increases: *e.g.*, octodecane ($C_{18}H_{38}$) melts at 28° C. The number of hydrogen atoms in a paraffin is always two greater than double the carbon atoms.

The paraffins are called saturated hydrocarbons, for the carbon atom has all four of its valences employed.

C_2H_4 is the first member of the ethylene series, or

olefines; acetylene (C_2H_2), of the acetylene series; and benzene (C_6H_6), of the benzene series.

Methane (CH_4) may be taken as a representative of the paraffin or saturated compounds. It is called marsh-gas because it is formed in marshes or pools, as a result of the decay of vegetable matter. It is frequently present in coal-mines, and is the dreaded fire-damp of the miner. When wood or coal is subjected to destructive distillation, large quantities of this gas are produced, coal-gas containing ordinarily from 35 per cent to 40 per cent by volume. Marsh-gas is a product of the decomposition of sewage, and may therefore accumulate in septic tanks along with air, constituting an explosive material. Some years ago there was a disastrous explosion in a septic tank at Ocean Grove, New Jersey, which was probably due to the accidental ignition of methane.

Methane is a colorless, odorless, tasteless gas, much lighter than air. Like other paraffins (Latin: *parum*, little + *affinis*, affinity), methane is not acted upon by most chemical reagents. We all know how inactive paraffin wax is. All hydrocarbons burn, forming water and carbon dioxide, accompanied by much heat.

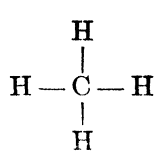
A mixture of methane and oxygen (or air) is extremely explosive, the maximum effect being obtained when two volumes of oxygen or ten volumes of air are mixed with methane.

Carbon atoms have great facility for combining with one another to form straight chains, branched chains, rings, or a combination of chains and rings; and to this is largely attributed the vast number of carbon compounds. Hydrogen is a constituent of a major-

ity of carbon compounds, and oxygen is often present. Some of these compounds are exceedingly complicated, for a single molecule may contain over two hundred atoms of carbon. Then, too, there are many illustrations of carbon compounds which contain the same numbers and kinds of atoms, but have different properties, as do ammonium cyanate and urea; that is, they illustrate isomerism. Thus, it has been calculated that 802 compounds of the formula $C_{13}H_{28}$ are possible. Innumerable isomers have been prepared.

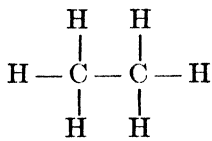
Chemists attempt to show something about the linkage of atoms in compounds by employing graphic or structural formulæ. The architecture of many of the molecules is most interesting. In certain cases it is very simple, and in other cases extremely complicated. When the chemist understands the structure or architecture of a molecule of a particular compound, he can undertake to construct it, very much as workmen follow an architect's plans in constructing a house. Structural formulæ are based upon experimental evidence.

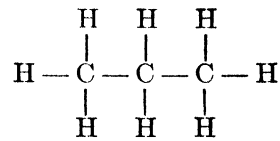
The paraffins are called "straight-chain" compounds, for it is believed that the carbon atoms are strung together in a chain. Since there is only one carbon atom in methane, the simplest hydrocarbon, its formula may be written thus:



Chemists really believe that the carbon atom of the methane molecule is situated at the center of a tetrahedron, with the four hydrogen atoms at the corner. (See "The Diamond" in Chapter XXI.)

The structural formulæ of ethane (C_2H_6) and propane (C_3H_8) may be written as follows:





As already stated, petroleum (Latin: *petra,* rock + *oleum,* oil), or "rock oil," consists principally of a mixture of hydrocarbons. It occurs largely in California, in Oklahoma, and in other states; also in Russia, Mexico, the Dutch East Indies, Galicia, Persia, and Rumania. In 1921, the United States produced nearly 470,000,000 barrels of 42 gallons each, while the world's production was 760,000,000 barrels. In 1925, the world's production of crude petroleum rose to 1,066,220,000 barrels, of which the United States supplied 764,000,000, or 71.6 per cent.

Oil is trapped in what the geologist calls an anticline, a sort of inverted bowl of clay or shale, and is reached by drilling wells. Colonel Drake dug the first petroleum well at Titusville, Pennsylvania, in 1859.

Russian petroleum occurs in and around Baku in the region of the Caspian Sea. As early as 600 B.C. the "eternal fires of Baku" attracted the fire-worshipers. The origin of petroleum is not known.

Petroleum is separated into various products by

fractional distillation. This means that the components of petroleum have different boiling-points, and may therefore be separated by distillation, the receiver of the still being changed from time to time.

Petroleum contains in solution gases, such as methane (CH_4) and ethane (C_2H_6). When the liquid is gently heated these gases are given off and are utilized as fuel and for the production of carbon-black. As the temperature is slowly raised heavier hydrocarbons are vaporized. After the separation of the true gases, the next product is the light liquids which are usually called naphthas. These consist largely of pentane (C_5H_{12}) and hexane (C_6H_{14}). This fraction is used as a solvent in the rubber and varnish industries. The next fraction is gasoline, which contains hydrocarbons having from six to ten carbon atoms in the molecule. It is employed extensively as motor fuel and as a solvent. The temperature of the still is now approximately 200° C., and it gradually rises to about 375° C., kerosene being obtained. In this fraction there are molecules containing from ten to fifteen carbon atoms. Kerosene is an excellent illuminant and fuel. Other fractions obtained are middle fractions and light and heavy paraffin distillates. The middle fractions are cracked to form gasoline. The paraffin distillates yield lubricating oil and paraffin. The tarry residue in the still is employed as artificial asphalt and as a source of a light, porous coke.

According to G. L. Wendt, mid-continent petroleum will furnish about 4 per cent of gas, 25 per cent of naphthas and gasoline, 15 per cent of kerosene, 40 per cent of gas oil, 12 per cent of paraffin and lubricat-

ing oils, and 4 per cent of coke. Before use, the gasoline, kerosene, and paraffin distillates must be refined.

Gasoline is the most prized derivative of petroleum. The use of gasoline has increased by leaps and bounds. Not many years ago the domestic production was about 4,000,000,000 gallons annually; but in 1925 our production was 10,886,127,000 gallons, an average of over 907,000,000 gallons per month. The domestic consumption amounted to over 7,362,000,000, and 12.2 per cent was exported. America is truly a "nation on wheels," for the registration of automobiles, trucks, and buses, passed the 21,000,000 mark in the spring of 1926.

According to W. C. Teagle, in 1924 our per-capita consumption was five and one half barrels as compared with one fifth of a barrel per capita for the rest of the world. This means that our consumption was twenty-seven times the consumption elsewhere.

Since the greatly increased demand for gasoline, chemists have been busy with the problem of increasing the yield. Immense quantities of gasoline have been produced by "cracking" processes which have been invented within recent years. The crude petroleum is first separated into fractions by the ordinary distillation methods, and then the middle fractions, which have a relatively low fuel value, are heated or distilled at very high temperature and pressure, whereby the heavier molecules break down to yield hydrocarbons of lower molecular weights. When the crude oil is heated in cracking coils at a pressure of from 350 to 600 pounds, it may yield as much as three times the amount of gasoline as would be obtained

under ordinary distillation. By the cracking process one barrel of crude petroleum ordinarily yields almost as much gasoline as was previously obtained from two. In 1924, the ratio of cracked gasoline to the primary distillation, or straight gasoline, was one barrel to three and two thirds.

Burning gasoline for energy is a most wasteful process, for our automotive engine has given us only 5-per-cent efficiency from the fuel consumed. President Coolidge's Federal Oil Conservation Board reported in September, 1926, that it is imperative for the United States to conserve its oil-supply. According to this board, the total of our reserve wells is about 4,500,000,0000 barrels—enough for six years' supply—if no oil is imported. In 1925, the Committee of Eleven of the American Petroleum Institute estimated the reserve to be 5,300,000,000 barrels, and believed there would be 26,000,000,000 barrels of oil left in the sands after the wells ceased to flow. It is hoped that by improved methods of extraction much of this oil can be recovered. The Committee of Eleven also estimated that our national petroleum reserves consist of over a billion acres of unexplored and undeveloped land. The President's board says that "the producing and proven area in the United States is asserted to be in excess of 3,000,000 acres."

Of the 9,000,000,000 barrels of oil produced in the United States up to June 30, 1926, about 3,000,000,000 barrels were produced in the last five years. The consumption of oil in the United States is about 70 per cent of the world's supply. We have vast deposits of the rock called oil shale. It is reported that the state

of Indiana has over 450,000,000,000 tons of the rock, and there are whole mountains of it in Colorado and in Utah. When heated in appropriate stills these shales yield from 10 to 50 gallons of oil per ton; but at present the expense of production is too high to compete with petroleum. In the future, however, they will no doubt be of great value. Furthermore, there are relatively few cases in which coal cannot satisfactorily be substituted for fuel oil. Then, too, colloidal fuel will materially aid in relieving the diminishing stores of petroleum, and will also lead to the utilization of coal waste and inferior fuels. It is also possible that synthetic fuel will be produced.

3 Ethylene and Acetylene

Ethylene is an important hydrocarbon gas, being the first member of a homologous series of compounds called the ethylene or olefiant-gas series. The gas may be produced by abstracting the elements of water from ethyl alcohol. This may be accomplished by heating alcohol with sulphuric or phosphoric acid, or by passing the vapor of alcohol over kaolin (a catalyst) at a high temperature:

$$\underset{\text{Alcohol}}{C_2H_6O} = \underset{\text{Ethylene}}{C_2H_4} + \underset{\text{Water}}{H_2O}$$

Ethylene gas is colorless and possesses an ethereal odor. It is extremely explosive when mixed with air or oxygen. Unlike methane, it combines directly with chlorine and bromine to form *addition products*. Thus, it unites with chlorine to form ethylene chloride

($C_2H_4Cl_2$), an oily liquid long known as Dutch liquid because it was first prepared by four Dutch chemists:

$$C_2H_4 + Cl_2 \longrightarrow C_2H_4Cl_2$$

Since ethylene has the property of forming addition compounds, it is called an unsaturated compound. Unsaturated compounds have the property of decolorizing a solution of bromine.

Ethylene is an important illuminant. During the World War the United States used large quantities of the compound in the manufacture of mustard gas, which is really a liquid with a boiling-point of 219° C. It was first employed in warfare by the Germans at Ypres, July 20, 1917.

Ethylene is an excellent anesthetic. In using the gas it must be borne in mind that it mixes with air to form a powerful explosive. A few years ago, in Baltimore, a patient was killed on the operating-table by an explosion of ethylene. The surgeon was using an electric needle.

It is an interesting fact, discovered a few years ago, that when carnations were shipped to Chicago, the flowers went to sleep, or closed up. It was demonstrated that this was due to ethylene. Experiments were then made on dogs, followed by experiments on man.

Ethylene is very useful in cutting and welding metals and for coloring green citrus fruit yellow.

Acetylene, another gas of the greatest importance, can be prepared very easily by treating calcium carbide with water:

$$\underset{\text{Calcium carbide}}{CaC_2} + \underset{\text{Water}}{2H_2O} = \underset{\text{Calcium hydroxide}}{Ca(OH)_2} + \underset{\text{Acetylene}}{C_2H_2}$$

Acetylene is a colorless gas, which, when pure, has an ethereal odor. The impure gas, however, usually has a disagreeable odor. It is slightly soluble in water and is somewhat poisonous. Acetylene burns with an exceedingly luminous flame, producing intense heat. It is dangerously explosive when mixed with air or oxygen, and the range of explosive mixture is great. Like ethylene, it readily forms addition products. Acetylene is therefore an unsaturated compound. Acetylene is not very stable, and may be exploded by shock. It is unsafe to compress acetylene in supply-cylinders. The gas, however, may be safely dissolved under pressure in acetone. This is the way it is compressed in the Prest-o-Lite cylinders. Acetylene is used extensively as an illuminant, for which a special burner with a fine hole is required. The oxyacetylene blowpipe flame is exceedingly hot (nearly 3,500° C.) and is utilized in cutting and welding metals. Wonders have been accomplished by its use: for example, it is very easy to cut through sixteen-inch armor-plate.

4 Fuel and Illuminating Gases

Large quantities of coal-gas are produced by the destructive distillation of coal at high temperatures. Coke, tar, and ammonia are the by-products. Bituminous coal is heated to a high temperature in retorts, from which a pipe leads to the hydraulic main, where

tar and water are condensed. The excess of tar flows into a tar-pit. The hot gases and vapors are next passed through a series of pipes called condensers, to condense more tar and to cool the gas for further purification. The liquids collected in the tar-pit separate into two layers, the lower being coal-tar and the upper gas liquor (an aqueous solution of ammonia and ammonium compounds). The cooled gas is passed from the condensers to the scrubber, where ammonia is dissolved by water, then from the scrubber to the purifiers, where hydrogen sulphide is taken out by hydrated ferric oxide or slaked lime. From the purifiers the gas passes to the holder, where it is stored over water, and piped to the consumer. Much gas is also obtained as a by-product of the modern coke-oven.

Water-gas, a mixture of hydrogen and carbon monoxide, is produced by passing steam through a bed of burning coke or anthracite coal:

$$C + H_2O = CO + H_2$$

The reaction takes place at a temperature of about 1,000° C., but in the course of a few minutes the temperature drops, so the steam must be turned off and the fuel burned with a forced draft until it is nearly white-hot. The process is then reversed. The production of water-gas is therefore intermittent.

Water-gas burns, producing a great deal of heat but very little light unless burned in connection with Welsbach mantles. The gas is largely used for cooking and lighting; it is also used in the production of methyl alcohol and hydrogen. To increase its luminosity, it may be mixed with unsaturated hydrocar-

bons, such as ethylene and benzene. Oil-gases are well adapted to this use. Water-gas thus treated is called carburetted, or oil-enriched, water-gas. Since water-gas contains a high percentage of carbon monoxide, it is much more poisonous than coal-gas.

Producer-gas (Figure 28) is manufactured when coal burns under such conditions as to yield a large

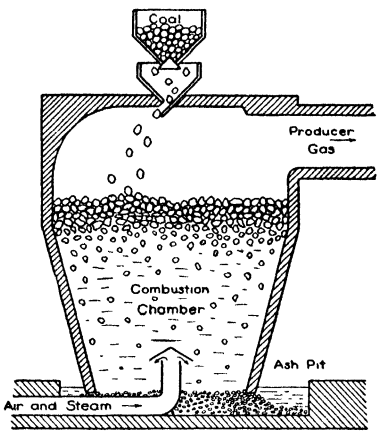


FIGURE 28
Manufacture of Producer Gas

quantity of carbon monoxide. As producer-gas contains nitrogen (from the air), it has low heating value, but the cost of production also is low.

When air and steam together are forced through beds of hot coal, a fuel gas containing hydrogen, as well as carbon monoxide and nitrogen, is obtained. These gases can be made from a low-grade coal, even lignite. They give a uniform heat and require no stok-

ing, and are extensively utilized for running gas-engines, and in connection with a large number of metallurgical operations.

A kind of producer-gas, called blast-furnace gas, is formed in the reduction of iron ore; it is taken from the top of the blast-furnace and is utilized to operate gas-engines.

5 Light-giving Flames; Gas-burners

It is a matter of common observation that some flames are very luminous and others are virtually non-luminous. Thus, ethylene and acetylene burn with luminous flames, while hydrogen, carbon monoxide, and methane (natural gas) in burning produce but little light. How may this fact be explained? An explanation to cover all cases of luminosity cannot be given. It may be stated in general, however, that the luminosity of flames is dependent upon, or influenced by, the following factors:

(1) The glowing of solid matter, such as carbon. A hydrocarbon such as ethylene breaks down when heated, yielding carbon. The luminosity of flames of burning hydrocarbons is due largely to solid particles of carbon heated to incandescence. This can be shown by holding a porcelain dish in the flame of burning ethylene or acetylene. A deposit of soot (carbon) is obtained upon the dish. Ethylene and acetylene are better light-producers than methane because they are richer in carbon. To increase the luminosity of the flames of natural gas and water-gas, the gases may be burned in contact with the Welsbach mantle, which consists

of 99 per cent of thorium dioxide (ThO_2) and 1 per cent of cerium dioxide (CeO_2). The oxides are heated to incandescence, and glow brilliantly.

(2) That the density of the burning gases has an influence upon the luminosity of flame, was observed by Frankland about 1868. He noticed that a flame of a candle burning on the top of Mont Blanc emitted much less light than when burning in the valley below. Frankland conducted various experiments, and arrived at the conclusion that dense gases and vapors become

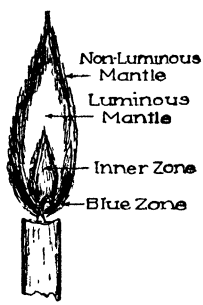


FIGURE 29
The Candle Flame

"luminous at a much lower temperature than the same gases in a more rarefied condition."

(3) The luminosity of a flame may be increased by heating the gas before combustion. The structure of flame is of interest. When a candle burns, the hydrocarbons are drawn up through the wick by capillary action, and vaporized. The inner zone consists of unburnt gas. Above and surrounding this zone there is a luminous mantle (partial combustion), and outside of this a non-luminous mantle (complete combustion). At the base of the flame there is a blue zone (Figure 29).

The Bunsen burner allows air to enter at the side holes and mix with the gas before combustion occurs, which results in a non-luminous flame, for the liberation of carbon is prevented, due to the fact that the air cools the middle zone of the flame, thus preventing the dissociation of the ethylene.

The upper oxidizing zone is at the top of the flame, and the fusing zone is somewhat more than one third from the bottom of the flame and equidistant from the inside and the outside of the mantle, which is

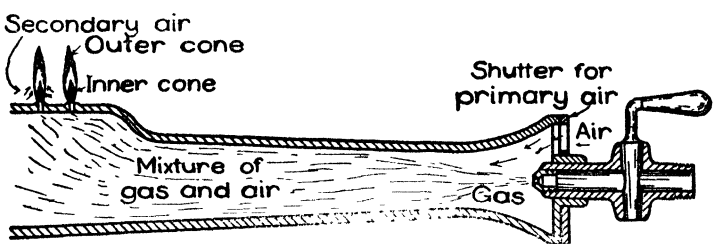


FIGURE 30

Burner for Gas Range
The air must be properly regulated

broadest at this point. This is the hottest part of the flame (1500° C.).

An important reducing zone is located in the inner border of the fusing zone, next to the dark cone. It may be shown that the inner cone of the Bunsen burner contains unburnt gas by inserting in it one end of a glass tube and igniting the gas as it issues from the other end. By lowering a wire gauze in the flame a red-hot ring is produced, showing that the interior of the flame is at a low temperature. Likewise, paper is charred in the form of a ring when pressed down for

a moment upon the flame of the burner. The flame of the Bunsen burner sometimes strikes back. This phenomenon can be produced by gradually turning off the gas until a point is reached where there is too much air in proportion to the gas. The result is that an explosive flame travels down the tube; *i.e.*, the flame strikes back. In order that the gas may burn quietly, it must be mixed with the proper proportion of air. The burners on a gas range are modified Bunsen burners (Figure 30). When the air-holes of the Bunsen burner are closed, the flame is luminous ("smoky"), due to incomplete combustion.

6 Coal-Tar and Dyes

Coal-tar, once regarded as a dirty, evil-smelling, useless material, is the source of about a dozen primary products, and from these thousands of compounds are produced, including aniline dyes, drugs, explosives, etc. Slosson says: "The chemist puts his hand into the black mass, coal tar, and draws out all the colors of the rainbow." The wonders of coal-tar are expressed in the following lines from "Punch":

> There's hardly a thing that a man can name
> Of use or beauty in life's small game
> But you can extract in alembic or jar
> From the "physical basis" of black coal-tar—
> Oil and ointment, and wax and wine,
> And the lovely colors called aniline;
> You can make anything from salve to a star,
> If you only know how, from black coal-tar.

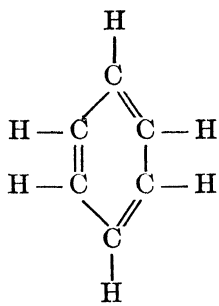
From coal-tar ten "crudes" (benzene, toluene, naphthalene, anthracene, carbolic acid, etc.) are obtained, and from these about three hundred "intermediates" are produced, and from the intermediates about nine hundred dyes, which yield about five thousand brands.

The first coal-tar dye, known as mauve, was produced by W. H. Perkin of England in 1856. As is well known, the Germans have led in the production of coal-tar dyes, but it is of interest to know that the American drug and dyestuff industry has developed rapidly in recent years. In 1914 the domestic product was valued at $2,500,000, but in 1917 the value was over $57,000,000. C. H. Herty reported in 1924 that fully 96 per cent of the American consumption is being supplied by the domestic industry, and that the quality of the dyes is fully equal to that of the foreign product. In 1917 the average price of dyes per pound was $1.26, but in 1923 it was less than $.55. The production of dyes of various hues and of excellent quality was the greatest triumph of American chemists in connection with the World War, for the problem was an exceedingly complicated one. The manufacture of dyes is closely related to the production of explosives: for instance, toluene (toluol) is the basic substance required in the production of trinitrotoluene, or TNT. From toluene numerous dyes may be produced. It took Germany about half a century to establish her dye industry, but in 1914 she monopolized it.

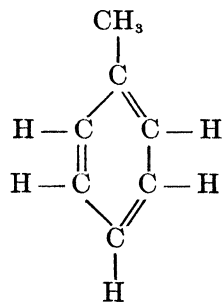
The substances produced from coal-tar are called the aromatic or closed-chain compounds. Benzene may be regarded as the starting-point in the preparation of

closed-chain compounds, just as we regard methane as the fundamental compound in building up straight-chain compounds.

The properties of benzene and its derivatives are best explained by assuming that the six carbon atoms of the compound are joined together in a ring. The structural formulas of benzene and toluene may be written thus:



KEKULE'S FORMULA FOR BENZENE



TOLUENE, OR METHYL BENZENE ($CH_3.C_6H_5$)

The use of benzene in motor fuel as an anti-knock takes the place of tetraethyl lead.

Aniline is a derivative of benzene and is the parent substance from which innumerable dyes may be produced.

Alizarin is the active principle of madder, which may be obtained from madder root. Madder is an Old World perennial plant which has furnished Turkey red for centuries. Alizarin is now produced more economically from anthracene, so the madder fields of France have been put to other uses.

Indigo is one of the oldest and fastest of dyes. As late as 1897 India devoted nearly a million acres to

the cultivation of the indigo-plant; but it is now produced principally from naphthalene, familiarly known as moth-balls.

The world owes a great debt to Perkin for the discovery of mauve, or aniline violet. According to C. M. Stine, more than two million men and women in the United States each year produce goods valued at more than three billion dollars, all dependent on dyes. In 1906, just fifty years after Perkin's discovery of the first coal-tar dye, a great jubilee celebration was held in London to commemorate the event. Following this celebration, Perkin accepted an invitation to visit the United States, and among the various gatherings held in his honor was a dinner tendered him in New York, at Delmonico's. On this occasion the writer well recalls that the chemists wore aniline violet ties with their evening clothes. Dr. W. H. Nichols presented Sir William with the first impress of the Perkin medal.

CHAPTER XXIII

THE FARMER'S DEPENDENCE ON CHEMISTRY

Consider the lilies of the field, how they grow; they toil not, neither do they spin.

And yet I say unto you, That even Solomon in all his glory was not arrayed like one of these.—Matthew VI. 28-29.

1 Food for Plants

Did you ever pause to consider the fundamental importance of agriculture? According to a recent report of the National Industrial Conference Board, Inc., our agricultural industry exercises normally a purchasing power of nearly ten billion dollars annually for goods and services produced by others. In 1919-20 the current value of the total capital invested in agriculture was seventy-nine billion dollars, which was greater than the combined investment in our manufacturing industries, railroads, mines, and quarries. We may regard agriculture as being the basic industry of mankind. The fundamental wealth and progress of a great country, such as the United States, depends in a large measure upon the fertility of the soil, and the growth of plants in field and garden are based largely upon the science of chemistry.

Plants, in their growth, are able to utilize the lifeless, inorganic materials found upon the surface of the earth, whilst animals are dependent either directly or

indirectly upon plants. A tree, for instance, stands in the same place, perhaps for centuries, receiving its food from the air and soil, the former supplying carbon dioxide and water and the latter inorganic salts. The foods required by plants are rather simple as compared with those utilized by animals. Plants have a much greater synthetic power than animals. Thus, they have the ability to synthesize starch and cellulose from carbon dioxide and water, and proteins from ammonium nitrate and other substances.

It is one of the marvelous facts of biology that the same soil, air, water, and sunshine are able to produce not only such useful plants as wheat and maize, but flowers of exquisite beauty and fragrance, such as the lily and the rose. They are supplied with the same elements, but we know virtually nothing about Nature's method of producing such a variety of plant life, nor really what life is. As expressed by Tennyson,—

> Flower in the crannied wall,
> I pluck you out of the crannies,
> I hold you here, root and all, in my hand,
> Little flower—but if I could understand
> What you are, root and all, and all in all,
> I should know what God and man is.

The ultimate source of our food is plants, which in turn are produced in Nature's laboratories exclusively from soil, air, water, and sunshine. In the growth of farm crops, only thirteen elements out of the ninety known ones appear to be necessary: namely, *hydrogen, oxygen, carbon, nitrogen, chlorine, potassium, sodium, calcium, magnesium, iron, phosphorus, silicon, and*

sulphur. Only five of these are metals. Hydrogen, oxygen, and carbon make up the bulk of the plant, and they are freely supplied by the air and water. The other elements are supplied in the form of their salts, and are assimilated from the soil by means of the roots of plants. In general, for most green plants, the salts of potassium, calcium, magnesium, and iron, supplied in the form of nitrates, sulphates, and phosphates, together with carbon dioxide and water, are usually adequate for complete growth and reproduction.

Protoplasm, a very complex, jelly-like material, is the basis of the cells of organisms. It is composed of carbon, hydrogen, oxygen, nitrogen, and other elements, being somewhat similar in composition to albumin, or the white of egg. Protoplasm circulates in the cells of plants as well as animals. Chlorophyll, the green coloring matter found in plant cells, is also a very complex material. Without it the higher orders of plants are not able to feed upon inorganic matter. Non-green plants, such as fungi and mildew, procure their food from other sources, such as dead organic matter. Magnesium is an essential constituent of chlorophyll, and iron is in some way associated with its formation. It is well known that when green plants are deprived of iron the leaves turn pale green or yellow, but health may be restored by adding iron to the soil or by spraying the leaves with salts of iron.

2 Photosynthesis

When a green plant is exposed to sunlight, certain rays are absorbed, and, in the presence of the little

bodies called chloroplasts, important carbon compounds are synthesized from the carbon supplied by the carbon dioxide of the air. This process is called photosynthesis. Carbon dioxide and water are very closely related to plant life, for they are the raw materials from which plants are able to synthesize such carbohydrates as cellulose, starch, and sugar. The formation of the carbohydrate glucose, a simple sugar, may be represented thus:

$$\underset{\text{Carbon dioxide}}{6CO_2} + \underset{\text{Water}}{6H_2O} = \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Oxygen}}{6O_2}$$

Professor Willstätter of Munich has made the interesting discovery that the chlorophyll of plants and the hemoglobin of blood may be regarded as being derived from a common substance, namely, ætioporphyrin ($C_{31}H_{36}N_4$). By chemical treatment of chlorophyll and of hemoglobin Willstätter is able to produce ætioporphyrin. Chlorophyll is a complex magnesium compound, while hemoglobin contains iron. It is noteworthy that chlorophyll releases oxygen from carbon dioxide, whilst hemoglobin takes up oxygen. It is also interesting to know that Willstätter has studied many flowers of variegated colors, and he finds that these colors have as their basis a common substance, namely, cyanidine.

The simplest carbohydrate capable of being formed by the action of a single molecule of carbon dioxide upon a molecule of water is formaldehyde (CH_2O). It is of much interest to note that formaldehyde has been found in plant tissues. In photosynthesis there is evidence that formaldehyde is formed and that six

molecules of this compound come together to form a molecule of a simple sugar, such as glucose:

$$\underset{\text{Formaldehyde}}{6CH_2O} = \underset{\text{Glucose}}{C_6H_{12}O_6}$$

E. C. C. Baly, an English chemist, succeeded in 1924 in producing formaldehyde by exposing carbon dioxide and water to short waves of ultra-violet light. When the solutions in which aldehyde is produced are made slightly alkaline, a syrup is obtained, which contains sugars very similar to those occurring in plants. Some day an abundant supply of sugar may be produced by synthetic methods. The fundamental fact of photosynthesis is that plants are able to convert carbon dioxide and water, which have no fuel value or energy value for life, into carbohydrates which possess a high fuel value, and are therefore available for the production of energy in organisms. Solar energy is stored up in the form of food and fuel. It has been said that thirty men in a factory the size of a city block can produce in the form of yeast as much food value as one thousand men working on seventy-five thousand acres under ordinary agricultural conditions. While this may be true, it should not lead us to the notion that factories and sunshine are going to produce most of the foods which are now grown on the farm.

The process of respiration is characteristic of all living things, whether animals or plants; and so far as we know all living plants give off carbon dioxide as do animals. Green plants absorb carbon dioxide in sunlight and give it off in darkness. Microscopic examination of the green pigment of leaves reveals the pres-

ence of exceedingly small particles of a body known as chloroplast, which is distributed through the protoplasm of cells. The chloroplast is the most important, at the same time the most minute, factory known; for without its operation all life would perish. In this tiny factory cellulose, starch, sugars, etc., are produced. Indeed, carbon fuels, which we burn to produce energy, were once synthesized in this factory. The chloroplast transforms the energy of sunlight into the storable form of carbon compounds.

Experiments have been carried out to determine the effect of artificial light upon the growth of plants; but no artificial light has been found that compares with sunlight in both intensity and quality. Chlorophyll is green because the green part of the spectrum is least absorbed, which suggests that it may be the red portion of the spectrum that is most effective in photosynthesis. It has been observed that when sunlight is employed as the source of light, photosynthesis is most marked in the red part of the spectrum. As the result of carefully conducted experiments, Fritz Schanz has concluded that light of short wave-lengths, and especially ultra-violet rays, are detrimental to the growth of plants. Schanz therefore recommends for use in greenhouses a yellow glass—Euphos glass—which cuts off the ultra-violet rays.

It should be added, however, that the intensity of the ultra-violet rays reaching the earth's surface is relatively low. It is an interesting and important fact that ultra-violet light is very effective in killing single-celled organisms and particularly bacteria. It may be employed, therefore, in sterilization. Scientists have

also conducted experiments to determine the effect on growing plants of increasing the carbon dioxide concentration of the air. At Essen, Germany, for instance, flue gases were purified and the resulting carbon dioxide piped into fields of sugar-beets. It is reported that there was an improved growth and yield of beets.

3 Chemistry and the Soil

Knowledge as to the nature of inorganic compounds required for the growth of plants is obtained by burning the plants and analyzing the ashes. Analysis of the ash of the rye-plant, for example, shows it to contain potash salts, lime, magnesia, phosphoric acid, silica, sulphuric acid, sodium chloride, and oxide of iron. In order, therefore, for such a plant as rye to grow, all these components must be in the soil. The ashes of other plants vary more or less in composition. Some of these components, such as oxide of iron and silica, are always available in abundance in the soil, whilst others are not. About 1840, Justus von Liebig showed for the first time that the soil will become exhausted unless phosphoric acid (as soluble phosphates), nitrogen (usually as nitrates or ammonium salts), and potash salts are supplied to it; hence the use of artificial fertilizers. Liebig discovered the connection between the soils and crops, or the principle "to give back to the soil by artificial means those substances which are removed by the growth of plants."

While it is true that many of the early classical writers, such as Cato, Vergil, and Pliny, wrote extensively on the practice of farming, very little was known

about the scientific care of the soil until after the year 1840 A.D. As stated by R. W. Thatcher, agriculture in all nations and in all ages was on a constantly declining scale as the first virgin fertility of the soil was exhausted, until the science of chemistry was developed and an exact scientific knowledge of what are the principles of plant-nutrition and of soil-exhaustion was developed.

4 Nitrogen, Potassium, and Phosphorus as Plant Foods

Sir Daniel Hall recently told the British Association for the Advancement of Science that there will be a world-wide shortage of food unless scientific research leads to an increased production. At present the agricultural system of the United States produces sufficient food to sustain about 140,000,000 people, which is probably approximately the population our country will have twenty-five years hence. It is estimated that the domestic food industry will be eventually called upon to support a population of 300,000,000. In order that such a vast quantity of food may be produced, it will be necessary to employ the most intensive and scientific methods of agriculture. Greater and greater demands will be made upon the chemist, not only to feed the plants, but also to protect them from diseases and pests.

Nitrogen is an essential constituent of all proteins and therefore of protoplasm, the active material present in every living cell. In order that plants may grow, the soil must be supplied with nitrogen, the ultimate

source of which is the atmosphere. In case of nitrogen starvation, the leaves of plants are yellowish and stunted in growth; but an abundant supply of nitrogen produces a rank growth and a rich green foliage. It is a common saying that nitrogen makes foliage.

The analysis of plant-ashes gives no information as to nitrogen, because the compounds of nitrogen are volatilized either unchanged or in combination with other elements when the plants are burned.

The "cycle" of nitrogen in nature has been considered. Plants cannot assimilate nitrogen by their leaves as they do carbon dioxide. In general, it may be stated that nitrates and ammonium compounds are the only sources of nitrogen for the majority of green plants.

It is estimated that a ton of wheat takes from the soil about forty-seven pounds of nitrogen. It is interesting to note that England has increased the average yield of wheat from six to thirty-two bushels per acre in the last seven hundred years, a part of this increase being due to fertilization. Belgium and Germany produced, in 1913, thirty-five bushels per acre, while in 1913, the average production in the United States was only fifteen bushels.

The chief nitrogenous fertilizers are sodium nitrate (Chile saltpeter), calcium nitrate, ammonium sulphate, and calcium cyanamide.

Nitrogen is also supplied by the decay of nitrogenous organic matter. Plant and animal residues are destroyed by bacteria, some of which produce ammonia, a portion of which is transformed by soil bacteria, first into nitrites and then into nitrates.

The soil is enriched by the growth of leguminous plants, such as clovers, peas, and beans. It was known before the Christian era that the yield of grain could be increased by growing a leguminous crop on a field the year before grain was produced. The principle of crop rotation is a very valuable one in farming.

Potassium is another soil element essential for the growth of plants, for without an adequate supply of it the general tone and vigor of the plants are lowered. Potassium is not a constituent of carbohydrates (starches, sugars, etc.), but in some mysterious way it is intimately associated with their production; hence the popular saying that potash makes starches and sugars. Potash is of great importance in the growth of sugar-beets, potatoes, etc. In case of potash starvation the vigor of the plant is much reduced, and it is more susceptible to attack by parasites. Potash was originally obtained as potassium carbonate by treating plant-ashes with water. This partially explains why wood-ashes are useful as fertilizer. Potash salts were expensive until 1860, or until the great Stassfurt deposits were utilized. Before the war Germany was producing potash salts (calculated as K_2O) at the rate of about one million tons per year. The chief potassium salt obtained from these deposits is the chloride (KCl); it is extensively used as a fertilizer. Considerable potassium sulphate is also employed as a fertilizer.

Phosphorus is of the highest importance in the feeding of plants. The exact function of this element in plant-nutrition is not understood, but an adequate supply of phosphorus stimulates the development of the roots and hastens the process of ripening. It is

especially abundant in the seeds of plants; hence the saying that phosphorus makes seeds.

Phosphoric acid is supplied to plants in the form of soluble phosphates. Phosphates are obtained chiefly from phosphate rock (Florida phosphate), bones, and the mineral apatite. These phosphates are virtually insoluble in water, but about 1840 Sir John Lawes of England discovered that when bone meal or phosphate rock is treated with sulphuric acid, the product is much more effective than the untreated material in the growth of plants; and in 1842 he took out a patent for the manufacture of superphosphate, or soluble phosphate. This process now demands enormous quantities of sulphuric acid, for superphosphate of lime is employed on a vast scale in the fertilization of plants.

5 Compost and "Indirect" Fertilizers

Barnyard manure, or compost, is most helpful in agriculture. A ton of manure usually contains about six pounds each of potash and phosphoric acid, and eight pounds of nitrogen (chiefly as urea and proteins). Bacteria play an important rôle in the transformation of manure. Urea, for instance, is transformed by an enzyme into ammonium carbonate:

$$\underset{\text{Urea}}{CO(NH_2)_2} + \underset{\text{Water}}{2H_2O} = \underset{\text{Ammonium carbonate}}{(NH_4)_2CO_3}$$

It is reported that Dr. James B. Sumner of Cornell University has isolated the enzyme (urease) which converts urea into ammonium carbonate. He obtained

it from the jack bean. It was prepared in the form of octahedral crystals, and is a protein. Urease is the first enzyme to be prepared in the pure state. The smell of ammonia is very common around barn-yards; for ammonium carbonate is unstable, one of the products of decomposition being ammonia. It may be that synthetic urea will be the chief nitrogenous fertilizer of the future. The proteins and similar bodies yield ammonia. When manure is scattered on the ground, soil bacteria assist in the oxidation of ammonia to nitrates.

Some substances which are added to the soil are not assimilated by the growing plants. Thus, gypsum ($CaSO_4.2H_2O$) is employed extensively as an indirect fertilizer, about one hundred pounds per ton of manure being used. The salt is very sparingly soluble in water, but it interacts with the ammonium carbonate produced from the urea, forming ammonium sulphate and calcium carbonate.

Ammonium sulphate is much more stable than ammonium carbonate, and calcium carbonate is only slightly soluble. While gypsum "fixes" the ammonia of manure-piles, slaked lime would liberate it.

The acidity of a soil may be neutralized by the addition of air-slaked lime or calcium carbonate. Soils may be naturally sour, or the acidity may be brought about by the use of too much fertilizer in the form of sulphates, such as sulphate of ammonia.

It should now be clear to the reader that the growth of plants depends upon chemical change. First, the inert, lifeless materials of the earth's surface are transformed into soluble matter and thus rendered available for plant-nutrition. Then, in the growth and

development of plants, a marvelous manufacturing process takes place whereby the plant fabric is built up and materials suitable for food are produced.

6 Bacteria on the Farm

There are many kinds of micro-organisms in the soil, bacteria being numerically the most important component of the soil micro-flora. It is now well known that micro-organisms play a major part in the production and maintenance of vegetation. The processes of decay, putrefaction, and fermentation, so important on the farm, are closely related to micro-organisms. The soil consists of innumerable earthy particles of varying sizes, each particle being surrounded by a thin layer of moisture. Within this film of moisture there are active micro-organisms, which play an important rôle in the growth of plants. The soil contains a mixture of culture media, which are ordinarily principally found within the five or six inches of the surface soil. In humic soils, very few bacteria are found at a depth below three or four feet.

According to J. G. Lipman, the average acre of cultivated land contains in the humid regions something like twenty tons of organic matter, which is constantly being attacked by micro-organisms, carbon dioxide, water, nitrates, sulphates, etc., being produced. While ammonia is produced, it does not accumulate in the soil, for it is oxidized to nitrous and nitric acids, the final product in the soil being a nitrate, most commonly calcium nitrate. This natural process of nitrification is of great importance, and it is brought about

by the agency of soil bacteria. The rôle played by symbiotic bacteria in the fixation of atmospheric nitrogen has already received adequate consideration (in Chapter XIII). It is estimated that cow-peas during a season of growth fix from ten to fifteen pounds of nitrogen per acre, while alfalfa or sweet clover may fix from two hundred to three hundred pounds of the element per acre. By plowing under clover, the soil is greatly enriched.

An immense quantity of carbon dioxide finds its way into the air as the result of chemical changes in organic matter, induced by micro-organisms. We have already seen how closely related carbon dioxide is to the growth of plants.

Science has devised ways and means for a certain amount of control over soil bacteria. For instance, such chemicals as formaldehyde, carbon disulphide, and copper sulphate are sometimes employed to rid soil or seed of a large part of their micro-organisms. Greenhouses are quite commonly disinfected with formaldehyde or carbon disulphide. Soil-inoculation is now not an uncommon practice. This means that large numbers of specific organisms are introduced into the soil in order to accomplish certain ends. Soil micro-organisms, lowly though they be, play the important part of restoring to circulation the elements locked up in plant and animal matter.

Our dependence on fermentation is very great, especially in agriculture. The formation of lactic acid by the souring of milk, the transformation of cider into vinegar, bread-making, the production of silage from green corn, and the disposal of sewage are based upon

fermentation processes, which involve many chemical changes. It should be stated that under the term micro-organisms are included many kinds of bacteria, yeasts, and the common molds and other fungi. All plants and animals contain enzymes. (See Chapter XI.) These are catalysts upon which fermentation and certain other processes depend.

Years ago bacteria were the butts of jokes—like that of the wag who said that "in Germany they were called germs, in France parasites, and in Ireland microbes." We now know that micro-organisms have to be reckoned with most seriously.

The production of silage from green corn affords an excellent illustration of the action of micro-organisms and enzymes. Silage is the chief food of dairy cows during the winter months. It is produced by a fermentation process. There are two classes of fermenting agencies associated with green corn—micro-organisms, on the outside of the plant, and enzymes, which are inside. While the corn is standing the micro-organisms are ordinarily dormant, and there is a sort of balance between these and the enzymes inside. But when the green corn is packed in silos, the equilibrium between the two classes of ferments is disturbed, and in the course of a few days acid-forming bacteria are in control. It is estimated that there are about two billion bacteria in a thimbleful of silage after the fermentation has gone on for from three to eight days. In the course of time the growth of bacteria is checked, and a product is obtained which keeps well for months. Silage is a cheap and nutritious food. There are about half a million silos in the United States.

7 Plant Pests and Diseases

Plants are subject to many kinds of diseases and pests, and it is partly the business of the chemist to find remedies for these. According to Lord Bledisloe, from 15 per cent to 20 per cent of the world's crops is lost through insects and fungoids; and it is estimated that the farmers of the United States spent $1,600,000,000 in the year 1925 to combat insects and grubs. C. R. Norton, of the Boyce Thompson Institute for Plant Research, at Yonkers, New York, has listed more than two hundred seed-borne parasites. It is necessary to wage an eternal chemical warfare to save the crops.

Insects which prey upon plants may be divided into two classes—sucking insects and chewing insects. The former puncture the plant or its fruit in order to obtain the juice, while the latter eat the foliage.

As a rule, insecticides and fungicides are chemical compounds or mixtures of compounds. Insecticides are divided into poison sprays, or stomach poisons, and contact poisons. The former kill when taken internally, while the latter destroy life by mere contact. Poison sprays usually contain some form of arsenic compound. Finely divided lead arsenate in suspension in water is used on a very large scale and is exceedingly effective. Calcium arsenate is cheaper than lead arsenate, and it is employed for fighting the boll-weevil, so destructive to the cotton-plant, and the potato-beetle. The cotton-plant is dusted with calcium arsenate in the form of very fine powder dropped from airplanes.

Pyrethrum is very effective as a contact insecticide.

It is prepared by pulverizing the flower heads of certain plants belonging to the genus chrysanthemum. Oil emulsions also are extensively used. The emulsion is prepared by adding chemicals, such as fish-oil soaps, to the oil. A soap film is formed around the droplet of oil. Nicotine, an alkaloid occurring in tobacco, is rapid and effective. Lime-sulphur is very extensively employed for scale insects. It may be prepared in concentrated form by boiling together water, sulphur, and slaked lime. The solution contains sulphides. Certain fumigants also are employed for destroying scale insects. Thus, hydrocyanic acid gas (Prussic acid) is used in greenhouses and on nursery stock. The liquid compound may now be purchased in glass cylinders. It should be borne in mind that it is a most poisonous substance! Carbon disulphide (CS_2) finds extensive application for insects that infest stored grain, or seed. Carbon disulphide, while very effective, is dangerously inflammable and is toxic to animals; so the United States Department of Agriculture now recommends for use a mixture of ethyl acetate and carbon tetrachloride. It is not inflammable, nor is it poisonous to man.

The loss from fungi is perhaps as great as that from insects. Sulphur and certain compounds containing sulphur and copper are generally employed. Sulphur was used more than a century ago for controlling mildew. Bordeaux mixture is very extensively employed as a fungicide, as in the growing of grapes. It is prepared by mixing a solution of copper sulphate with slaked lime. Its discovery was made by accident by Professor Millardet of Bordeaux, France. One day, while passing through a vineyard, he observed that

some of the vines had lost their foliage, while others had not. On investigation Professor Millardet learned that it was the practice of the master of the vineyard to cover the grapes along the border with a mixture of copper sulphate and lime in order to keep away marauders.

It is now fairly common to treat seeds, before planting, with certain chemicals in order to kill fungus spores. For this purpose a solution of formaldehyde or corrosive sublimate or powdered copper carbonate may be employed.

It is reported that the farmers of France are utilizing certain of the deadly "war gases" in fighting plant diseases and pests. Among these chloropicrin is quite promising.

CHAPTER XXIV

THE HOUSEWIFE'S DEPENDENCE ON CHEMISTRY

Nothing lovelier can be found
In woman, than to study household good.
—MILTON.

1 CHEMISTRY AND FOOD AND NUTRITION

THE dependence of the housewife on chemistry is very great, for chemistry is most intimately connected with everyday life. Whether we realize it or not, we are constantly carrying on chemical operations. The comfort and attractiveness of the modern home are largely dependent on chemistry. In a material sense, our homes would be poor indeed if the chemist should step out.

Some of the most valuable contributions of modern chemistry have been made in the field of food and nutrition; and it is now well recognized that a proper diet is closely related to the health and happiness of human beings.

Early man ate anything and everything available, such as meat, fish, grubs, insects, vegetables, and fruits. Before the discovery of fire and its application to cooking, food was eaten in the raw state. Primitive man lived very simply. John the Baptist had his raiment of camel's hair, and a leathern girdle about

his loins; and his food was locusts and wild honey. For many centuries civilized races have given much thought and attention to the preparation of innumerable articles of diet designed to satisfy the most refined taste and appetite. According to Doctor Johnson, "a man seldom thinks with more earnestness of anything than he does of his dinner." The selection of diet in accordance with scientific principles is, however, quite modern. It has come in connection with the marvelous development of chemistry, a great deal being due to chemical analysis and to animal experimentation. A brief study of food and nutrition should be profitable.

Food may be defined as "that which taken into the body, either builds tissue or yields energy."

The body may be compared to a machine, the material which is oxidized in each case furnishing power and heat. There are important differences, however, between the human machine and a steam-engine. The former is self-building, and self-regulating. The steam-engine is dependent solely upon the fuel which is supplied to it, while in the human organism the reserve material may be drawn upon to supply energy. Furthermore, a portion of the food supplied to the body is utilized in its repair or growth.

The food of man consists of the following constituents:

(1) *Proteins* (albuminous or nitrogenous foods). These form the chief constituents of lean meat, egg white, fish, the gluten of flour, etc. They build and repair tissues, and if only a little fat and carbohydrate is present, they serve as fuel.

(2) *Carbohydrates* (including starch and sugar) serve as fuel; partially transformed into fat.
(3) *Fats* (including certain animal and vegetable oils) serve as fuel; partially stored as fat.
(4) *Mineral Salts* (sodium chloride, phosphates of potassium and calcium, etc.) share in forming bone; assist in digestion; necessary for normal activity of tissues.
(5) *Water.* Constitutes more than two thirds of the body.
(6) *Vitamins* (accessory food substances) are necessary to health and growth.
(7) *Oxygen:* The "breath of life."

There are about fifteen chemical elements in the human body, oxygen furnishing about 65 per cent. Carbon, hydrogen, and nitrogen are also abundant. Calcium is the most abundant metal (2 per cent), and there is about 1 per cent of phosphorus. Some of the elements—*e.g.,* iron and iodine—are present in exceedingly small amounts, but they are vital.

According to the Food (War) Committee of the Royal Society, a diet must meet the following requirements:

(1) Its calorie (energy) value must be sufficient.
(2) It must contain certain minimum amounts of adequate proteins, carbohydrates, fats, mineral salts, and vitamins.
(3) It must correspond so far as practicable to the dietetic habits of the nation.

Animals are absolutely dependent upon plants for their food; also, the food of animals is, as a rule, much more complex than that of plants. The proteins, carbo-

hydrates, and fats are characterized by their high molecular weights, and some of them have very complicated structures. The synthetic power of animals is very limited. They are able, however, to synthesize fats from carbohydrates.

2 Proteins

The proteins are nitrogenous compounds. Without nitrogen there can be no flesh and no protoplasm, in fact, no life. The word protein is derived from a Greek word meaning "to take the first place," due to the fact that the great physiological importance of this group of substances was early recognized. Proteins are found in all living matter, and are present, therefore, in varying amounts in all natural foodstuffs. Since they form the main constituents of living animal tissues, they are most plentiful in animal foods such as meat, eggs, and fish. Proteins are the most complicated substances which have ever been investigated. The molecular weight of hemoglobin appears to be over 16,000.

All proteins contain carbon, hydrogen, nitrogen, oxygen, and sulphur, and a few contain phosphorus. Small quantities of other elements are found in certain proteins. The proteins are utilized mainly for building up animal tissues; but they are also very useful as a source of bodily energy. For providing the material for growth in the young animal and for repairing the waste tissues in the full-grown animal, they cannot be replaced by other foods. The animal proteins—meat, eggs, milk—are more valuable for this

purpose than are vegetable proteins; but the proteins of certain edible leaves are of good quality. Milk is of special value among protein-containing foods, particularly for children. There are thousands of proteins, which differ more or less in structure and quality. During digestion the giant protein molecules are split up into a large number of products known as amino-acids, which contain the amino group ($-NH_2$). These are absorbed and recombined in new proportions, forming other proteins which possess different properties and architectures. The proteins of food are therefore different from the proteins of the body.

3 Carbohydrates, Fats, and Oils

Carbohydrates and fats are the chief sources of energy. The term carbohydrate, as commonly used, refers to certain compounds containing carbon, hydrogen, and oxygen, in which the ratio of hydrogen to oxygen is the same as in water. These compounds might be represented, then, as being composed of carbon and water; hence the name carbohydrate (or hydrate of carbon). For example, the formula of glucose, $C_6H_{12}O_6$, might be written $6C.6H_2O$. This does not mean that a carbohydrate contains water, but only the elements of water.

The carbohydrate group is supplied by plants and is closely related to life, for it contains substances used as food and from which important fabrics, such as clothing and paper, may be manufactured. The carbohydrates are divided into the following classes:

The sugars (cane-sugar, glucose, levulose, etc.)
The starches (the most abundant of foods)
The celluloses (the principal substances of cell membranes and plant tissues)

Cane-sugar, or sucrose, is found chiefly in the sugar-cane and the sugar-beet; it also occurs in the sugar-maple and in honey. The sugar-cane was originally grown in India, Persia, and Arabia, and was introduced into southern Europe by the Arabs. The sugar-cane contains from 16 per cent to 18 per cent of sugar. Sugar was discovered in beet-root by the German chemist Marggraf in 1747. At that time there was about 6 per cent of sugar in the beet, but by cultivation the percentage has been increased from 14 per cent to 18 per cent.

Sugar is obtained from the sugar-cane by crushing the stalks between rollers; but the beets are cut into slices, and the sugar extracted by a diffusion process. After appropriate preliminary treatment, the sugar solution is evaporated under reduced pressure at about 65° C. to prevent decomposition of sugar. The syrup obtained, upon cooling, yields crystals of brown sugar, which can be refined by dissolving in water, filtering through bone-black, and evaporating in vacuum pans until sugar crystallizes out. Great progress has been made in the production of sugar, due largely to rigorous chemical control. In 1924-25, the world's production of sugar was over 23,000,000 tons, 35.4 per cent of which was from the beet. Americans are the greatest consumers of sugar. A century ago our average per capita consumption was about eleven

pounds, but to-day it is about one hundred pounds. The candy bill alone for the United States, in 1924, was estimated to be $500,000,000.

Glucose, or grape-sugar, is another sugar of much importance. It occurs in many sweet fruits, particularly the grape; also in honey. Glucose is manufactured on a large scale by boiling starch with a dilute acid. We may regard a molecule of water as uniting with one of starch to form a molecule of glucose:

$$\underset{\text{Starch}}{C_6H_{10}O_5} + \underset{\text{Water}}{H_2O} = \underset{\text{Glucose}}{C_6H_{12}O_6}$$

Glucose is a useful food, but it is not so sweet as cane-sugar. When glucose is persistently present in the urine, it is indicative of diabetes. In case of this disease there is a deficiency of insulin supplied by the pancreas, and the carbohydrates are not thoroughly burned. Just how the insulin acts is not known. When metabolism of sugar fails, fats and proteins cannot be properly digested or utilized. In case of diabetes, insulin is now administered subcutaneously, thanks to Dr. Banting and others, to make up for the deficiency of the substance in the body. Undoubtedly this treatment has already saved thousands of lives.

When a glucose solution is treated with yeast, alcohol and carbon dioxide are produced. Fermentation (Latin: *fervere,* to boil) is brought about by the catalyst zymase, an enzyme furnished by yeast. Glucose finds extensive use in the manufacture of confectionery, jams, and jellies.

Starch is the most abundant of all foods. It occurs in various plants, being stored largely in the seeds of

grains and the tubers of the potato. The following are the average percentages of starch present in the potato, cereals, maize, and rice:

Potato	15–20 per cent
Wheat, and other cereals	60–65 " "
Maize	65 " "
Rice	75–80 " "

Starch consists of minute colorless granules, which differ somewhat in appearance according to its source. In the United States, starch is obtained chiefly from maize, whilst potatoes are the source in Germany, and rice in England. The process of manufacture is largely mechanical. The softened or crushed material is washed so as to pass the granules of starch through a fine wire or silk sieve, leaving the gluten behind.

Starch is insoluble in cold water, but when it is treated with hot water the granules burst and the substance goes into colloidal solution; *i.e.*, the very finely divided particles are suspended in water. Colloidal solutions of starch are used in the laundry. Colloidal starch turns blue in the presence of iodine. Starchy foods are made more digestible by cooking. During the process of digestion, starch is first converted into the simpler sugars by the agency of the digestive fluids.

Fats and animal and vegetable oils contain the elements carbon, oxygen, and hydrogen. Like carbohydrates, they burn or undergo oxidation to form water and carbon dioxide, accompanied by a large output of energy. A fat may be formed by allowing a fatty acid, such as stearic or palmitic, to interact with glycerine, which is an alcohol. Fats belong to a class of organic

compounds known as esters. Now, an ester is formed by the interaction of an acid and an alcohol, just as a salt is formed by the interaction of an acid and an alkali. Ethyl acetate, for instance, is an ester produced by allowing acetic acid and ordinary alcohol to interact. It is a colorless liquid with a fruity smell, and is used in perfumery. Esters occur in plants, and are the sweet-smelling ethereal oils. They are now manufactured for use in perfumes and fruit essences.

In general, fats and animal and vegetable oils are mixtures of esters. When they are decomposed by heating with a solution of an alkali, soap and glycerine are obtained:

$$\text{Fat} + \text{Alkali} = \text{Soap} + \text{Glycerine}$$

Among important fats are stearin, palmitin, olein, and butyrin.

In almost every diet carbohydrates are the main source of energy, being especially abundant and cheap in the temperate climates. Indeed, they are by far the cheapest variety of food.

4 The Energy Value of Foods

The energy value of a food is determined in a bomb calorimeter, which means that we find out its heat of combustion. The bomb calorimeter consists of a closed vessel lined with a refractory material such as platinum or enamel. Oxygen under pressure is run into the combustion chamber, and the material to be burned is ignited electrically by means of a fuse-wire. The heat of combustion is imparted to a known mass

of water in which the bomb is submerged. The increase in the temperature of the water is noted by a thermometer. A calorie is the amount of heat required to raise the temperature of one gram of water one degree Centigrade. In the study of food and nutrition a calorie one thousand times greater is generally employed. It is the amount of heat required to raise one thousand grams (one kilogram) of water one degree Centigrade, and is written "Calorie." Professor W. O. Atwater and others have measured by means of the respiration calorimeter the amounts of energy evolved by foods during combustion in the body. Experiment has shown that the material which is thus oxidized yields the same amount of energy as it would if burned in the bomb calorimeter.

Fats yield about 4000 Calories per pound, carbohydrates 1800, and proteins about 1800. This means that a pound of fat (*e.g.*, butter) is equivalent in heat energy to a little more than two pounds of either a carbohydrate or a protein.

Fats are utilized mostly in the form of stearin, palmitin, and olein. Oily fats are more easily assimilated than are hard fats. Carbohydrates are more easily oxidized than fats. In order to secure complete oxidation of fat in the body, carbohydrates should be oxidized at the same time. Proteins assist the Eskimos in the complete combustion of fats. Fats are more sustaining than carbohydrates, but carbohydrates are more economical. The athlete is quickly supplied with energy after eating sugar, while a hibernating animal is sustained for a long period of time by the slow oxidation of stored-up fat. Sugar is readily absorbed from

the alimentary canal and is most useful for producing muscular effort. An examination of the blood of Marathon runners showed that the sugar content was below normal at the end of the race. The following year the contestants ate sugar during the race, which enabled them to finish in far better physical condition than formerly. The value of chocolate and other sweets to soldiers is well recognized. In case vigorous muscular effort has to be undertaken and sustained, it is necessary that the diet should contain not less than 25 per cent of its energy in the form of fat. For instance, the Canadian lumberman lives on a diet containing a large proportion of fat pork, the fat representing from 35 per cent to 40 per cent of the total energy of the food.

The value of a food to the body may be determined by finding its calorific value. In case the total energy given off by an individual in the course of a day is known, it suffices to supply him with a food capable of yielding the same number of utilizable calories. In reckoning the food requirements it is of course necessary to take into account waste and refuse. Under ordinary conditions this may be taken as about 10 per cent; *i.e.*, the food as purchased should have a utilizable calorific value about 10 per cent above that actually required by the individual. The energy requirement of a person depends, of course, upon his size, age, and occupation. A man at rest requires much less food than a man at work.

The Food (War) Committee of the Royal Society arrived at the following figures:

	Energy requirements	*Food requirements*
Tailor	2500 Calories[1]	2750 Calories
Bookbinder	2800 "	3100 "
Metal-worker or carpenter	3200 "	3500 "
Painter	3250 "	3600 "
Stone-mason	4400 "	4850 "
Wood-cutter	5000 "	5500 "

[1] Calorie = 1,000 calories.

These are the requirements for the "average man"—*i.e.*, a man from twenty-five to fifty years of age, weighing (unclothed) 145½ pounds, and 5 feet 7.4 inches tall. In these figures 300 Calories are allowed to cover the energy expended in traveling from a man's house to his place of work, and 10 per cent to cover the difference between food as digested and food purchased. The average food requirement for the seven classes of workmen is about 3300 Calories. The average brain worker is abundantly supplied by a diet yielding from 2200 to 2600 Calories, or approximately 1000 less than the average bodily worker.

The average working woman requires about 2650 Calories per day, while the requirement of the sedentary woman may be placed at 2100 Calories.

The diet of the brain worker should be light and digestible and should contain relatively more protein and less fat than that of the individual who earns his living by the work of his muscles.

The protein in the diet of the "average man," doing moderate work, may be placed at about 80 grams. According to the Royal Society Food Committee, the composition of the diet for the average man, at moderate work, should be as follows:

Protein	70 grams	=	280 Calories
Fat	90 "	=	810 "
Carbohydrates	550 "	=	2200 "
	Total		3290 Calories

This refers to that part of the diet actually utilized.

C. F. Langworthy gives the following dietary standard for a man in full vigor at moderate muscular work:

Condition Considered	*Protein—Grams*	*Energy—Calories*
Food as purchased	115	3800
Food eaten	100	3500
Food digested	95	3200

The average calorific value per gram of the three classes of foods may be taken as follows: Proteins, 4 Calories; carbohydrates, 4 Calories; and fats, 9 Calories. The values per pound may be obtained by multiplying these numbers by 453.6 (the number of grams in one pound).

5 Composition of Common Foods

The composition of food products varies greatly. That of some of the most common foods may be seen by reference to Figure 31 (see the Langworthy Charts, United States Department of Agriculture). The calorific value per pound is also shown. Thus, white bread has a calorific value of 1180 per pound; butter, 3405; whole milk, 315; and beefsteak (edible portion), 1090. According to these figures, one pound each of white bread, milk and beefsteak, and four ounces of butter would yield, when burned in the body, a total of 3436 Calories. It is quite easy to calculate from such charts

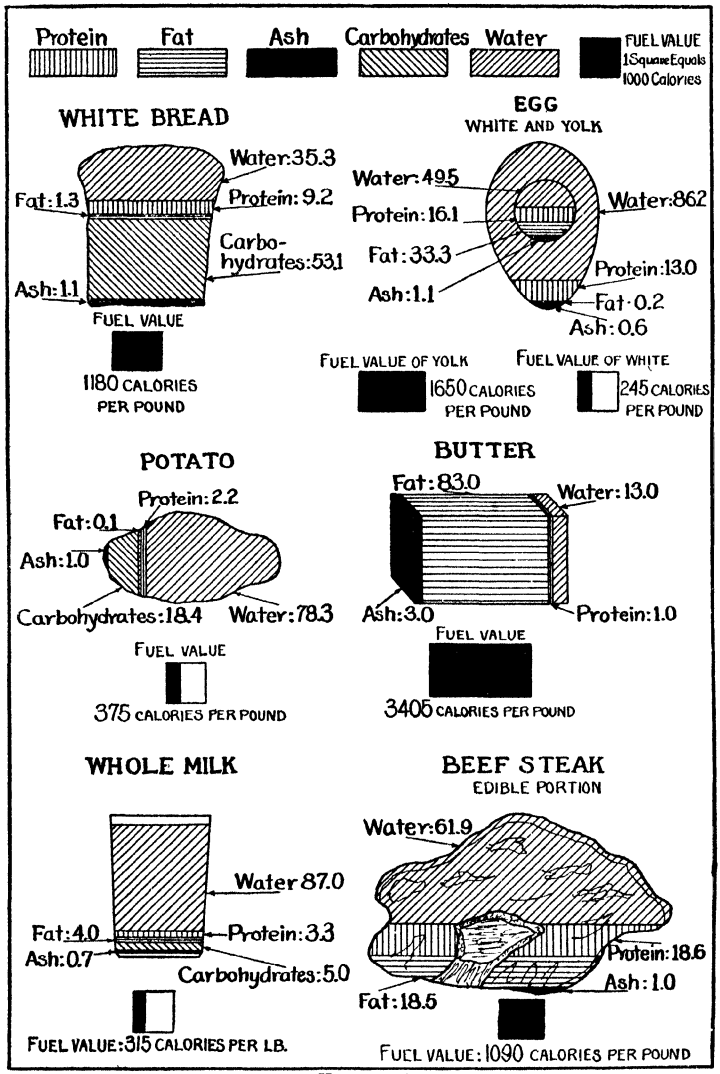


FIGURE 31

Chart Showing Composition of Food (see the Langworthy Charts, United States Department of Agriculture)

the total proteins, carbohydrates, and fats supplied by a diet; also, the total cost of food required to supply the bodily needs, provided the market value of each kind of food is known.

The composition of a few other common foods is given in the table below (Langworthy):

Food	*Protein*	*Carbo-hydrates*	*Fat*	*Water*	*Ash*	*Calorific val. per lb.*
Bacon	9.4	....	67.4	18 8	4.4	3090
Oatmeal (cooked)	2 8	11 5	0 5	84 5	0.7	280
Cream cheese	25 9	2 4	33.7	34 2	3 8	1885
Mackerel (fat fish)	18.3	....	7.1	73 4	1.2	620
Navy bean (dry)	22 5	59 6	1 8	12 6	3 5	1560
String-bean (green)	2 3	7.4	0 3	89 2	0 8	190
Apple (edible portion)	0.4	14 2	0 5	84 6	0 3	285
Corn	10 0	73 4	4 3	10 8	1 5	1685
Rice	8.0	77 0	2 0	12 0	1 0	1620
Peanut	25.8	24.4	38 6	9.2	2.0	2485

6 Vitamins and Mineral Matter

In recent years it has been discovered that animals require for their growth and health small quantities of certain accessory food substances termed vitamins. These substances are present in traces in nearly all fresh foods. In their absence growth may cease, and various diseases, such as scurvy, beri-beri, or rickets may be produced.

The vitamins are difficult to prepare, and their chemical nature and constitution have not been fully determined. Dr. E. V. McCollum has designated the various known vitamins by the letters of the alphabet, pending the time when their composition shall be exactly determined. They may be described as follows:

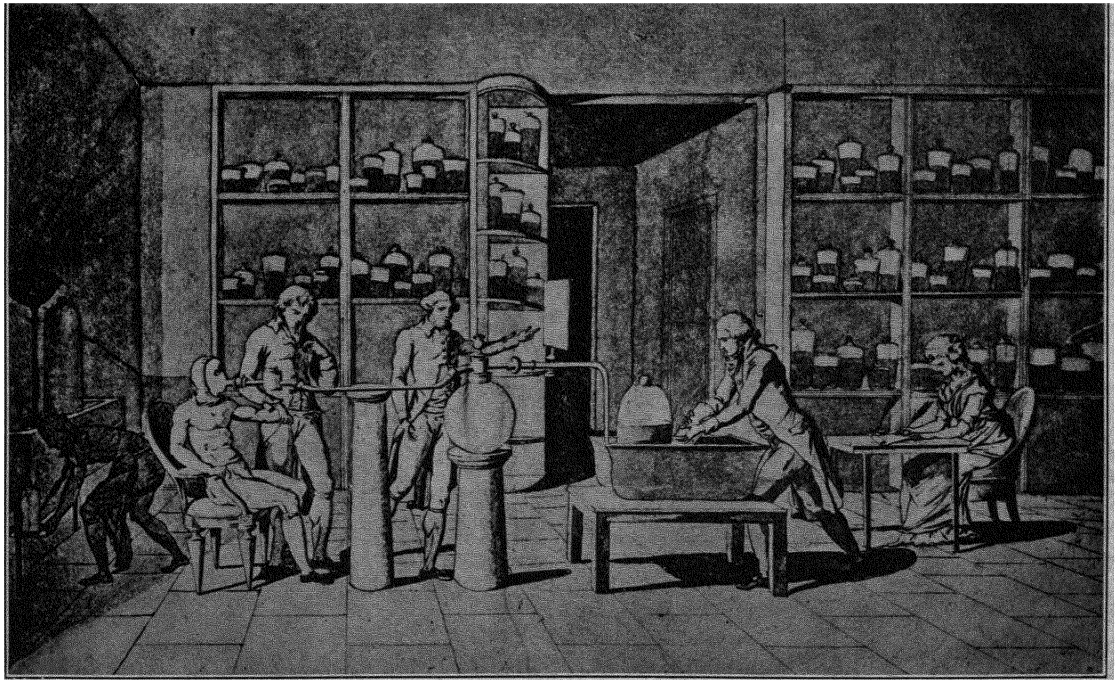
Vitamin A: growth-producing; prevents blindness.
Vitamin B: antineuritic; appetite-promoting.
Vitamin C: antiscorbutic (scurvy-preventing).
Vitamin D: antirachitic (prevents rickets).
Vitamin E: fertility-promoting.

Vitamin A (*fat-soluble A*). Where there is a deficiency of this the animal fails to grow; so the vitamin is called the growth-promoting accessory food factor. It accompanies certain fats and oils, such as cod-liver oil, butter, and fat of egg yolks. It is also present in whole milk, and is especially abundant in liver, sweetbreads, and kidney. Certain green leafy vegetables, such as spinach, lettuce, celery, and beet-tops, are especially rich in vitamin A. Children, in particular, require this vitamin. In the ordinary cooking of foods vitamin A is fairly stable; but prolonged heating in contact with air causes its oxidation and therefore its destruction. If the diet is deficient in vitamin A for a prolonged period, a disease of the eye known as xerophthalmia, of dietary origin, may develop, in certain cases leading to blindness. According to McCollum, a grandmother remedy long used in Japan consisted of giving the sufferers chicken livers or eel fats.

Vitamin B (*water-soluble B*). A lack of this vitamin leads to stunted growth, and to beri-beri in human beings. It is closely related to the nervous system; hence it is called the antineuritic vitamin. Beri-beri is a disease common in Asiatic countries where the people live largely on rice. Polished rice is lacking in vitamins. For instance, when birds are fed exclusively on polished rice, symptoms (including paralysis) typical of

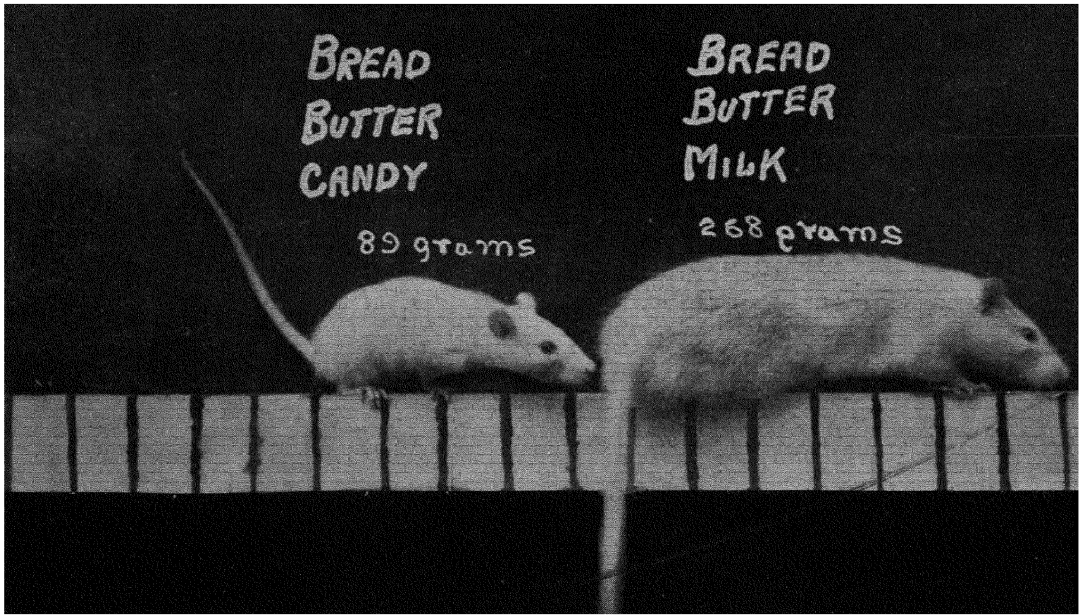
beri-beri develop. The disease is rapidly cured, however, by feeding the birds whole rice or rice polishings. The true cause of the paralysis of the nervous system of animals was discovered in 1897 by Dr. Eijkman, of Holland. Vitamin B is relatively abundant in plants, such as unpolished rice, tubers, and roots, leafy vegetables, fruits, in glandular organs of animals, and in cereal grains. It is lacking in refined mill flours and in animal and vegetable oils. Vitamin B is not readily destroyed by heating the foods in which it occurs.

Vitamin C (water-soluble C). This is the scurvy-preventing (antiscorbutic) vitamin. Scurvy was known to the Greeks and other ancient people. It has been very common in armies and navies. Captain Cook, in 1772, recognized the value of fresh food, and therefore supplied his crew with it. During his voyage of three years there was an absence of scurvy. Recognition of the vitamin character of the substance which prevents scurvy was not accomplished, however, until 1919-20. Fresh fruits and green vegetables are the chief source of vitamin C. We may mention in particular the citrus fruits, the tomato, celery, raw cabbage, and lettuce. There is little in nuts, meats, and grains, and especially in flour and cereal foods prepared by refining methods. Vitamin C is the least stable of the vitamins, and is liable to be destroyed when food is cooked, especially in contact with air. Pasteurized milk might lead to scurvy in the case of children unless given with orange juice or tomato juice, the latter being quite digestible and cheaper. According to Kohlman and Eddy, the antiscorbutic properties of canned fruits and vegetables may be preserved,



Courtesy of Dr. C. F. Languorthy

LAVOISIER'S RESPIRATION APPARATUS
From a Drawing by Madame Lavoisier.



Courtesy of Chemical Foundation, New York

A PRACTICAL LESSON IN DIETETICS

This illustration shows that it is better for under-nourished children to eat less candy and drink more milk.

provided they are protected from atmospheric oxygen in canning, which destroys vitamin C by oxidation. This may be accomplished by immersing the fruits or vegetables in water, slightly salted, for a few hours, which shuts off the air and also results in the removal of the oxygen of the vegetable tissues.

Vitamin D. This is the antirachitic vitamin, or the one which prevents rickets, a disease very common to children, particularly in certain industrial districts. Children suffering from rickets have abnormal bones and are anemic. Vitamin D is most abundant in cod-liver oil, and is contained in appreciable amounts in butter and in egg yolk. Rickets does not occur in the Arctic regions where the diet is principally fish or animals which feed upon fish. It is also true that the disease is very uncommon in the tropics, where the body is subjected to strong irradiation. The very short rays, or the ultra-violet rays, are the effective ones. It is believed that the antirachitic vitamin D is a modified cholesterol. It has been discovered that irradiation with ultra-violet light causes inactive vegetable oils to take on antirachitic properties. It also appears that the antirachitic potency of butter fat is owing to the consumption by the mother of irradiated food materials; and the irradiation of green vegetables, such as spinach and lettuce, increases their value as preventives of rickets. It should be noted that glass does not allow the ultra-violet rays of sunlight to pass; therefore, sunlight which has passed through glass has very little effect, if any, in preventing rickets.

H. M. Evans has discovered a fertility-promoting vitamin, which he termed vitamin X, but McCollum

calls it vitamin E. This vitamin is present in the wheat germ, oats, alfalfa, lettuce, and meat.

W. H. Eddy and his associates have prepared from yeast a white, crystalline substance called bios. It contains carbon, oxygen, hydrogen, and nitrogen. Bios is a powerful stimulant to growth, and it may be vitamin B.

To keep the body in health, it is necessary that it be supplied with an adequate amount of mineral matter. In the case of rickets there is a marked disturbance in the assimilation of calcium and phosphorus. These elements are especially necessary for the growing child in order that the skeleton may be properly formed. Calcium is the element which is most constant in amount in the blood. In case of rickets, the phosphorus content of the blood is below normal. Calcium and phosphorus are supplied by milk. Cheese is rich in calcium. Phosphorus is supplied by many other foods, such as eggs and meats; but in many cases the diet is deficient in calcium, as in the white bread, meat, potato, and sugar diet. Of the vegetable foods, only the leaves of plants are rich in calcium; they are also rich in vitamins. The leaves of certain plants are, indeed, a complete food. For instance, the bison, which once flourished on American plains, lived solely on grass, which reminds us that "all flesh is grass." It has been suggested by eminent authorities that it might be well to add a certain amount of calcium carbonate in the form of precipitated chalk to the common salt for use in shakers, thus insuring an adequate supply of calcium for the skeleton, teeth, etc.

The selection of a proper diet is a matter of prime

importance. According to the dictum of W. M. Bayliss, the English physiologist, "Take care of the calories, other things will take care of themselves." This means that if any reasonable diet be taken, including fruits, sufficient vitamins will be automatically obtained.

Chemistry has been of great service to the housewife in numerous other ways. For instance, it has made wonderful contributions toward furnishing metals and alloys for household use. It was just a century ago that aluminium was first isolated, and very little of the metal was produced before 1886. At one time it sold for $140 per pound, but now it is cheap, and common in every kitchen. Chemistry has been of great service in the sanitation of the home and in the disposal of sewage. Chemistry has also made scientific baking and cooking possible. It has provided us with a greater variety of clothing and household furnishings as well as with innumerable dyes that rival the rainbow in beauty. Likewise, it has furnished us with synthetic perfumes and flavors, thus turning certain products of black coal-tar into substances with odors as sweet as the rose. This fast-growing science has also supplied innumerable other things for the household, such as drugs and medicines for the closet, gaseous fuel, materials for extinguishing fires, soaps and bluing for the laundry, and with a great variety of toilet preparations.

*Those interested in a fuller study of diet could not do better than read an excellent little book entitled, "Food, Nutrition and Health," by McCollum and Simmonds, of the School of Hygiene and Public Health, Johns Hopkins University, Baltimore.

CHAPTER XXV

THE PHYSICIAN'S DEPENDENCE ON CHEMISTRY

Within the boundaries of even a minute cell there are dozens of different principles, myriads of molecules which defy the power of the finest optical instruments, but yield their secrets to the patient analytical and synthetic quest of the chemist.—J. S. HALDANE.

1 History of Medicine

THE medical art is commonly divided into internal medicine, or medicine proper, and external medicine, or surgery. Internal medicine is the province of the physician, while external medicine remains to the surgeon. In the present chapter, however, the term physician will be used in its widest meaning; *i.e.*, it will include anything pertaining to the art of healing or the treatment of disease.

The art of healing is very ancient. Before the periods of consecutive history the headmen of the tribes and the leaders of the religious orders prescribed for the sick. In ancient Egypt and India, medicine was subordinated to religion, the priests having been charged with medical functions. As we saw in Chapter I, some scholars hold that the name chemistry refers to the land of Chêmi (Egypt), which was the cradle of chemistry. It is said that chemistry had its origin in temples where priests conducted experiments for the prepara-

tion of medicines. Other scholars hold that the word chemistry is derived from a Greek word, signifying a mingling or infusion; for chemistry was employed in extracting the juices from plants for use in healing the sick.

The ancient Greeks and other ancient people possessed some knowledge of drugs and their uses. In Homeric poems there are references to the art of healing, and certain of Homer's heroes were skilful in surgery. In the age of Pericles lived Hippocrates (460-377 B.C.), the great physician, who is known as the "father of medicine." Hippocrates had a sound system, for it was based largely on observation. It has been truly said that "the medical art as we now practice it, the character of the physician as we now understand it, both date from Hippocrates." While 265 drugs were mentioned in his writings, he chiefly relied on diet, exercise, and natural methods.

Due to Greek influence, the Alexandrian schools in medicine became famous, probably surpassing the Greek original in the study of anatomy. Bodies of living persons—criminals condemned to death—were opened, and much was learned concerning the structure and functions of organs. It is believed that the Alexandrian practitioners in surgery and obstetrics could compare very favorably with those of modern ones.

Medical knowledge and practice were carried by the Greeks to Rome, about 200 B.C., and ultimately to the whole Roman world. Celsius was a renowned Roman physician, "the Cicero of medicine." Galen, a Greek who became the imperial physician at Rome, was

a most remarkable man. He dissected animals, propounded medical theories, enriched *materia medica* by the addition of about two hundred plants, and wrote extensively.

Two thousand years later Dr. O. W. Holmes said in a lecture before the Harvard Medical School: "I firmly believe that if the whole *materia medica* could be sunk to the bottom of the sea, it would be all the better for mankind and all the worse for the fishes."

Medicine declined in Europe during the Dark Ages, but the Arabians did much to preserve and advance the art during this period. They dominated medicine from the ninth to the close of the fourteenth century. Schools of medicine, often connected with schools of pharmacy and hospitals, arose in the Mohammedan empire.

During the monastic period of the Middle Ages pharmacy was largely in the hands of religious orders. Monks were forbidden to shed blood, so surgery was turned over to barbers, who advertised their calling by means of a spiral decoration representing the application of bandages. The familiar barber's pole is a survival of that early practice.

In the first half of the sixteenth century Paracelsus made an attempt to join medicine and chemistry. He taught that "the object of chemistry is not to make gold but to prepare medicines." Paracelsus was the great precursor of the medical chemists or of the iatrochemical school. He introduced into medicine mercury, iron, lead, arsenic, sulphur, and copper sulphate; also drugs, such as laudanum, still in use. In the course of time, however, the chemist and the doctor parted

company, and the former turned his attention to applied or industrial chemistry. Very little real chemistry was known before the days of Robert Boyle (1627-91).

2 Surgery and Anesthetics

Ancient surgery was extremely barbarous. The flow of blood was stopped by the application of a red-hot iron, and operations were commonly performed without anesthetics. Certain substances were known to produce anesthesia, but surgeons generally regarded them with disfavor. While ether was discovered in the thirteenth century, it was not until 1842, at Athens, Georgia, that the compound was first employed as an anesthetic in surgery. In 1800 Sir Humphry Davy discovered that nitrous oxide, or laughing-gas, has anesthetic properties. After breathing the gas, he wrote:

> Not in the ideal dreams of wild desire
> Have I beheld a rapture-wakening form;
> My bosom burns with no unhallowed fire,
> Yet is my cheek with rosy blushes warm;
> Yet are my eyes with sparkling luster fill'd;
> Yet is my mouth replete with murmuring sound;
> Yet are my limbs with inward transport fill'd
> And clad with newborn mightiness around.

The inhalation of ether is accompanied by a feeling of suffocation, which is lessened by starting the anesthetic with nitrous oxide. Sir James Y. Simpson employed ether in obstetrics in 1847. The same year he discovered that chloroform has anesthetic properties. The use of chloroform was suggested to him by a

Liverpool chemist named Waldie. Chloroform was prepared as early as 1831 by Samuel Guthrie, of Sackett's Harbor, New York. Mankind is greatly indebted to chemistry for pure anesthetics, which have done so much to prevent suffering. In certain cases chemists have been able to improve upon natural products. For instance, cocaine, a powerful alkaloid contained in coca, has been employed for years as a local anesthetic, thus making possible painless operations without recourse to a general anesthetic, such as ether or chloroform. Unfortunately, cocaine has certain defects, the most serious of which is that it is poisonous, and has therefore been the cause of deaths, even when used in a minor operation such as the extraction of a tooth. By great industry and perseverance chemists have learned the arrangement of the atoms in the cocaine molecule, and it has been discovered that it is one particular part of the molecule which has the beneficent action of cocaine. Another part of the molecule is related to nicotine, and the third part to a deadly alkaloid found in hemlock, which Socrates was forced to drink.

Thanks to modern chemistry, local anesthetics are now being produced which have the useful properties of cocaine without its excessive poisonous qualities. Among these we may mention procaine (novocaine), eucaine, and benzyl alcohol. The use of local anesthetics in surgery is growing rapidly. They are now being employed for certain major operations, such as for hernia and appendicitis. Cocaine and its derivatives are very remarkable drugs.

3 Pasteur and the Germ Theory of Disease

The nineteenth century witnessed a great development in medicine and surgery as well as in chemistry and other sciences. Dr. William Osler writes:

> At the middle of the last century we did not know much more of the actual causes of the great scourges of the race, the plagues, the fevers, and the pestilences, than did the Greeks. Here comes in Pasteur's great work. Before him Egyptian darkness; with his advent a light that brightens more and more as the years give us ever fuller knowledge.

Louis Pasteur began his scientific work as a pure chemist, and it will always be a source of pride to chemists that "to no man has it ever been given to accomplish work of such great importance for the well-being of humanity." He began, about the middle of the last century, the study of certain biological problems and applied his knowledge of chemistry in solving them. In a report to the French Government, Paul Bert formulated Pasteur's wonderful discoveries under the following heads:

(1) Each fermentation is caused by the development of a specific micro-organism.

This discovery has been of untold value in the brewing and baking industries. Certain microbes are ferments of disease, thus leading to alterations in the products. It is now possible to control fermentation so as to secure pure cultures. This discovery that beers could be preserved by the application of heat, gave rise to the word pasteurize.

(2) Each infectious disease is due to the development within the organism of a special microbe or germ.
(3) The germ of an infectious disease culture, under unfavorable conditions, is weakened in its disease-producing activity. This means that from a virus it has become a vaccine.

While studying fermentation Pasteur discovered the microbes of fermentation, but the discovery of germs had been made previously. He observed the similarity between fermentation and the changes which take place in infected wounds. While Pasteur applied his discoveries to improving the quality of wine and beer, it remained to Lister to introduce the antiseptic system of surgery. This system is based upon the germ theory of putrefaction. Lister and his associates employed antiseptic solutions, particularly a solution of carbolic acid, for killing the germs. The disinfectant must not be too powerful, however, for it might injure or even kill the patient. In operating, bacteria may be avoided by boiling or heating the instruments, heating the bandages, etc., and by covering the hands with clean gloves. This is known as asepsis—*i.e.*, without septic germs. Asepsis is based upon absolute cleanliness, while antisepsis is the defense against germs by killing them or arresting their development with a germicide, such as corrosive sublimate or carbolic acid.

There are many kinds of disease-producing germs or parasites. Blood-poisoning, for example, is produced by pus-forming bacteria, which gain access to the blood and multiply on an enormous scale. Unless in an impoverished condition, the blood has strong germi-

cidal properties and if the invading organisms are not too numerous they are ordinarily destroyed.

Such diseases as typhoid fever, pneumonia, influenza, and diphtheria are caused by specific vegetable microbes or parasites. Malaria, amœbic dysentery, syphilis, scarlet fever, and hydrophobia are due to animal parasites.

W. T. Helmuth, in his "Ode to the Bacillus," wrote:

> Oh, powerful bacillus,
> With wonder how you fill us,
> Every day!
> While medical detectives,
> With powerful objectives,
> Watch your play.

In the case of such diseases as smallpox, measles, mumps, and whooping-cough no specific parasites have been found; that is, these infectious diseases are not proved to be due to micro-organisms. But J. A. Thomson says, "Nowadays the serpent that bites man's heel is in nine cases out of ten microscopic."

4 Toxins and Antitoxins; the Blood

Chemists have made invaluable contributions in finding out the chemical composition and action of the blood and in providing vaccines, antitoxins, etc., so efficacious in preventing and curing diseases. Marvelous things have been accomplished in immunity. Why are certain individuals immune to certain diseases, and how may immunity to diseases, say diphtheria or typhoid fever, be conferred? When pathogenic organ-

isms invade the body in sufficient numbers, disease results, for toxins or poisons are produced. In general, the blood develops bodies or substances known as antitoxins, which oppose the invading germs. In case antitoxins are produced in sufficient quantity, the fight may be a short one, the person quickly recovering; but if the germs get the ascendency, the fight will be prolonged, or even death may follow.

Those having in their blood plenty of antibodies for certain diseases are naturally immune. In case of diphtheria the Schick test is of great value in determining immunity. This test consists of injecting a small amount of diphtheria toxin into the skin. If the individual is immune, there is no reaction; but if there is not immunity, the toxin irritates the skin, a localized inflammatory condition being produced, which is readily recognized. One may be rendered immune to diphtheria by treatment with diphtheria toxin-antitoxin. Antitoxin, the material used in treating persons ill with diphtheria, is obtained from the horse. A small dose of the virus or toxin of diphtheria is injected into the animal, and the blood responds by producing antitoxins. By repeated treatment the horse can be made to stand larger and larger quantities of the toxins. When sufficient antitoxins have been formed in the blood, a portion of it is withdrawn from the animal, and is then properly treated to secure a serum for injection into the human body.

It is quite within the range of possibility that diphtheria may become a disease of the past. It is now called a conquered disease. According to Dr. S. J. Crumbine, immunization of school-children and those

below school age in Auburn, New York, a city of 37,000 inhabitants, was begun in 1922, with the result that where the cases once reached the hundred mark annually, with from ten to twenty deaths, not a death occurred in the entire city from this cause from March, 1924, to the summer of 1926. There were fifteen cases reported in the year 1925, but not a single case occurred among those immunized. In a similar way typhoid has been conquered, and scarlet fever has also been robbed of its terrors. We have the Dick test for scarlet fever, which is of value in determining immunity.

The blood is a marvelous fluid containing numerous components, some of which are exceedingly complex. Chemists have devoted a great deal of attention to the study of the blood, knowing that health depends upon a proper adjustment of its components. It is estimated that there are about twenty-five trillion red cells or corpuscles in the blood of the average man. Anemic persons have too few red cells, or else the cells are deficient in iron. The blood also contains white cells, or leucocytes. These cells are not so numerous as the red cells and are not very well understood. There are different kinds of white cells, one variety being known as phagocytes, or eater-cells. These cells are active in ingesting and destroying waste and harmful material and bacteria from the blood. The blood normally contains a substance called opsonin, which whets the appetite of phagocytes for bacteria, so that they are eaten in bunches rather than one at a time. It is thus seen that phagocytes play an important part in combating germ diseases.

5 Syphilis, Leprosy, and Sleeping Sickness

Chemists are being called upon more and more to prepare specific drugs to cure specific diseases. We have a splendid illustration of this in the famous "606," or salvarsan (arsphenamine), an arsenic compound synthesized by Paul Ehrlich, a German bacteriologist who applied chemical principles to his work. This is one of the outstanding achievements in the field of medicine. Syphilis is one of the most ancient, wide-spread, and dreadful of diseases. It is startling to know that not long ago it was estimated that there were about ten million cases in the United States alone, which was about 10 per cent of the population. According to a report of the Royal Commission, there was a similar state in England. The disease is caused by an animal parasite, a single-celled protozoan. Ehrlich discovered that when certain dyes are injected into the body they have an affinity for certain cells, being taken up by them. It therefore occurred to him that healing drugs might be carried to diseased cells, or chemical specifics or poisons to invading disease-producing organisms. The specifics behave like dyes in that certain parts of the body take them up. To use a simile of Percy May's:

> The chemical specific may be likened to a poisoned arrow, the point being the particular dye which has a selective affinity for the parasite, and therefore fixes it. If a poison can be attached to such a dye or to the anchoring group of such a dye, the arrow will be not merely a dye, but also the desired chemical specific.

Erhlich discovered that the syphilis germ is one of the cells having an affinity for dyes. In the treatment of syphilis he therefore handed to the messenger a dose of salvarsan, which killed the microbe without injury to the sufferer. This mode of treatment is known as the "messenger system." The greatest success in the treatment of syphilis has been attended by a combination of salvarsan, or a similar preparation, and the old mercurial treatment. The public should know that the disease is cured with difficulty. Ordinarily, repeated injections are required, and the treatment may be expected to extend over a period of two years or even longer.

Sleeping sickness, so prevalent in the great continent of Africa, is also caused by an animal parasite. Fortunately, a drug, similar to salvarsan, has been discovered which has robbed the germ of sleeping sickness of its sting, thus opening up Africa to civilization.

Amœbic dysentery, a disease prevalent in tropical and subtropical countries, is also caused by an animal parasite. This one-celled organism usually gains access to the body in impure drinking-water. It often produces chronic dysentery or an abscessed liver. The chemist has extracted from ipecac its active principle, called emetine, which quickly destroys the amœba.

Leprosy, like syphilis, is an ancient and dreadful disease. It is caused by a vegetable organism, a tissue parasite, and is known as a chronic infective disease. For many years chaulmoogra oil has been used in India in the treatment of leprosy. This natural product is, however, nauseating and irritating. Due to the skill and industry of the chemist, pure acids have been

prepared from the disagreeable chaulmoogra oil, and these have been combined with ethyl alcohol, giving us a new, agreeable drug which has been employed with great success in the treatment of leprosy. With improved sanitation and increased cleanliness, coupled with the use of modern drugs, leprosy should be eradicated.

6 Glands; Giants and Dwarfs

In recent years chemists, pharmacologists, and pathologists have devoted considerable attention to the study of glands, or organs of secretion. Glands of the animal body are divided into two groups—glands with ducts and ductless glands, or endocrines (Greek: within + separate). Glands having ducts pour their secretions into the stomach, intestines, or elsewhere, for purposes of digestion. These are well illustrated by the salivary glands and the pancreas. The ductless glands, or endocrines, pour their secretions directly into the blood-stream. The ductless glands supply hormones (Greek: excite), or chemical messengers. These substances circulate in the blood-stream and produce activity in, or exert control over, various parts of the body. Some of the hormones act like very powerful drugs. The organs of our bodies contain many principles and their study is opening up a new chapter in medicine and life. There are a number of ductless glands, some of the most important of which are the suprarenal, the pituitary, the thyroid, and the islands of Langerhans in the pancreas.

The suprarenals, or adrenals, owe their name to

their situation, which is just above the kidneys. Adrenalin (epinephrin) is a pure principle which was first prepared from the suprarenal glands. Its chemical structure has been determined, and the complex compound is now produced artificially. Adrenalin is a very powerful and extremely useful drug. For instance, when injected hypodermically, it allays very quickly the spasms of acute bronchial asthma. It also has great potency in arresting hemorrhage, and is a powerful heart stimulant. The power of the drug is graphically told by G. A. Dorsey in the following words:

> It influences some tissues when diluted to one part in 100,000,000. It depresses the intestinal canal when diluted to one part in 330,000,000! What such dilution means has been worked out in terms of street sprinklers each of 625 gallons capacity. A procession of such sprinklers twenty miles long and 200 to the mile would hold just enough water to dilute one ounce of adrenalin down to one dose.

According to the theory of W. B. Cannon, adrenalin comes to our aid in time of emergency, enabling us to fight harder and to accomplish almost superhuman tasks.

The pituitary gland is located near the center of the head, and is about the size of the tip of the little finger. Starting with this gland, Dr. J. J. Abel has recently prepared a tartrate which is extremely potent. To quote Dorsey again, "Recall the twenty-mile procession of street sprinklers required to reduce an ounce of epinephrin [adrenalin] to a test dose: to reduce an equal amount of Abel's pituitary hormone would require not twenty miles of sprinklers, but 5,000 miles!"

It is believed that giantism is caused by too much activity in the anterior lobe of the pituitary gland. Machnow, a Russian, was exhibited in London in 1905, at the age of twenty-three; he then stood 9 feet, 3 inches in height and weighed 360 pounds. The gland appears to be closely related to growth. Magrath, the famous Irish giant, had a pituitary as large as a hen's egg. On the other hand, certain noted dwarfs have been known to have abnormally small pituitary glands.

The thyroid gland was mentioned in connection with goiter (in Chapter VIII). Thyroxin, the active principle of this gland, was isolated several years ago by Dr. E. C. Kendall. Thyroxin regulates the combustion of our food. It is a powerful drug, an occasional dose of only a fraction of a milligram being sufficient to cure cretinism and myxedema. As stated before, thyroxin has been prepared synthetically.

The islands of Langerhans, in the pancreas or sweetbreads, supply the important hormone called insulin, which is so closely related to diabetes mellitus. Insulin feeding is a very efficacious remedy for diabetes; but the diet must also be controlled. It is estimated that there are more than one million sufferers from diabetes in the United States alone.

Pneumonia and tuberculosis are responsible for a very large number of deaths in the world, and cancer also claims its tens of thousands. Thus far no specifics have been discovered for these scourges. We may confidently expect that in the course of time the patient and systematic investigations of chemists, biologists, pharmacologists, and physicians will find cures for them.

Not only has the chemist been of the greatest service in preparing medicaments to allay suffering and to cure diseases, but chemical analysis and tests are of much value to the physician in the diagnosis of diseases, such as those connected with digestion or the blood. Chemicomedical research is really in its infancy, but we may confidently expect that with close coöperation the solution of many problems for the benefit of mankind will be reached.

Voltaire pays the following beautiful tribute to the physician:

> But nothing is more estimable than a physician who, having studied nature from his youth, knows the properties of the human body, the diseases which assail it, the remedies which will benefit it, exercises his art with caution, and pays equal attention to the rich and poor.

CHAPTER XXVI

THE MANUFACTURER'S DEPENDENCE ON CHEMISTRY

> Almost all the investigations upon which modern industry nas been built would have been crushed at the outset if immediate practical value had determined what work should be undertaken. Science brings back new seeds from the regions it explores, and they seem to be nothing but trivial curiosities to the people who look for profit from research, yet from these seeds come the mighty trees under which civilized man has his tent, while from the fruit he gains comfort and riches.—SIR RICHARD GREGORY.

1 CHEMISTRY IN INDUSTRY

THE story of the dependence of the manufacturer on chemistry, or of chemistry in industry, is a fascinating and romantic one. Chemistry is so intimately connected with many industries that a large number of volumes would be required to tell of its great achievements. The thrilling story relating to dyes, drugs, camphor, rubber, plastics, textiles, essential oils and perfumes, nitrogen-fixation, alcohols and ethers, petroleum-refining, fuels, fats and oils, metals and alloys, and innumerable other things is largely the story of chemistry and chemical engineering. Formerly, many manufacturing industries were run more or less by rule-of-thumb methods; but more and more they are being based on and controlled by chemistry. The necessity of this will become greater as our natural resources diminish.

Since chemistry is concerned with the transformation of matter, there is scarcely an article in common use which does not owe its existence, directly or indirectly, to chemistry.

In a previous chapter attention was called to some of the marvelous materials produced from bituminous coal, and there is perhaps no better illustration to show the dependence of the manufacturer on chemistry. For many generations it was known that coal is black and dirty and that it burns with a bright flame; but it was only recently that, under the magic hand of the chemist, it yielded up its rich treasures, a veritable chemical rainbow; terrific explosives needed in time of peace and war; medicines of great potency in relieving suffering, inducing sleep, and healing disease; synthetic flavors and perfumes which rival those of fruits and flowers; and saccharine, a substance hundreds of times sweeter than sugar or honey. Not many people fully realize the dependence of manufacturers on dyes or know that there are exceedingly complicated chemical problems connected with their production. There are thousands of possible coal-tar colors, no one of which can be produced without chemistry.

German chemists, engineers, and manufacturers spent half a century in building up a great dye industry. When the war broke out in 1914, other nations were largely dependent on Germany for an adequate supply of fast dyes. In 1915 a single keg of dye sold for $1500, while the normal price had been about $15. The story of the trips of the submarine *Deutschland* with its cargoes of aniline dyes, valued at millions of dollars, reads like a romance, so full is it of adventure.

Dyes were so scarce in the United States that hundreds of chemists were put to work to solve the problem of producing them on an industrial scale; and it will always be a bright page in the history of American chemistry that before the war ended we had an independent dye industry destined to rival that of Germany.

By-product coke and the products accompanying its manufacture are of vast economic importance. The first plant of modern by-product ovens built in the United States was a battery of twelve ovens erected at Syracuse, New York, in 1892. In the year 1923, the total value of our by-product coking was about $517,000,000, of which over $153,000,000 was for by-products. In the same year over 65 per cent of the domestic coke was the output of by-product ovens. The by-product oven, which is controlled by chemistry, means a great deal for the conservation of our natural resources. By employing the wasteful beehive oven, over a quarter of the mass of the coal is vaporized and utterly lost in the coking process. The Gary (Indiana) plant of the United States Steel Corporation operates twelve blast-furnaces, the coke for which is supplied by the by-product oven. According to official figures, the modern oven enabled the plant to save in a recent year 1,190,000 tons of coal.

According to "Science Service," Washington, D. C., scientists are now busy trying to produce a new fuel, called semi-coke, from coal. The proposed new fuel will be smokeless and almost wasteless, and is expected to save a large portion of the three fourths of coal which now passes up the chimney from coal burned in

the ordinary way. An attempt is being made to produce semi-coke by low-temperature carbonization. Professor S. W. Parr, an American chemist, has been a leader in this investigation. The by-products obtained by low carbonization are different from those of the ordinary by-product oven, and as yet their economic value is not known. Great Britain hopes to get fuel oil for her navy from the portion of coal which is now wasted. By this new process it is proposed to recover the gases, oils, and ammonia which now escape in smoke. It is predicted by certain scientists that the solution for a world problem is in sight, but it is too soon to say what the final outcome will be.

Dr. F. Bergius and other European scientists have perfected a process for the transformation of coal into oil. The essential principle of the process consists in chemically combining hydrogen gas with coal by means of high temperature and pressure. A complex mixture of gaseous, liquid, and solid compounds is produced, and these compounds are similar to the hydrocarbons obtained from natural wells.

According to W. E. Treat of New York, coal may be pulverized to the consistency of talcum powder; when heated, it flows like water, giving virtually a liquid fuel.

It is possible that these products may be utilized on a large scale as motor fuels.

When cotton cloth is treated with a solution of sodium hydroxide, it takes on a high silky luster, and the cloth becomes stronger, more durable, and has an increased affinity for many dyes. The process is known as mercerization. This discovery was made by John

Mercer, of England, in 1844, but it was many years before its great importance was realized. Mercerized goods are now produced on a large scale. To prevent shrinkage, the cloth is kept under tension while being treated.

The manufacture of the so-called artificial silk, or rayon, from cellulose derived from wood or cotton linters, is another great triumph which we owe to chemistry. This industry has gone forward by leaps and bounds. The output of rayon in 1925 was 197,000,000 pounds, of which 50,000,000 pounds were manufactured in the United States, now the leading producer. This new industry during the year 1926 returned more profits than the entire cotton industry.

In the production of artificial silk the chemist has learned a valuable lesson from the silkworm, which ejects through two very fine spinnerets a semiliquid material that hardens quickly into fiber. Various processes are employed to produce the fiber of rayon, but at present about 80 per cent is manufactured by the viscose process. When wood cellulose or cotton linters is treated with a solution of sodium hydroxide, it becomes mercerized. By treatment of the mercerized product with carbon disulphide, xanthate of cellulose is formed, which dissolves in an alkali yielding a liquid called viscose. Artificial silk is spun by forcing viscose through round holes having a diameter of about 0.004 inch, into a coagulating bath, the product being obtained in the form of a flat ribbon-like thread, which is desired for the production of soft, pliable material. Rayon may be dyed very uniformly, giving

colors of great brilliancy and beauty. According to M. G. Luft, artificial silk is never weighted, while natural silk is generally weighted with metallic salts, usually of tin—in some instances up to 300 per cent of the original yarn. Natural silk is brittle and it rots from perspiration and turns yellow, but artificial silk is not brittle and remains white. Rayon has many uses. For instance, with cotton, it is employed on a large scale in the manufacture of hosiery, underwear, ribbons, etc. It is also mixed with real silk to form yarn for various articles.

It is of interest to know in this connection that the work of the great chemist Pasteur about the middle of the last century saved the silk industries of Europe from utter ruin. At that time the silkworm was attacked by a disease known as pébrine, which was caused by a microscopic organism. In the course of a few years the state revenue derived annually from the silk industries fell from 130,000,000 to 8,000,000 francs; "and the mulberry plantations on the slopes of the Cévennes mountains, which had for long given employment to a happy and contented people, were completely abandoned; and the once radiant faces of men became sad and melancholy because misery and poverty prevailed where before happiness and plenty had reigned." In this time of despair the Government requested Pasteur to undertake the solution of the problem. The silkworm cultivators expressed regret that the Government should choose a "mere chemist." Pasteur undertook the task. By the exercise of great patience, industry, intuition, and his "imagination,

which equaled any poet's," he succeeded in saving the silk industry. Natural silk is an animal product, while rayon is of vegetable origin.

Starting with cellulose, the chemist has also been able to produce many other materials of great importance, such as explosives, celluloid, artificial leather, photographic plates, lacquers, and enamels.

Chemistry has made possible the production of bakelite. This is a synthetic product, a phenol-formaldehyde resin, which was invented by Doctor L. H. Baekeland after years of systematic research. "Its invention is an impressive tribute to the united power of knowledge, system, and hard work, and is the result of their complete interaction." Bakelite is produced by heating together under suitable conditions solutions of carbolic acid (phenol) and formaldehyde. The resin obtained has remarkable properties. It is a hard, strong, odorless, tasteless, inert material, impervious to water, and a good insulator. When pure, it is transparent, being amber-like in appearance. It has innumerable uses, such as for insulation, pipe-stems, cigarette-holders, pencils, beads, camera-cases, and radio parts.

Chemistry has also contributed much to the production of metals, steel, and alloys, for the reactions carried out in furnace and crucible are of a chemical nature. In the manufacture of iron and steel, complete chemical control is exercised from beginning to end. It is the business of the chemist to see to it that the steel contains the proper amount of carbon, manganese, and other alloying elements; also, that the content of sulphur and phosphorus is kept very low.

It is worthy of note that Andrew Carnegie gained an early advantage over his competitors because he secured the services of chemists to show him how steel could be produced more economically. In recent years manufacturers have employed expert metallurgists, and by means of the microscope and the photomicrograph they are securing information of vast importance concerning the structure and properties of steel. This is work of the highest value, for a defect in a steel rail may be the cause of a terrible accident.

Our dependence on alloy steels is not generally realized. An alloy steel contains one or more elements other than carbon, in sufficient quantity to modify or improve substantially some of its useful properties. As stated in Chapter XVIII, manganese steel is very tough. A steel containing from 12 per cent to 14 per cent of the metal is excellent for rock-crushers and burglar-proof safes. Nickel steel possesses great elasticity and tenacity, being used in the construction of armor-plate. Chromium increases the hardness of steel, and also renders it rustless. The "stainless" steels therefore contain a considerable proportion of chromium. Cutting-tools, armor-plate, and projectiles, also contain chromium. High-speed lathe tools usually contain tungsten, for this metal prevents the loss of the temper of the steel when heated to a high temperature. Vanadium steel finds extensive use in the production of automobile parts, and titanium steel is valuable for car rails and steel castings. We thus see that modern civilization with its many comforts and advantages is largely dependent on alloy steels. There are also numerous alloys into which iron does not enter. Indeed,

there are over one hundred alloys in use. Some of these are very light and are therefore essential in the construction of aircraft. Other alloys are non-corrosive and still others find favor for ornamental use.

2 Artificial Lighting

Chemistry has also played an important rôle in artificial lighting. Half a century ago our homes were lighted by candles, kerosene lamps, and flat-flame gas-lamps. Not a single home was wired for electricity, for the incandescent lamp had not been invented. This epoch-making invention was made by Thomas A. Edison in 1878, but it was three more years before the carbon-filament incandescent lamp became a practical success. The wire-drawn tungsten lamp was introduced in 1910, and the gas-filled tungsten lamp four years later, thus virtually making it possible to turn night into day. According to M. Luckiesh, the average luminous efficiency of all filament lamps sold in 1926 was about ten times that of Edison's early carbon lamps. This is a fact of great importance, for it means that light is now produced more economically. In 1925 there were sold in the United States 278,600,000 large incandescent lamps, 123,000,000 automobile lamps, 43,000,000 Christmas-tree lamps, and 30,000,000 flash-light lamps. The progressive farmer now uses the flash-light instead of the dangerous lantern.

It should be added that Auer von Welsbach in 1884 invented the incandescent gas-mantle, which has been of great value in increasing the luminosity of flame. This mantle consists of the oxides of thorium and

cerium which the chemist has been able to prepare from the monazite sands of Brazil, India, and the United States.

3 Chemistry and the Cotton-Plant

It has been said that the cotton-plant won the war; for it furnished food, clothing, housing, and ammunition—four indispensable things for a soldier. Cotton-seed oil was changed into solid fat by a chemical process, so it was substituted for lard; it was also employed in the production of oleomargarine, which took the place of butter. Cotton-seed oil was also a source of glycerine and explosives. Cotton cloth was utilized in the manufacture of clothing, tents, and bedclothes; and cotton linters found use for stuffing mattresses, and for producing felt for hats. Nitrocellulose, a cotton derivative, supplied material which forms the basis of celluloid (buttons, combs, etc.), artificial leather, and explosives.

The main products of cotton-seed are the linters, meal, hulls, and oil. Half a century ago cotton-seed was almost a waste product; but to-day, thanks largely to researches of chemists, the cotton-seed industry is one of the most important manufacturing industries in the South. There is complete chemical control of the crude-oil mills; and cotton-seed products are sold on quality as determined by chemical analysis.

4 Catalysis Transforming Industry

The importance of catalysis in industrial development has already been discussed (in Chapter IX). Within twenty years the catalytic chemist has done a

great deal to transform industrial and commercial life. Hugh S. Taylor, an expert on catalysis, says:

> Gone are the indigo plantations of India; they fell a victim to the discovery of synthetic indigo. This synthesis required for its fulfillment the contact sulphuric acid process. . . . Indigo required also the oxidation of naphthalene to phthalic acid, and this has twice been revolutionized catalytically. . . . An enormously expanded whaling industry in Arctic and Antarctic seas, new tracts of cocoanut plantations in tropical regions of Africa and America, an expanding market in cottonseed oil—all these are reflex actions of the discoveries of Sabatier and Normann that hydrogen molecules could readily be added to unsaturated hydrocarbon chains, liquid or gaseous, when in contact with finely divided nickel as catalyst. Fixed nitrogen for fertilizer and explosives is an indispensable adjunct of peace as well as war. Two decades ago the ships of all the nations hurried their cargoes of saltpeter from Chile to home ports. Today all the great nations are drawing supplies of fixed nitrogen from the air, whether as ammonia, cyanamide, or nitride. The hurrying pace of motor transport facilities creates a need for solvents and enamels; the catalytic chemist produces alcohols and acids and esters in response to the demand.

Other parts of the marvelous story of the dependence of the manufacturer on chemistry have been briefly told in previous chapters. In general, the manufacturer transforms raw materials into the manifold products needed in a busy world. While the chemical transformation of matter demands the guiding hand of the chemist, it is only fair to say that other scientifically trained men—the physicist, the mathema-

tician, the biologist, and the engineer—are, in many cases, equally important. The sciences are closely related and by close coöperation on the part of scientists we may confidently expect even greater discoveries to be made.

Years ago, M. Berthelot, the great French chemist, stated that the food problem is a chemical problem, and he was bold enough to predict that the time will come when we shall be able to subsist on synthetic foods. He prophesied:

> On that day chemistry will have accomplished a world-wide revolution that cannot be estimated. There will no longer be hills covered with vineyards and fields filled with cattle. Man will gain in gentleness and morality because he will cease to live by carnage and destruction of living creatures. . . . The earth will be covered with grass, flowers and woods, and in it the human race will dwell in abundance and joy of the legendary age of gold—provided that a spiritual chemistry has been discovered that changes the nature of man as profoundly as our chemistry transforms material nature.

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II MELTING POINTS OF THE MORE IMPORTANT METALS

Mercury	−38.8° C.	Calcium	810.0° C.
Potassium	62.3	Barium	850.0
Sodium	97.5	Arsenic	850.0
Lithium	186.0	Silver	960.5
Tin	232.0	Gold	1063.0
Bismuth	271.0	Copper	1083.0
Cadmium	321.0	Manganese	1230.0
Lead	327.0	Nickel	1452.0
Zinc	419.0	Cobalt	1480.0
Antimony	630.0	Iron, wrought	1530.0
Magnesium	651.0	Chromium	1615.0
Aluminium	659.0	Platinum	1755.0
Radium	700.0	Tungsten	3400.0

The following formula may be used to change from the Centigrade scale of temperatures to the Fahrenheit scale:

$$F.^\circ = \tfrac{9}{5}(C.^\circ) + 32.$$

3400° C. = 6152° F., the melting point of tungsten.

III THE SYMBOLS AND ATOMIC WEIGHTS OF THE ELEMENTS

	Symbol	*At. Weight*		*Symbol*	*At. Weight*
Aluminium	Al	26 97	Molybdenum	Mo	96 0
Antimony	Sb	121.77	Neodymium	Nd	144.27
Argon	A	39.91	Neon	Ne	20.2
Arsenic	As	74.96	Nickel	Ni	58 69
Barium	Ba	137.37	Nitrogen	N	14 008
Beryllium	Be	9.02	Osmium	Os	190 8
Bismuth	Bi	209.00	Oxygen	O	16 000
Boron	B	10.82	Palladium	Pd	106.7
Bromine	Br	79 916	Phosphorus	P	31 027
Cadmium	Cd	112 41	Platinum	Pt	195 23
Calcium	Ca	40 07	Potassium	K	39 096
Carbon	C	12.000	Praseodymium	Pr	140 92
Cerium	Ce	140 25	Radium	Ra	225 95
Cesium	Cs	132 81	Radon	Rn	222
Chlorine	Cl	35.457	Rhodium	Rh	102 91
Chromium	Cr	52.01	Rubidium	Rb	85 44
Cobalt	Co	58 94	Ruthenium	Ru	101.7
Columbium	Cb	93.1	Samarium	Sm	150 43
Copper	Cu	63.57	Scandium	Sc	45 10
Dysprosium	Dy	162 52	Selenium	Se	79 2
Erbium	Er	167.7	Silicon	Si	28 06
Europium	Eu	152.0	Silver	Ag	107 880
Fluorine	F	19 00	Sodium	Na	22.997
Gadolinium	Gd	157.26	Strontium	Sr	87 63
Gallium	Ga	69.72	Sulfur	S	32 064
Germanium	Ge	72.60	Tantalum	Ta	181 5
Gold	Au	197 2	Tellurium	Te	127 5
Helium	He	4.00	Terbium	Tb	159 2
Holmium	Ho	163 4	Thallium	Tl	204 39
Hydrogen	H	1.008	Thorium	Th	232.15
Indium	In	114.8	Thulium	Tm	169.4
Iodine	I	126.932	Tin	Sn	118 70
Iridium	Ir	193.1	Titanium	Ti	48.1
Iron	Fe	55.84	Tungsten	W	184.0
Krypton	Kr	82.9	Uranium	U	238.17
Lanthanum	La	138.90	Vanadium	V	50.96
Lead	Pb	207.20	Xenon	Xe	130.2
Lithium	Li	6 940	Ytterbium	Yb	173 6
Lutecium	Lu	175.0	Yttrium	Y	88.9
Magnesium	Mg	24.32	Zinc	Zn	65.38
Manganese	Mn	54.93	Zirconium	Zr	91
Mercury	Hg	200.61			

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