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Mineral Industries Series

FERROUS METALLURGY

Volume I

INTRODUCTION TO FERROUS METALLURGY

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MINERAL INDUSTRIES SERIES

Introduction to Ferrous Metallurgy

FERROUS METALLURGY

VOLUME I

by

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Currently Metallurgist, E. G. Budd Mfg. Co.

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FOREWORD

Every person is imbued with a desire to live comfortably. To accomplish this desire, some are willing to work and some are content to let Nature take its course. For the former, there lies ahead a path of opportunity for advancement and, through this advancement, the attainment of those things most desired in every life.

The United States with its vast mineral industries offers a wide field for study. The mining of iron ore and fuels, and the processing of iron and steel are two major industries of the nation. The results of research and the exacting demands of the purchasing public necessitate constant change and improvement in iron founding and steel mill practice. This change necessitates a better informed operating force, one that embraces every opportunity to increase its efficiency and knowledge to meet the changing conditions in industry. The best possible method of improvement is through study.

This is the first book of a three-book series prepared by E. J. Teichert, supervisor of Metallurgy Extension of The Pennsylvania State College, to provide a three-year course of training for persons interested in the iron and steel industry. It covers those fundamentals essential to an understanding of the work to follow and includes the primary processing of iron ore in the blast furnace and the manufacture of cast iron, wrought iron, and crucible steel. Every known care has been exercised to present the subject matter as clearly and concisely as possible. The extent of the work, however, prevents a treatment of all subject matter in minute detail. The student is expected to read the many references given for a more detailed description of the processes covered.

In an effort to embody in the text the latest and best information available on operating practice, it was necessary to secure that information where such practice existed. Grateful acknowledgment is hereby extended to the following for their helpful assistance and cooperation in furnishing material included in the

text: The Jones and Laughlin Steel Corporation, The Philadelphia Drying and Machinery Company, The Wellman Engineering Company, The Youngstown Sheet and Tube Company, The Koppers Construction Company, The Harbison-Walker Refractories Company, Leeds and Northrup Company, William A. Haven of Arthur G. McKee and Company, The Detroit Electric Furnace Company, A. M. Byers Company, and National Malleable and Steel Castings Company. Acknowledgment has been extended in the text for all material excerpted from current literature.

H. B. NORTHRUP, *Director,*
Mineral Industries Extension.

THE PENNSYLVANIA STATE COLLEGE,
December, 1943.

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INTRODUCTION

Schools of mineral industries are concerned with the exploration, development, and conservation of all mineral resources, and with their production, preparation, processing, and utilization. It is natural that Pennsylvania with its long-established prestige of leadership in the production and processing of mineral products should be the first to organize and operate a school of this type in which all branches of instruction and research are united.

The mineral fuels, the metals, and the nonmetallics are nonreplaceable. Their efficient utilization is therefore of the utmost importance in the industrial life of the nation. The interrelated problems concerned with their production and use constitute a distinct division of education. This may be divided into earth sciences, mineral engineering, mineral technology, and mineral economics. The existence of our mineral industries is dependent upon three divisions of service: resident instruction, research, and extension and correspondence instruction.

Ferrous Metallurgy is presented in a series of three texts, which were prepared originally for extension classes in metallurgy covering a three-year curriculum in that subject. They have been maintained up to date by frequent revisions and improvements and have withstood the test of metallurgical critics and teachers for the past ten years, during which time thousands of students have completed the series.

It is recognized that no one text or series of texts can hope to present fully all existing information on ferrous metallurgy. The aim of this series is to present a curriculum in the subject which shall be fundamental in nature, factual in text, sufficiently extensive in scope, and arranged in a manner that experience has found to be most effective in the classroom and in home-study courses.

The Mineral Industries Series, in which these three texts are included, has been developed as a part of The Pennsylvania State College extension service to meet the current economic and

social needs of the nation. There are similar texts in other subjects and advanced special courses in coal-mine mechanization and meteorology. Through this service the principles and truths developed by study and research are translated and carried to the people and applied to the industries. Educational processes taken into the mills, mines, and processing plants result in the promotion of mutual understanding between employers and employees, which is imperative for efficiency, safety, and economy of operation.

EDWARD STEIDLE, *Dean,*
School of Mineral Industries.

THE PENNSYLVANIA STATE COLLEGE,
November, 1943.

FERROUS METALLURGY

VOLUME I

CHAPTER I

GENERAL INORGANIC CHEMISTRY

All industrial processes are based, at least in part, on the science of chemistry. Although industries originated in the old days before the extensive application of chemistry, our present methods of production have been brought to a high point of efficiency during the past fifty years through our increased knowledge of the principles of chemistry along with advances in other sciences. Chemistry has undoubtedly been the greatest tool in the evolution of industry from the methods of trial and error to those of scientific planning and control. It is necessary, therefore, that the students in these industries have a sufficient familiarity with chemistry and the methods used in chemistry so that they will be able to understand the scientific principles underlying them.

Chemistry has three main objectives:

1. The study of the properties of every known substance so that they may be distinguished from each other.
2. The separation of substances into their simple components to determine their origin.
3. The transformation of these substances into substances of other kinds.

The science of chemistry deals with all forms of matter, regardless of whether they are obtained from beneath the surface of the earth (rock, ores, minerals), or from the surface of the earth (plants, animals, the sea), or from the air. It also deals with artificial materials not found in nature but made by man, such as paints, explosives, and steel. The chemist is concerned primarily with the composition and changes in composition of the materials that man finds about him, as well as their energy relations. He is also interested in the preparation and utilization of materials. The chemist has developed a technical language

and a point of view all his own, both of which must be understood by the student before the science of chemistry can be clear to him.

MATTER AND ENERGY

Each of us, from the moment we were born, has begun to acquire chemical information, not consciously perhaps, but from common experience. These experiences have taught us that all material things with which we are acquainted are constantly undergoing some sort of change. Thus, when we observed that milk turns sour, that silverware is stained by eggs, that metals rust away, that solid rocks weather and disintegrate, we were learning chemical facts. Such changes in nature are almost limitless in number, but in all of them there are two things involved: the matter that undergoes the change and the energy that causes the change or results from it.

MATTER

When we think of matter, we immediately form a picture of a substance that has both mass and weight. Fundamentally, these are its characteristics.

Mass.—If we were to apply a given force to a body, such as a cube of iron, which is free to move, this cube of iron would gain a certain acceleration. Similarly, should we apply the same force to a cube of wood of the same volume as the cube of iron, we should find that it would acquire a much greater acceleration than the iron. Thus we can say that "the property of a body that determines the acceleration it will acquire when acted upon by a given force is called its mass."

Weight.—We are most familiar with this characteristic through the spring balance which records this quantity mechanically. Just what is it that we are really measuring? We are measuring the intensity of the earth's attraction for the body, or the acceleration it tends to impart. The force, or earth's attraction, being that force with which we are all familiar, *gravity*. The measure of the earth's attraction for a body is called its *weight*.

The unit of weight or mass is the gram (g.), which is defined as the weight of 1 cubic centimeter of distilled water at 4° centigrade. At this temperature, water has a maximum density and the above temperature was chosen for this reason. For

large measurements, the kilogram, containing 1,000 grams, is used.

These terms of measure with which we have defined the gram are from the metric system. As this system is not so familiar as the English system, Table I shows in a condensed form many of the terms from the metric system with their English equivalents.

TABLE 1-I.—METRIC UNITS AND ENGLISH EQUIVALENTS

LENGTH AND AREA

1 meter (m.) = 10 decimeters (dm.) = 100 centimeters (cm.) = 1,000 millimeters (mm.) = 39.37 inches.
1 kilometer (km.) = 1,000 meters = 0.6217 mile.
1 meter = 1.094 yards = 3.281 feet.
1 square centimeter (sq. cm.) = 0.155 square inches.
1 square meter = 10.764 square feet.
1 inch = 2.54 centimeters.

VOLUME AND DENSITY

1 liter = 1,000 cubic centimeters (cc.) = a cube 10 cm. × 10 cm. × 10 cm. on a side.
1 cubic meter = 35.315 cubic feet.
1 liter = 0.03532 cubic feet = 61.02 cubic inches = 1.057 quarts = 33.81 fluid ounces.
1 fluid ounce = 29.57 cubic centimeters.
1 gram per cubic centimeter = 62.428 pounds per cubic foot.

WEIGHT

1 gram (g.) = weight of 1 cubic centimeter of distilled water at 4°C.
1 kilogram = 1,000 grams = 2.205 pounds.
1 gram = 10 decigrams = 100 centigrams = 1,000 milligrams.
1 metric ton = 1,000 kilograms = 2,205 pounds.
1 pound = 453.6 grams.
100 grams = 3.5 ounces.

Conservation of Mass.—In our experiences we have observed that the outward appearance of matter is constantly changing, so that it would be reasonable to assume that its mass is also undergoing some sort of change. To test this assumption let us take a lump of coal and burn it. The mass of this lump is certainly much greater than the ashes that result from its burning, but, should we collect the gases formed and account for all the other materials concerned in the burning and weigh them, we should find that the total mass has remained unchanged. All the experience accumulated in the study of every ordinary change

in matter shows that in all ordinary changes the total mass is neither increased nor diminished.

The Properties of Substances.—The chemist and the engineer are interested in the properties of substances not only as a means for distinguishing them from one another but also because the properties determine uses. It is well to consider these properties from two classifications. The physical properties are those which may be observed, measured, or determined without considering the possibility of a transformation of the material into materials of other kinds. The most familiar of these properties are the color, taste, odor, relative heaviness, and the physical state (*i.e.*, whether solid, liquid, or gas). The other physical properties which call for measurements are those of engineering importance. Examples of this group are hardness, solubility, melting point, boiling point, electrical conductivity, heat conductivity, tensile strength, ductility, and density.

The chemical properties of a substance are those which express its capacity for being transformed into other materials. Thus, if we expose iron to a very moist atmosphere, it has the chemical property of transforming into iron rust. Similarly, if we burn iron in air, it has the chemical property of uniting with the oxygen of the air to form a red powder similar to iron rust.

The physical properties of a substance are often the easiest and most convenient means of identification, but the chemical properties are the most conclusive. Thus, we can take a lump of coke, a pencil lead, and a diamond and say that physically they differ in their color, hardness, relative heaviness, etc., but chemically they are the same since they all burn completely in oxygen to form an invisible gas, known as carbon dioxide.

ENERGY

When we consider this great physical universe of ours, we find that it reveals itself to us as matter and energy. All our natural phenomena are found to be an inseparably connected and intimate mixture of matter and energy. Energy itself determines the properties of matter; and every change in matter involves a change in energy. Since our entire universe is so intimately connected with energy, it is very important that we consider some of its characteristics before we study the changes brought about in matter.

We have all at some time or other used the expression that a certain person is full of "pep" and energy, meaning that he has the capacity for doing work. This same thing may also be recognized in inanimate things, such as steam which has been highly compressed in a boiler. It possesses energy, for when it is admitted to the cylinder of an engine it will push back the piston and propel the dynamo of our electric plants. The power lines connected to this dynamo will also contain energy, for should we connect a motor to them it will rotate, or should we connect an electric lamp it will be made to glow. Energy may therefore be defined as the ability to do work.

This energy may make its appearance in a number of forms such as heat energy, electrical energy, chemical energy, radiant energy (that emitted from a lamp), kinetic energy (energy possessed by moving bodies), or potential energy (energy possessed by a body through its position).

Experiments carried out over a long period of time have shown that energy is like mass in that energy in all the ordinary transformations is neither created nor destroyed. This generalization is known as the *law of conservation of energy*. The distribution of this energy between bodies, however, is altered without a great deal of difficulty. For example, if a piece of hot metal is placed into cold water, the metal is cooled and the water is heated so that the metal loses energy and the water gains it. We also find that energy can be freely transformed from one variety to another. Thus the heat energy derived from the burning of coal may be changed into the kinetic energy of the locomotive. Similarly, the kinetic energy possessed by falling water can be transformed into electricity. If we were to make a close study of all such transformations, we should find that a definite quantity of energy of one kind always gives a definite equivalent quantity of another.

Chemical Energy.—When we consider such substances as wood or coal, we find that they possess energy not because of their position or motion but because of their ability to burn or undergo combustion. The process of burning these substances in air consists in the union of these substances or their constituent parts with the oxygen that is present in the air. The result of such burning is the evolution of both heat and light energy. From the law of conservation of energy, it is quite apparent that the energy evolved must be accounted for. The most reasonable

assumption that could be made is that the substances undergoin the burning and the oxygen of the air must possess a certai amount of energy which is released in the form of heat and light This form of stored-up energy is known as chemical energy.

To illustrate chemical energy further, let us burn iron in air The result of such burning will be the disappearance of the metal. In its place we have a reddish powder very similar to iron rust. This reddish powder is composed of a combination of iron and oxygen. According to our assumptions both the iron and the oxygen possess a certain amount of chemical energy which will be transformed to heat and light energy when the iron burns. This red powder may also be separated again into iron and oxygen but experiments have shown that in doing so we must restore as much energy to the iron and oxygen as was evolved when they united. Thus, our expectation which is limited by the law of conservation of energy has been satisfied.

Chemical energy, therefore, refers to that form of energy which makes itself apparent when substances combine with each other and we say that they combine because of the force of chemical attraction or affinity. We do not, however, know any more about the nature of chemical energy than we do about potential energy. In other words we do not know how the energy is stored but we do know that it exists and we name it chemical energy, potential energy, etc. Similarly, we know little more about the force of chemical attraction than we know about the force of gravity.

Measurement of Energy.—In view of the great importance of energy and its changes, it becomes quite important that we devise units for its measurement as well as methods for making the measurement. In general, each kind of energy must have its own units just as with matter which, in the metric system, has its meter for length, liter for volume, and gram for weight. Energy in some of its forms is very difficult to measure directly. In the case of chemical energy neither units nor methods have been devised for its direct measurement. Thus, it is necessary to change this type of energy into a form more convenient for measurement. This is accomplished by changing it into heat or electrical energy and these then are measured in appropriate units.

In a qualitative way we are judges, through the sensations produced, of what we mean by hot and cold and we know that a

thermometer is a much better index of these qualities than are our sensations. The thermometer in this case measures the intensity of the heat and not the quantity of its heat energy. The measurement of the heat energy of a body is made by observing to what extent this body will change the temperature of a given mass of some standard substance. The units of measurement and methods involved are discussed more thoroughly in the section on Heat in Chap. IV.

The thermometer used for measurement of ordinary temperatures depends for its operation on the fact that a substance expands when its temperature is increased. Liquid mercury is the substance most commonly used, but any substance that expands uniformly between suitable temperatures may be used. Assume now that we have a mercury thermometer properly filled, but not provided with a scale, and that we have no other thermometer with which to compare it. It is necessary therefore to determine certain fixed reference points, mark them on the stem of the thermometer, and lay off a scale divided into equal divisions called degrees. If a series of marks or numbers started at zero, then the number of marks indicates the difference in temperature between the temperature at the mark and the temperature selected as zero. The two fixed points that are ordinarily chosen for a thermometer are the melting point of ice and the boiling point of water. The point at which the mercury stands when immersed in ice is marked and used as one of the fixed points on the thermometer. This point is called 0° on the centigrade temperature scale and arbitrarily called 32° on the Fahrenheit scale. The point at which water boils at atmospheric pressure (normal atmospheric pressure at sea level is equivalent to the pressure produced by a 760 mm. column of mercury) is marked and used as the second fixed point. This point is

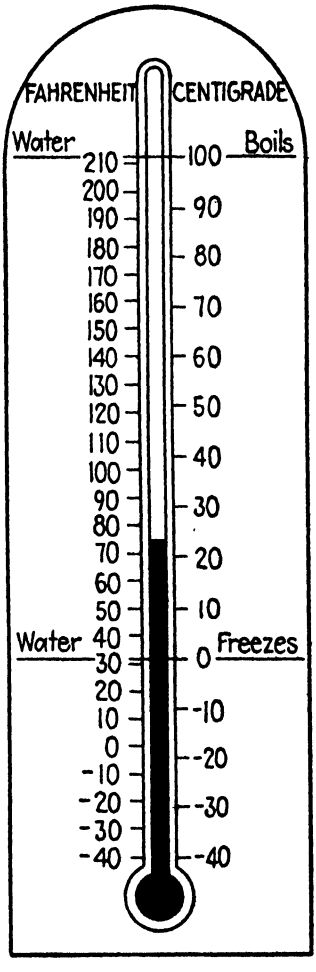


FIG. 1-I.—A thermometer.

called 100° on the centigrade scale and 212° on the Fahrenheit scale.

The two thermometer scales commonly used are illustrated in Fig. 1-I. These scales have been graduated in degrees and, as can be seen, their graduations differ considerably. Thus, the boiling point on the Fahrenheit scale is 212 degrees (212°F.) and on the centigrade scale 100 degrees (100°C.). The freezing point on the Fahrenheit scale is 32 degrees (32°F.) and on the centigrade 0 degrees (0°C.). Hence 100 divisions or degrees on the centigrade scale correspond to 180 on the Fahrenheit scale and 1° on the Fahrenheit scale equals only five-ninths of 1° on the centigrade.

To convert temperature readings from one scale to the other, the following formulas are used:

From Fahrenheit to centigrade, use $C = \frac{5}{9}(F - 32)$.

From centigrade to Fahrenheit, use $F = \frac{9}{5} C + 32$, where F and C are degrees Fahrenheit and centigrade, respectively.

Example: The reading of a thermometer for the temperature of a room is 75°F. What is the reading on the centigrade scale?

$$C = \frac{5}{9}(F - 32)$$
$$= \frac{5}{9}(75 - 32) = 24°$$

Example: The temperature of a furnace is 1000°C. What is the reading on the Fahrenheit scale?

$$F = \frac{9}{5} C + 32$$
$$= \frac{9}{5} 1000 + 32 = 1832°$$

VARIETIES OF MATTER

The forms assumed by matter in the myriad of natural transformations are almost infinite and the classification of these forms may be made in a number of different ways according to the purpose in view. The chemist centers his interests chiefly on the composition of substances and in their chemical energy, together with the changes that take place in both of these. From this standpoint they may be classified into three groups: compounds, elements, and mixtures. The distinction among these three may best be explained by some experiments.

Experiment 1.—Let us first of all familiarize ourselves with the chief characteristics of the two substances with which we are

going to work, namely, iron and sulfur. Iron when finely powdered is found to be dark in color and strongly attracted by a magnet. When it is treated with hydrochloric acid, the iron goes into solution and a colorless gas, known as hydrogen, is evolved along with a considerable amount of heat. Sulfur in its most common form is a light yellow powder which will not dissolve in hydrochloric acid and is not attracted by a magnet. It is, however, quite soluble in a liquid known as carbon disulfide. If this solution is allowed to evaporate, the sulfur is again deposited in the form of yellow crystals. Iron is not soluble in this liquid.

If we take these two substances and thoroughly grind them together, a greenish-black powder is obtained which is quite different from either of the individual substances. If, however, we apply tests to this powder which we have found to characterize these two materials, it is found that in many respects the powder acts like these two taken separately. Thus, hydrochloric acid dissolves the iron and evolves hydrogen and heat, leaving the sulfur unchanged; a magnet rubbed through the powder withdraws the iron and leaves the sulfur; and carbon disulfide dissolves the sulfur but not the iron. The iron and the sulfur, therefore, act just the same as they did before they were mixed, and with the same energy.

Now let us take a portion of this powder, place it in a test tube, and heat it. We soon see that the mixture has started to glow at the point of greatest heat and, even though the flame be withdrawn quickly, the glow will continue to spread through the entire content of the test tube and give off a great deal of heat. Upon examination of this product it is found that there has been quite a modification of the characteristics as shown individually by the iron and by the sulfur. Carbon disulfide no longer dissolves the sulfur and leaves the iron; a magnet does not affect the material; hydrochloric acid dissolves the entire product and evolves a very disagreeable smelling gas which is different from hydrogen; and the heat liberated by the action of the acid is not the same in quantity as in the case of its action on iron alone. Many of the properties of the product differ from those of the constituents, among those being density, color, hardness, solubility, and melting point. In this experiment we have taken two unlike substances and united them to form a third known as iron sulfide. This change is described as a <u>combination.</u>

Experiment 2.—In the previous experiment we noted that when the action of the iron and sulfur was once started, it went on to completion. Such is not the case when we heat a small quantity of sugar in a test tube. In this case the sugar melts, turns brown in color, gives off vapors, and finally dries to a solid black residue which can be identified as carbon. If the vapors that were emitted were collected, they would be found to consist largely of water. The complete transformation of sugar in this case demands that we apply heat continuously. Thus, one substance with the continued application of heat has given rise to at least two other substances of very different properties. This change is described as a decomposition.

It is very easily seen that the two experiments just described differ from each other in many ways, but they do have several common characteristics. We can see that the properties of the materials have changed and that the products formed are different from the original materials, but the most important characteristic is that the chemical energy has been changed. In the case of the iron and sulfur a large amount of heat was evolved which must have come from the chemical energy contained in the iron and sulfur. It is quite apparent that the iron sulfide contains less chemical energy than the two original materials as it is necessary to do work on the sulfide if we regain the iron and sulfur. In the case of the decomposition of sugar it was necessary to apply heat continuously and this heat must be transformed into some other form of energy. A part of it is converted to chemical energy, so that if we were to take the energy possessed by both the carbon and the water we would find that they possess more energy of this kind than did the original sugar. Thus we can say that any transformation in matter, whether combination or decomposition, which involves a change in the chemical energy of the substances concerned is called a *chemical reaction.*

Chemical Compounds.—Since most of the substances with which we shall be concerned belong to this class, it is very important that we know the characteristics of the group. In a general way the characteristics are as follows: (1) A compound is always composed of at least two different substances. Thus in the case of iron sulfide we know that it is composed of the combination of iron and sulfur. (2) The composition of any given compound is always perfectly definite. Considering iron sulfide again, we

find that it contains iron and sulfur in the proportion of almost exactly seven parts by weight of iron to four parts of sulfur. If a mixture of iron and sulfur containing a larger proportion of iron is heated, some of the metal will remain uncombined. Similarly, if too much sulfur is present, all of it will not combine with the metal and the excess may be volatilized by heat or extracted by carbon disulfide. (3) The chemical energy of a compound is always different from the sum of the chemical energies of its constituents taken separately. (4) Finally, a compound has its own characteristic properties, which differ in many respects from the properties of its constituents. Thus, we have seen that iron sulfide has properties different from those of the iron and sulfur of which it is composed.

In all the chemical reactions that we shall study, in fact in every chemical reaction, there is always a change in chemical energy, which change, whether loss or gain, is usually indicated by an evolution or an absorption of heat. However, under the proper conditions, chemical action also involves other energy changes. Thus, we find that chemical energy may be converted into electrical energy. For example, in connecting a plate of zinc by a wire to a plate of carbon and dipping the two into a hydrochloric acid bath, the acid will attack the zinc, and some of the chemical energy set free will appear as an electric current in the wire. In other cases it may be partly transformed to light energy, or into kinetic energy. We must, however, not come to the conclusion that a change in energy is evidence of chemical action. Chemical energy is only one of the many forms of energy that may be changed to our more familiar forms, such as heat and electrical energy. For example, the radiant energy emitted from an electric lamp has its source in the mechanical energy of an engine that may be driven by water power and hence involves no chemical action.

Chemical action may under many conditions be either promoted or hindered. A temperature increase is usually quite favorable to chemical action as in the case of iron and sulfur; in the case of sugar it promotes decomposition. Other forms of energy, such as light, mechanical pressure, and electricity may also promote chemical combination or decomposition.

Elements.—Robert Boyle, a famous chemist, was the first to use this term element or elementary substance to mean a sub-

TABLE 2-I.—THE CHEMICAL ELEMENTS

Element	Symbol	Atomic weight
Aluminum	Al	27.10
Antimony	Sb	121.77
Argon	A	39.94
Arsenic	As	74.93
Barium	Ba	137.36
Beryllium	Be	9.02
Bismuth	Bi	209.00
Boron	B	10.82
Bromine	Br	79.916
Cadmium	Cd	112.41
Calcium	Ca	40.07
Carbon	C	12 000
Chlorine	Cl	35 457
Chromium	Cr	52.01
Cobalt	Co	58.94
Copper	Cu	63.57
Fluorine	F	19 00
Gallium	Ga	69.72
Gold	Au	197.2
Helium	He	4 00
Hydrogen	H	1.008
Iodine	I	126.932
Iridium	Ir	193 1
Iron	Fe	55 84
Lead	Pb	207 22
Lithium	Li	6 940
Magnesium	Mg	24.32
Manganese	Mn	54.93
Mercury	Hg	200 61
Molybdenum	Mo	96.0
Neon	Ne	20.183
Nickel	Ni	58.69
Nitrogen	N	14.008
Oxygen	O	16.000
Palladium	Pd	106.7
Phosphorus	P	31.04
Platinum	Pt	195.23
Potassium	K	39.10
Radium	Ra	225.97
Rhodium	Rh	102.91
Silicon	Si	28.06
Silver	Ag	107.88
Sodium	Na	22.997
Strontium	Sr	87.63
Sulfur	S	32.06
Tantalum	Ta	181.5
Tellurium	Te	127.5
Thallium	Tl	204.39
Thorium	Th	232.12
Tin	Sn	118.70
Titanium	Ti	47.90
Tungsten	W	184.0
Uranium	U	238.14
Vanadium	V	50.96
Zinc	Zn	65.38
Zirconium	Zr	91.22

stance that could not be decomposed. To illustrate this fact, let us return to the experiments previously discussed. Chemists have found that their efforts over many years have failed to decompose carbon, iron, and sulfur but have been able to decompose water into two invisible gases, oxygen and hydrogen, which cannot be further decomposed. There are several hundred thousand of these decomposable substances known to the chemist but, after many years of experimenting, it has been determined that there are 92 elementary substances into which the compounds may be decomposed.

In a few instances elements appear actually to have been decomposed by sources of energy of extraordinary intensity. Radium and a few other elements (the radioactive elements) actually decompose of their own accord, at a rate that we are unable to control. These, however, are not removed from the list of elements for they are far more stable than any compound. To be recognized as an element, a pure substance must have properties that give it a definite place in the periodic table (to be studied later).

Table 2-I gives a list of the more common elements together with their symbols. The symbols are the abbreviations, as designated by the chemist, for the elements. For reasons that will be explained later, the chemist considers that any given quantity of an elementary substance is composed of a vast number of distinct, identical unit particles called *atoms.* The symbol of an element, therefore, stands for one atom of the element. Thus, Fe represents an atom of iron; O, an atom of oxygen; etc. The atomic weight listed for each element is the weight, in any units, of one atom of the element with respect to the atom of oxygen which is arbitrarily given an atomic weight of 16.

The distribution of the elements in nature are, as far as we can judge, of very unequal occurrence. According to Table 3-I, we see that oxygen makes up over half the earth's crust including the solid rocks, soil, ocean, and atmosphere. Most of it is in chemical combination with the other elements. In the atmosphere, however, oxygen is for the most part uncombined. Silicon is the second most abundant element. This element exists in combination with oxygen as quartz (white sand) and is an important constituent of many other minerals. Adding to these two

elements the six most common metals—aluminum, iron, calcium, sodium, potassium, and magnesium—we have 98 per cent of the earth's crust. The other elements make up the remaining 2 per cent.

TABLE 3-I.*—RANK OF THE ELEMENTS IN THE EARTH'S CRUST

Element	Average of 10 miles of crust	Average of igneous rocks, 10 miles crust
O_2	49.52	46.59
Si	25.75	27.72
Al	7.51	8.13
Fe	4.70	5.01
Ca	3.39	3.63
Na	2.64	2.85
K	2.40	2.60
Mg	1.94	2.09
H_2	0.88	0.13
Ti	0.58	0.63
Cl	0.188	0.048
P	0.12	0.13
C	0.087	0.032
	99.705	99.59

* CLARK and WASHINGTON, *U.S. Geol. Survey, Prof. Paper* 127, p. 34, 1924.

Mixtures.—It is quite possible to prepare, from elements or compounds or both, a substance which is not itself a compound but is merely a mixture. Ordinary concrete is such a material, as in a broken piece we are able to distinguish the crushed stone, the sand, and the cement that compose it. In many cases mixtures and compounds are not so easily distinguished. For example, alcohol and water mix in all proportions to form a homogeneous liquid; copper and zinc when melted together form a brass, which has different properties from the original metals, yet it has no fixed percentage composition. We can see then that it is possible to have a series with water as the perfectly definite compound on one end, concrete on the other, and between these two every combination of these extremes.

GASES—THE GAS LAWS

Gases are distinguished from liquids and solids by their much smaller weight per unit volume and also by the fact that they

will completely fill any vessel in which they are placed. Gases have no definite volume or surface other than that of the vessel in which they are contained. Experiments have shown that every known substance tends to pass into the gaseous state if its temperature is raised sufficiently, but this is not always possible, as the temperature of gasification may be so high that it cannot be attained or the substance may decompose before the temperature is reached.

Gases are constantly increasing in importance in our modern industry. This importance is exemplified when we consider a few applications. Air not only supports respiration and combustion but supplies motive power in engineering applications and is an important source of nitrogen and oxygen which are used in large quantities in the chemical industries. Then, there are the myriad uses of such gases as chlorine, ammonia, sulfur dioxide, and carbon dioxide, which are compressed and shipped in steel cylinders. Consider one other large application which is so important to the field of ceramics—fuel gases. It is difficult to conceive of the quantities of natural gas, coke oven gas, water gas, and coal gas used in these industries.

Characteristics of the Gaseous State.—A gas may be characterized in four ways: (1) Probably its most striking characteristic is its tendency to expand indefinitely, so as to distribute itself uniformly throughout the space in which it is contained. (2) A second characteristic is its compressibility. If we were to take a volume of gas and alter only slightly the pressure on this volume, it would be very greatly changed. In comparison, it is found that liquids and solids are comparatively little affected by pressure. (3) If a gas is liberated in an evacuated container, it quickly distributes itself throughout this space. This characteristic is known as diffusion. If this gas were liberated in a similar container occupied by another gas, the former would distribute itself throughout the latter. This intermingling of the two gases was brought about by diffusion, and the gases are said to be permeable to one another. (4) Each pure gas is a homogeneous body. There is no tendency for it to settle.

Variation of Volume with Pressure; Boyle's Law.—Let us visualize a quantity of gas confined within a cylinder fitted with a gastight, movable piston. If we should apply a weight or force (pressure) to the piston, it would cause the piston to descend and

confine the gas within a proportionately smaller volume. It is found that, if the pressure is doubled, the volume will be diminished by one-half, the temperature in this case being constant. Similarly, if we diminish the pressure by one-half, the volume will double. This effect was first studied by Robert Boyle (1660) who, by careful measurement, found that the volume which a given mass of a gaseous substance occupies is inversely proportional to the pressure under which it is measured, provided the temperature remains constant. Stated in algebraic terms, we have the equation:

$$P_1V_1 = P_2V_2 \qquad \text{or} \qquad V_2 = \frac{P_1V_1}{P_2}$$

where P_1 = original pressure.
P_2 = new (increased or decreased) pressure.
V_1 = original volume.
V_2 = new (increased or decreased) volume.

It should be understood that this law and the following law of Charles are like most laws of science in that they are only an approximate statement of facts, since all gases do not act in exactly the same way, and extreme conditions produce irregularities. These laws are, however, within the ordinary accuracy required and hence are a satisfactory statement of facts.

The pressure under which a gas is confined may be expressed in one of many ways, such as pounds per square inch, grams per square centimeter, inches of water, in atmospheres, or centimeters of mercury. An atmosphere is practically the average pressure due to the weight of the air at sea level. For practical purposes we must choose some standard pressure to which all gas volumes may be referred (if no reference conditions are given). The most convenient one is the average pressure at sea level as indicated by the barometer reading. The barometer reading is chosen since the exact pressures to which gases are subjected vary directly with its readings. Standard conditions (reference conditions) are those in which the gas is supporting a pressure of one atmosphere or a mercury column 760 mm. high, at a temperature of 0°C.

Variation of Volume with Temperature; Charles's Law (Gay-Lussac's).—Let us return to the cylinder used in the study of Boyle's law and again consider that a quantity of gas has been confined therein, but this time keep the pressure constant and

increase the temperature. The gas will in this case expand and drive the piston outward. If, on the other hand, we lower the temperature, the gas will contract and occupy a smaller volume. The piston will then descend.

Experiment has shown that if a quantity of gas is confined under this piston at 0°C., a drop of one degree of temperature will diminish its volume by $\frac{1}{273}$ of its volume at 0°C. With the temperature at 100° below 0°C., the decrease would be $\frac{100}{273}$ of its volume at 0°C. The reverse effect will take place with any increase of temperature above 0°C. If we were to cool the gas 273° below 0°C., we could deduce that the gas would disappear altogether, but this does not happen as gases always condense to a liquid, or even freeze to a solid, before this temperature has been reached.

From these facts it has been found desirable to use what is known as the absolute scale of temperatures rather than the Fahrenheit or centigrade. On this scale the divisions are the same size as on the centigrade scale, but the zero point is at −273° centigrade. Therefore, the freezing point of water, which is at 0° on the centigrade scale, is equal to 273°A. (absolute). To convert centigrade degrees to absolute degrees, add 273; conversely to convert absolute degrees to centigrade degrees, subtract 273. For example, 20°C. = 20° + 273° = 293°A. On this scale the volume of gas is proportional to the temperature at every point. Add 460°F. to obtain F.° Abs.

Charles in 1787 and Gay-Lussac studied independently the variation of volume of a gas with temperature and formulated the following general statement: The volume of a given sample of gas varies directly as the absolute temperature (if the pressure is kept constant). Stated algebraically we have the following equation:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \quad \text{or} \quad V_2 = \frac{V_1 T_2}{T_1}$$

where V_1 and V_2 are the volumes at the absolute temperatures T_1 and T_2.

Variations of Volume with Changes in Both Pressure and Temperature.—In case both the pressure and the temperature change, the corrections for each may be made in succession, but it is more convenient to combine the equations expressing Boyle's

and Charles's laws for the solution of such problems. The summation of these two equations is as follows:

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

Example: To apply the laws of Boyle and Gay-Lussac in problems involving volumes of gases, let us assume that a gas occupies 25.45 cc. at 20°C. and 740 mm. pressure. Required, the gas volume at standard conditions.

Original conditions:

$$V_1 = 25.45 \qquad T_1 = 20 + 273 = 293°\text{A.} \qquad P_1 = 740$$

Final conditions:

$$V_2 = ? \qquad T_2 = 273°\text{A.} \qquad P_2 = 760$$

First of all, we notice that the gas is cooled from 20 to 0°C. or from 293 to 273°A. Therefore, the gas will contract and occupy a smaller volume than before. We also note that the pressure is increased from 740 to 760, which means that the gas is compressed and will occupy a smaller volume than before. In each case then the original volume must be multiplied by a fraction smaller than one. The final volume will be

$$V_2 = 25.45 \times {}^{273}\!/_{293} \times {}^{740}\!/_{760} = 23.10 \text{ cc.}$$

Volumes, Pressures, and Temperatures in the English System. The calculations in the preceding sections have all been in the metric system. It should be emphasized that all these calculations may be accomplished equally as well in the English system. The relations between metric and English units have been given and the only thing necessary to know is how to change from one system to the other.

Temperature.—In connection with Charles's law it was shown that for each centigrade degree change in temperature the volume of any gas changes its volume by $1/273$ of its volume at 0°C. or 273°A.

In the English system there is also an absolute temperature scale in which the size of each degree is the same as the size of the Fahrenheit degree. This absolute temperature scale is often called the Rankine temperature scale to differentiate it from the

other absolute scale which is often called the Kelvin temperature scale (1°K. = 1°C. = $\frac{9}{5}$°F. = $\frac{9}{5}$°R.). Absolute zero (0°R.) is equal to −460°F. Zero degrees Fahrenheit is equal to 460°R. To convert Fahrenheit degrees to the absolute Rankine scale add 460° to the Fahrenheit temperature.

The volume of any gas changes $\frac{1}{460}$ of its volume at 0°F. (460°R.) for each 1°F. change in temperature. The formula given under Charles's law applies equally well when the temperatures are in Fahrenheit; the only precaution to observe is that the absolute temperature must be obtained by adding 460° to obtain the Rankine scale rather than 273° as in the case of changing the centigrade to the Kelvin scale.

Pressure.—In the metric system the pressure exerted by the atmosphere at sea level is capable of supporting a column of mercury 760 mm. high. If the height of this same column is measured in inches, it will be found to be 29.92 in. high. In industrial installations pressures are often given in inches of mercury and the volume of a gas bears the same relation to inches of mercury as it does to millimeters. The only difference is the difference in the size of the units used in measuring the column. The relation between inches and millimeters is 1 inch = 25.4 millimeters. In the English system pressures are also frequently expressed in pounds per square inch and also in inches of water.

The pressure of the atmosphere will support a column of water nearly 34 ft. high. The exact height of the column of water may be calculated by multiplying 29.92 in. of mercury by 13.6 (mercury is 13.6 times as heavy as water).

$$29.92 \times 13.6 = 406.9 \text{ in. of water}$$

or approximately 33 ft., 11 in. Since the column of water supported by a given pressure is much greater than the column of mercury that would be supported by the same pressure, water is often used for measuring small pressures, for the longer column can be measured more accurately.

A column of mercury 1 in. high exerts a pressure of 0.491 p.s.i. 29.92 in. of mercury exerts a pressure of 14.69 p.s.i. Thus the pressure exerted by 1 atm. is approximately 14.7 p.s.i. The volume of any gas is inversely proportional to the pressure in any of the units described. The following factors may be used to convert values expressed in one set of units to another:

1 atm. = 760 mm. of mercury
1 atm. = 29.92 in. of mercury
1 atm. = 33.9 ft. of water
1 atm. = 14.7 p.s.i.
1 in. of mercury = 25.4 mm. of mercury
1 in. of mercury = 1.13 ft. of water
1 in. of mercury = 13.6 in of water
1 in. of mercury = 0.491 p.s.i

Volume.—The volumes of gases are usually expressed in cubic feet in the English system. One cubic foot equals 28.3 liters or 28,300 cc. Standard conditions in the English system are 32°F. and 1 atm. pressure.

Example: If a certain gas occupies 89.7 cu. ft. at 29.1 in. of mercury and at 68°F., find its volume at standard conditions (32°F. and 29.92 in. of mercury).

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

Original conditions:

$V_1 = 89.7$ $T_1 = 528°\text{R.}\ (460° + 68°)$ $P_1 = 29.1$

Final conditions:

$V_2 = ?$ $T_2 = 492°\text{R.}\ (460° + 32°)$ $P_2 = 29.92$

$$V_2 = 89.7 \times \frac{492}{528} \times \frac{29.1}{29.92} = 81.29 \text{ cu. ft.}$$

THE KINETIC-MOLECULAR HYPOTHESIS

We know that when a gas is compressed, *i.e.*, its volume decreased, it is under a higher pressure than before compression. Also, we know from experience that when a fixed volume of gas is heated, its pressure also increases. If the pressure is kept constant and the gas is heated, an increase in volume takes place. These facts require explanation and can be explained most completely by the conception of the internal structure of matter known as the *kinetic-molecular hypothesis*.

This hypothesis first assumes that all matter is composed of exceedingly minute particles called *molecules*, the molecules of any particular substance being all alike in nature and weight. In solids and liquids these molecules are packed closely together—

more so in solids than in liquids. In gases, however, the molecules are widely scattered with much vacant space between them. In the second place, the hypothesis assumes that the molecules of all substances under ordinary conditions are in rapid motion and consequently possess *kinetic energy*. Whereas in liquids and solids this motion occurs within a definite and limited volume, the molecules of a gas are free to distribute themselves throughout all of the containing vessel. The bombardment of the molecules of a gas on the walls of the containing vessel produce the effect commonly known as *pressure*. The hypothesis gets its name from these two assumptions and has been found to be true in all respects.

According to the foregoing ideas of the internal structure of a gas, compression of the gas involves only compression of the empty space between the molecules. Since the molecules are in rapid motion in straight lines except when they come in contact with other molecules or with the walls of the vessel, compression of the gas increases the *frequency* (number of times per second) with which the molecules strike the walls of the vessel. This is because the compression has reduced the space through which the molecules must travel before striking the walls of the vessel.

There is no tendency for a gas to settle in its containing space because the pressure of a gas on the top and bottom of its container can be found to be exactly equal. Because of this fact, we must assume that the molecules of the gas are in constant motion without loss in energy because if they slowed down some settling would take place. We must further assume that each molecule of any one gas is exactly like every other molecule of that gas, because if any difference in energy or weight were present, settling would again occur. We therefore reason that the molecules are perfectly elastic, *i.e.*, they bounce back from contacts with other molecules and from the walls of the container without loss of energy. This property of molecules is unlike any aggregate substance, because a rubber ball, for example, when dropped on the floor will lose energy at each bounce until it comes to rest. It is therefore not perfectly elastic. The speed of motion of molecules of a gas is very high; in fact the velocity of a hydrogen molecule at room temperature is about 1,840 m. per sec.

The fact that the pressure of a gas at constant volume increases with increase in temperature can be explained by assuming that

the velocity of each molecule is increased as the temperature is raised, an assumption that can be proved. This increase in velocity increases the kinetic energy of the molecules and, therefore, the pressure, since the frequency of bombardment of the constant number of molecules against the walls of the container increases with an increase in their velocity.

At ordinary pressures, the molecules of a gas show almost no desire to stick together (to *cohere*). At very high pressures, however, the empty space between them reaches such a low value that the molecules are close enough together to show some cohesion. We find experimentally that all gases can be liquefied (changed to the liquid state) if the temperature is sufficiently low and the pressure great enough. When the kinetic energy (energy of motion) of the molecules is reduced low enough by cooling and the molecules are brought close enough together by compression, the gas will condense to a liquid state. It is further found that the kinetic energy must be reduced to a certain low value for each gas in order that liquefaction may occur at any pressure, however great. This means that the gas must be cooled to a certain temperature, called the *critical temperature* for that gas, and the farther below this temperature the gas is cooled, the smaller the amount of pressure necessary to liquefy it. The critical temperature of hydrogen is −234°C. (−389°F.), of oxygen −118°C. (−180°F.), of carbon dioxide 31.35°C. (88°F.), and of water 374°C. (705°F.). By changing the pressure and further cooling the liquefied gas, the liquid can be frozen to the solid state. For example, the melting point of solid hydrogen is −260°C. (−436°F.).

In the liquid state, the molecules are packed so closely together that compression takes place only by using enormous pressures. The molecules are so close together that cohesion is quite pronounced and the liquid hangs together in drops and, when present in a container of larger size than its volume, does not completely fill the container but possesses a surface at its upper boundary. The liquid does possess, however, the general properties of a gas to a modified degree and, as the temperature of the liquid is raised, the differences between the liquid and the gas become less and less until, at the critical temperature, they become identical. The temperatures at which the solid changes to the liquid state and the liquid changes to the gaseous or vapor state are known

as *transition points* and each occurs at a definite temperature for each substance at a fixed pressure. The temperature at which the solid-to-liquid change occurs is known as the *melting* or *freezing point* and the temperature of the change from liquid to gas the *boiling point.*

For the purpose of studying the relations between the liquid and the vapor state in greater detail, let us assume that a quantity of liquid water is introduced into a previously evacuated container of greater volume and in such a way that a vacant space exists above the liquid. Let us further assume that the temperature remains constant. In spite of the great cohesive forces existing between the molecules in the liquid state, the motion of the molecules causes some of them to break through the surface layer of the liquid and enter the previously empty space above where they move around as molecules of a gas. As soon as a few of them are present in the vapor space, they begin to exert a pressure upon the liquid below by their bombardment of its surface. In so doing, some of them reenter the liquid but their places are immediately taken by other molecules shooting forth from the liquid. At first, emission of molecules from the water takes place while there are no molecules in the vapor state to reenter the liquid. The pressure of the vapor increases, however, as the concentration of molecules in the vapor space becomes greater. Also, the number of vapor molecules plunging back into the liquid increases in proportion to the degree to which they are crowded together in the vapor space. The rate at which molecules return to the water begins at zero and increases steadily, while the rate at which molecules leave the water maintains a constant value. Hence the rate (number per unit time) at which vapor molecules enter the water must finally equal the rate at which water molecules leave the liquid. A greater number of molecules cannot leave the liquid than return to it because the pressure in the vapor space is too high for additional molecules to overcome. Likewise, if more molecules enter the liquid in a given time than leave it, the pressure of the vapor space decreases sufficiently to allow the escape of more molecules from the liquid. A balanced state, therefore, sets in, in which the number of molecules leaving the vapor space is exactly balanced by the number entering it, and the pressure in the vapor space remains at a fixed value. This pressure can be measured and is known

as the *vapor tension* of the liquid and, in the case of water, is known as the *aqueous tension.*

Such a balanced state as that just described is known as a *state of equilibrium.* It is emphasized that this condition is not a *static* state (at rest) but a *dynamic* one (in motion). There are three important characteristics of a state of equilibrium:

1. There are always two opposing tendencies which, when equilibrium is established, exactly balance each other. In the previous case, one tendency is the hail of molecules leaving the liquid, a constant value that represents the *vapor tension of the liquid.* The other tendency is the hail of returning molecules which increases from zero to its final value. This is known as the *vapor pressure of the vapor.* These have the effect of opposing pressures and, when they become equal, equilibrium is reached. We can symbolize the two opposing tendencies by arrows, thus,

$$\text{Water (liquid)} \rightleftarrows \text{water (vapor)}$$

2. Although their effects neutralize each other at equilibrium, both tendencies are still *in full operation.* The opposing streams of molecules are still at work but neither can bring about any visible change in the state of the system. Equilibrium, therefore, is a state of balanced activity, not one of rest.

3. A slight change in the conditions produces instantly a correspondingly small change in the state of the system. The change in conditions accomplishes this by favoring or disfavoring one of the two opposing tendencies. For example, when the temperature of liquid water is raised in the previous case, the motion of its molecules is increased, the rate at which they leave its surface becomes greater, the vapor tension increases, and hence a greater concentration of vapor can be maintained. The system, therefore, quickly reaches a new state of equilibrium at which a higher vapor pressure exists.

Avogadro's Hypothesis.—From the previous study we have found that all kinds of molecules possess the same average kinetic energy and that, regardless of their kind, must all exert the same pressure on the sides of the confining vessel. It therefore proceeds from a consideration of the gas laws and the kinetic theory of gases that equal volumes of all kinds of gases contain the same number of molecules. This assumption was suggested by the Italian physicist Avogadro and is known as Avogadro's hypoth-

esis. Thus, we can say that a liter of hydrogen contains just as many molecules as a liter of oxygen, a liter of chlorine, or a liter of any gas measured under the same conditions of temperature and pressure.

LAWS OF CHEMICAL COMBINATION

In the previous section we studied two of the laws governing chemical action:

1. The law of conservation of mass, which states that within the limits of experimental accuracy no change in the total mass of matter can be detected as a result of any transformation that matter may undergo; and

2. The law of definite composition, which states that the composition of a pure compound is always precisely the same.

In this section we extend these laws.

Combining Weights.—In the law of definite composition we found that the elements making up a compound did so in a definite weight ratio. These combining weight ratios are easily

TABLE 4-I.—A FEW COMBINING WEIGHTS

Substance	Percentage composition by analysis	Number of parts of the element uniting with 8 parts of oxygen
Magnesium oxide:		
Magnesium	60.32	12.16
Oxygen	39.68	
Copper oxide:		
Copper	79.90	31.80
Oxygen	20.10	
Water:		
Hydrogen	11.19	1.008
Oxygen	88.81	
Aluminum oxide:		
Aluminum	52.94	9.00
Oxygen	47.06	
Carbon dioxide:		
Carbon	27.27	3.00
Oxygen	72.73	
Calcium oxide:		
Calcium	71.43	20.03
Oxygen	28.57	

calculated from the analysis of pure compounds. Since most of the elements combine directly with oxygen, it is possible to learn from experiment what weight of each will combine with a fixed weight of oxygen. These weight numbers may then be compared.

Table 4-I shows a list of relative weights in which some of the elements combine with 8 g. of oxygen. We immediately wonder why the chemist has chosen oxygen and exactly 8 g. of oxygen. Since the combining weight of each element is a true constant of nature, it was essential to select one element as a standard and determine what weight of every other element will combine with some fixed weight of this standard. Convenience has been the chief guide in selecting oxygen as the standard. Convenience again has been the factor in assigning the value of eight to oxygen. Any number might have been chosen since the combining numbers are merely relative to the arbitrary value assigned to the standard. This integer of eight is the smallest convenient one since it is found that 8 g. of oxygen unite directly with 1.008 g. of hydrogen to form water. Any smaller value would make the combining weight of hydrogen, the lightest known substance, less than unity and it is well to have all values at least as great as unity.

From this table we may derive a partial list of combining or equivalent weights:

Oxygen	8.0	Hydrogen	1.008
Magnesium	12.16	Aluminum	9.0
Copper	31.8	Carbon	3.0
Calcium	20.03		

From this table we might postulate that, since 1.008 g. of hydrogen are equivalent to 8 g. of oxygen, the weight of any element uniting with 1.008 g. of hydrogen would probably unite (if at all) with exactly 8 g. of oxygen. Thus, it is found that 35.46 g. of chlorine will unite exactly with 1.008 g. of hydrogen, and, according to our above postulation, this amount of chlorine should combine with 8 g. of oxygen, which it does do.

Fluorine will not combine with oxygen, but it will combine with silver to form silver fluoride. It is possible to find the combining weight of fluorine by using equivalent weights. Thus we can say

Oxygen	Hydrogen	Chlorine	Silver	Fluorine
8 g.	1.008 g.	35.46 g.	107.88 g.	19 g.

This table states that 19 g. of fluorine are equivalent to 8 g. of oxygen since 19 g. of fluorine combine with 107.88 g. of silver, which combine with 35.46 g. of chlorine, which combine with 1.008 g. of hydrogen, which combine with 8 g. of oxygen.

There are many instances where two elements combine in different proportions to form a series of compounds. It would seem possible then for some of the elements to have at least two combining weights. Let us take the two oxides of hydrogen, for example.

	Hydrogen, g.	Oxygen, g.
Water	1.008	8 (= 1 × 8)
Hydrogen peroxide	1.008	16 (= 2 × 8)

Similarly, we may consider the two oxides of carbon.

	Oxygen, g.	Carbon, g.
Carbon dioxide	8	3 (= 1 × 3)
Carbon monoxide	8	6 (= 2 × 3)

Considering the combinations of nitrogen and oxygen, we find that five oxides are formed with radically different properties.

	Nitrogen, g.	Oxygen, g.
Nitrous oxide	14	8 (= 1 × 8)
Nitric oxide	14	16 (= 2 × 8)
Nitrogen trioxide	14	24 (= 3 × 8)
Nitrogen tetroxide	14	32 (= 4 × 8)
Nitrogen pentoxide	14	40 (= 5 × 8)

From these illustrations we can see that the elements combine in the ratio of their combining weights or simple whole multiples of these. Thus the *law of multiple proportions* may be stated in the following way: In a series of compounds that are made up of the same elements, a simple ratio exists between the weights of any one element that combine with a fixed weight of another

It should be emphasized again at this point that the law of multiple proportions applies equally when the units of weight are in the English system, expressed as ounces, pounds, or tons. The principal thing to remember is that a simple ratio exists between the weights regardless of what the units are, provided all weights are expressed in the same units.

ATOMIC HYPOTHESIS

We have found in the previous study that the combining weights are different for different elements. There is apparently something significant in the fact that, in the compounds of oxygen with hydrogen, the amount of oxygen combined with a given weight of hydrogen is eight, or twice eight, times the weight of the hydrogen.

Since water is composed of 8 parts by weight of oxygen and 1 part of hydrogen, the smallest masses of water must have this composition. For the same reason, the smallest masses of hydrogen peroxide must contain 16 parts by weight of oxygen to 1 of hydrogen. Why is eight the characteristic of oxygen, and why is there no compound of these elements in which the ratio is 10:1 or 20:1? These facts may be explained by the atomic hypothesis.

It was John Dalton, an English scientist, who made certain assumptions in looking for an explanation for the facts to describe the laws of definite composition and of multiple proportion, from which the atomic theory has been developed. His theory is as follows:

1. The ultimate particles of a pure substance, simple or compound, are alike in size and weight.

2. The "simple atoms" of an elementary substance are indivisible, and can neither be created nor destroyed.

3. The "compound atoms" of a chemical compound are formed by the union of two or more elementary atoms.

4. Combination between atoms takes place in the simplest possible ratios, *e.g.*, one atom of *A* with one, two, or three atoms of *B*.

If we now think of the universe as being composed of atoms, we immediately ask the question whether there is an infinite number of different kinds of atoms, corresponding to the almost endless variety of material things or whether all material things

are composed of relatively few different kinds of atoms. In answer, we believe now that there are only 92 kinds of atoms, as many as there are elements. From these elements or atoms the thousands of complex materials are formed by bringing them into special groupings or arrangements, each having the characteristics of a given material.

Such combinations, formed by atoms entering into chemical union with one another, are now called *molecules*. A molecule is, therefore, the smallest particle of any pure substance. If we were to take a molecule of sugar apart, we should have particles that no longer taste like sugar. They would merely be atoms of carbon, hydrogen, and oxygen. The smallest particles of elements taking part in chemical reactions are thus called *atoms*. A chemical reaction, then, is merely a regrouping of the atoms in new combinations. Two or more atoms of the same kind may unite to form molecules of an elementary substance.

This theory explains the law of conservation of mass since a reaction taking place between substances in a closed vessel is found neither to gain nor to lose weight. In other words, all the atoms in the reacting substance are accounted for in the new substance.

It explains the law of definite composition for, when one element unites with another, the combination always takes place between a definite number of each kind of atom. In the formation of water it is found that the percentage of oxygen and hydrogen by weight is always the same.

It also explains the law of multiple proportion in that, when two atoms of hydrogen unite with two atoms of oxygen, instead of one as in water, a new compound is formed which is quite different from water. This compound is called hydrogen peroxide.

Modern Atomic Theory.—Dalton's atomic theory did not explain why some elements react with each other and others do not, what forces hold atoms together in molecules, and how the constituent atoms are arranged. It has been only in recent years that scientists have been able to obtain information on the structure of the atom and this has been done principally through the use of the X-ray beam and the study of radioactive elements. Although the ideas of scientists vary somewhat as to the details, the following concept is fairly well established at the present time.

According to the modern concept an atom consists of a positively charged nucleus which is very small compared to the size of the atom. In this nucleus is located nearly all of the mass of the atom. Around this nucleus there is a distribution of planetary particles called *electrons* in orbital motion. The atom, therefore, consists of small particles each of which has an electrical charge. The positively charged particles are called *protons* and the negatively charged particles *electrons*. All the protons in the atom are identical and each possesses one unit of positive electricity. Likewise all electrons are identical and each possesses one unit of negative electricity. The nucleus is found to be made up of both protons and electrons, closely associated in a group. The nucleus contains all the protons and, since there are always a greater number of protons than electrons in the nucleus, it has a net positive charge. The total charge on the planetary electrons is just equal to the net positive charge on the nucleus. This atom is like a planetary system with the nucleus replacing the sun and the electrons replacing the planets. The size of these central suns differs from atom to atom and the number of planetary electrons also differs from atom to atom.

It has been found that the positive charge of the nucleus is different for each element and that this nuclear charge is equal to the sequence number of the element in the periodic system. If we examine the periodic table shown on page 46, we shall note that the figures appearing above the abbreviations of the elements start with hydrogen as unity and that successive values differ from each other by unity. The elements, thus, are arranged in a general order from 1 to 92. This arrangement and interpretation were made possible through the studies by Moseley. He was able to show that this regularity was due to regular changes of the charge on the nucleus. The charge on the nucleus of the hydrogen atom is found to be 1, of the helium nucleus 2, etc. This number is known as the atomic number and represents the number of positive charges on the nucleus of an atom of the element and denotes its position in the series of elements. To illustrate: The number of hydrogen is taken as 1, which means that the hydrogen atom is made up of one proton as a nucleus and one electron in orbital motion about this nucleus (Fig. 2-I). In this case the positive charge on the proton is just equal to the negative charge on the electron so

that the atom in the normal condition is neutral. When we pass from hydrogen, which has an atomic weight, atomic number, and atomic charge of unity, we next come to helium with an atomic weight of 4 and an atomic number or nuclear charge of 2. The helium nucleus, with which is associated most of the mass of the helium atom, consists of four hydrogen nuclei or protons. These four protons would give a nuclear charge of four units, but the nuclear charge is 2 so that there must also be two electrons in the nucleus. The effective nuclear charge is thus two units of positive electricity (Fig. 2-I). The atoms of larger atomic weight are thus formed by adding additional units to the core of the atom and additional electrons to the region outside the core.

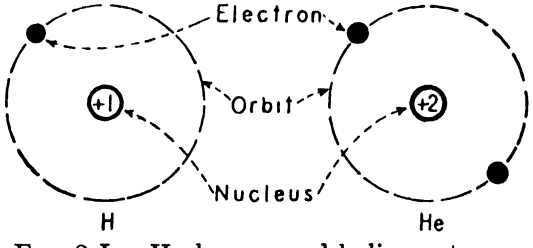


FIG. 2-I.—Hydrogen and helium atoms.

The entire chemical behavior and most of the physical properties of the atoms are determined by the planetary electrons. Even though there is an electrical attraction between the electrons (negative) and the protons (positive), some of the outer planetary electrons are known to escape to other atoms. For example, some of the most active atoms like those of the metals sodium and potassium have a very great tendency to give away their outer electrons, while some of the most active nonmetallic atoms like those of fluorine and chlorine have a reluctance to give away electrons but have a strong tendency to take on electrons. Thus we can see why two such active metallic atoms will not react with each other—each of these two types is trying to do the same thing, throw off an electron. To illustrate this tendency, let us consider a typical chemical reaction. We find that sodium reacts with chlorine, because of the fact that the chlorine atom takes the electron that the sodium atom is willing to give away and we have a chemical reaction to form a molecule of sodium chloride (salt). This electron transfer is shown in Fig. 3-I. Here we see that the electrically neutral sodium atom loses

an electron and leaves an excess of one proton, or positive charge, on the atom, while the neutral chlorine atom gains an electron and makes that atom negatively charged. Thus we have two oppositely charged atoms held together in the molecule of salt by electric attraction.

In some types of reaction outer planetary electrons are shared by the atoms in pairs. In the simplest case two atoms share a single pair of electrons. For example, two fluorine atoms combine to form a fluorine molecule. Before combining, each fluorine atom has the desire to take on one electron, so rather than one rob the other they compromise by sharing electrons. This sharing of electrons is also true of a few other elements, such as

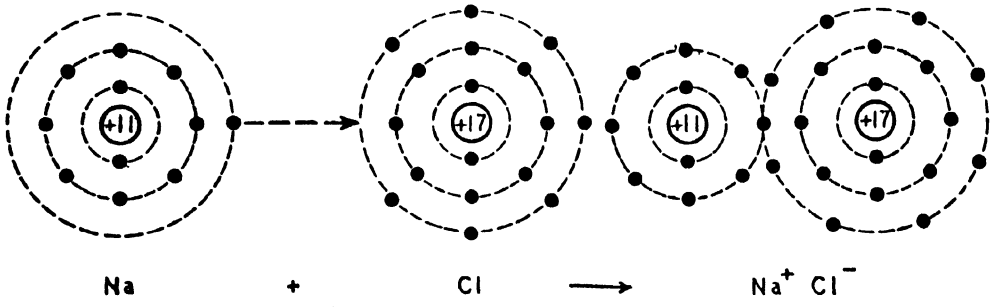


FIG. 3-I.—Electron transfer and chemical reaction.

oxygen, hydrogen, nitrogen, and chlorine. Hence the molecule of these elements is composed of two atoms.

The atoms of inert gases like helium, neon, and argon are so stable that they neither gain nor lose planetary electrons; consequently they never react with anything and thus form no compounds. With these gases, therefore, one atom constitutes a molecule.

Atomic Weights and Molecular Weights.—We have seen how the combining weights of the elements can be determined with accuracy and how the atomic theory interprets these combining weights to be the relative weights of the atoms. The difficulty is, however, that nearly all elements combine in more than one ratio and, therefore, have more than one combining weight. For example, hydrogen and oxygen unite in the ratio of 1:7.94 to form water and in the ratio of 1:15.88 to form hydrogen peroxide. To determine whether 7.94 or 15.88 is the relative atomic weight of oxygen, we must first know the relative weight of the water molecule and how many atoms of each element it contains.

According to Avogadro's hypothesis, we found that equal volumes of gases under identical physical conditions contain the same number of molecules. From this we can deduce that the weights of equal volumes of two gases are in the same ratio as the weights of their molecules. Thus, if we find that a liter of carbon dioxide gas is about one-third heavier than the same volume of oxygen gas under the same conditions of temperature and pressure, we know that the molecule of carbon dioxide is about one-third heavier than a molecule of oxygen. It must be noted that this method applies only to gases and vapors and not to liquids or solids. Other methods which will not be described have been found for obtaining the relative weights of the molecules of substances that are not readily gasifiable.

Oxygen has been chosen as the standard of comparison in finding the relative weights of atoms and molecules, since it can be made to combine with nearly all the elements. A molecule of oxygen is arbitrarily taken as 32 units of weight so that the lightest known substance (one atom of hydrogen) comes out with a weight very close to 1.

The average weight of the molecule of a given substance, in comparison with a molecule of oxygen, taken as 32 units, is called the *molecular weight* of the substance. Thus, when we say that a gas has a molecular weight of 64, we imply that one of its molecules is twice as heavy as a molecule of oxygen.

Having determined the relative weights of molecules, we can now find the relative weights of the atoms of which they are composed. Such relative weights of atoms—in comparison with a molecule of oxygen, taken as 32—are called *atomic weights.*

The approximate atomic weights of an element may be determined by noting the least weight of each element found in a molecular weight of any of its compounds. The least weight of an element in a molecular weight apparently then corresponds to the least possible number of atoms in a molecule, or one atom. For example, in the analysis of carbon compounds the least weight of carbon ever found in any of them is 12. Therefore, this is the relative weight of one atom of carbon on the scale that makes a molecule of oxygen weigh 32. Atomic weights have thus been determined for all the elements except the inert gases, which have been determined by other means. The approx-

imate atomic weights are found to range from 1, which is the atomic weight of hydrogen, to 238, which is that of uranium.

The atomic weight of oxygen, hydrogen, and nitrogen is just one-half of the molecular weight and accordingly there must be two atoms in a molecule of each of these elements.

The atomic weights have been referred to as approximate ones. This is due to the fact that the molecular weights from which they were determined were also slightly in error. However, when a very pure compound is very carefully analyzed, the chemist has been able to correct the atomic weights of the elements it contains. The accurate atomic weights may be found by referring to the periodic table on page 46.

Molar Volume.—Having adopted the arbitrary value of 32 as the molecular weight of oxygen, we should like to know what volume 32 g. of oxygen gas would occupy. One liter of oxygen weighs 1.429 g., so $32/1.429 = 22.4$, the number of liters occupied by 32 g. of oxygen. For convenience, let us imagine a cubic tank that will hold exactly 22.4 liters. If this tank were filled with oxygen or any other gas under standard conditions, the weight of the contents in grams must be the formula weight of that gas, since we see that it is true for oxygen. Thus, according to Avogadro's hypothesis, since this tank must hold the same number of molecules of any gas, the weights vary as the weights of the single molecules. If, therefore, the tank were filled with hydrogen, it would weigh 2.016 g. and the molecular weight would be and is 2.016. The gram-molecular volume of ammonia weighs 17 g. Thus, the molecular weight of ammonia is 17.

In practice it would be very awkward to weigh exactly 22.4 liters, so we simply weigh any convenient volume, say 100 cc. and calculate the weight of 22.4 liters.

By the English system the molar volume may be calculated as follows: One cubic foot of oxygen weighs 0.089 lb., so

$$\frac{32}{0.089} = 359$$

the number of cubic feet occupied by 32 lb. of oxygen. This number, 359 cu. ft., is generally called the *pound-molar volume* to distinguish it from the molar volume found by using grams and liters (22.4) which is called the *gram-molecular volume.*

Both these figures hold for any gas regardless of its composition, providing its molecular weight is known.

SYMBOLS, FORMULAS, AND EQUATIONS

Chemical Symbols.—We have seen that each element is represented by its symbol. Not only does each symbol stand for a certain element, but it also represents a definite weight of the element, namely, a weight proportional to its atomic weight. If we employ the gram as our standard of weight, then the symbol O indicates 16 g. of oxygen; H indicates 1.008 g. of hydrogen. Such a weight is called the symbol weight or *gram-atomic weight* of an element.

If we employ the pound as our standard of weight, then the number representing its atomic weight also indicates the number of pounds for which the symbol stands. Thus O stands for 16 lb. of oxygen and H equals 1.008 lb. of hydrogen. When the pound is used as the unit of weight, the atomic weight is known as the *pound-atomic weight.*

Chemical Formulas.—A chemical formula is a group of symbols showing what kinds of atoms and how many of each are present in any given molecule. Symbols refer to atoms. Formulas refer to molecules. To represent the formula of a compound, we simply join the symbols of the constituent elements and attach small subfigures to represent the actual number of atoms in the molecule. In expressing the composition of the compound, we might use the symbols merely to indicate the elements present in the compound and also give the percentage of each, thus: H, 11.19 per cent; O, 88.81 per cent. It is much more convenient and concise to make use of the atomic weights of the elements constituting the compound. The united symbols H_2O represent the formula for water and tell us that two atoms of hydrogen and one atom of oxygen make up a single molecule of water. The weight of the molecule, 18.016, is the sum of the weights of all the atoms in it; thus $(2 \times 1.008) + (1 \times 16) = 18.016$. Since this weight represents the sum of the atomic weights of the elements in the formula, it is called the *formula weight* or *molecular weight* of the compound that the formula represents.

In the case of the formulas for the elements, we have already found in the study of the atom that the molecule of such elements as oxygen and hydrogen is composed of two atoms; hence the

molecular weights of these elements are twice their atomic weights. The formulas for these elements, when existing as gas or vapor and when uncombined with other elements, are always represented as O_2, H_2, N_2, Cl_2, etc. In the case of the inert gases, where one atom constitutes a molecule, the atomic weight is identical with the molecular weight.

When we deal with a solid element, such as carbon, sulfur, phosphorus, or solid metals, in the crystalline state, there is no definite number of atoms in the molecule and no definite molecular weight. We therefore usually represent solid elements by the symbols of their individual atoms and do not try to indicate their true, or molecular, formulas.

The formula for a substance may be found in several different ways, depending upon what is known. For example, if we are unable to determine the molecular weight of a compound by experiment, we can still deduce its simplest formula from its percentage composition alone, though we cannot be sure that some multiple of this simple form is not the real formula. We know by experiment that water is composed of 88.81 per cent of oxygen and 11.19 per cent of hydrogen. If we divide the percentage of oxygen by its atomic weight (16), the quotient (5.55) will be the relative number of oxygen atoms in 100 parts of water. Similarly, if we divide the percentage of hydrogen by its atomic weight (1.008), the quotient (11.10) will be the relative number of hydrogen atoms in 100 parts of water. The two numbers 5.55 and 11.10 represent the ratio between the number of oxygen and hydrogen atoms in 100 parts of water. This ratio reduced to its simplest form is

$$11.10 \div 5.55 = 2 \qquad 5.55 \div 5.55 = 1$$

The ratio of hydrogen atoms to oxygen atoms in a molecule of water is therefore 2:1, and the simplest formula of water, as well as the real formula in this case, is H_2O.

If we are able to determine the percentage composition of a compound and its molecular weight, we can therefore deduce the formula of the compound as follows: Suppose we know that the molecular weight of water vapor is approximately 18. This represents the sum of all the atomic weights in the molecule. Multiplying 18 by the percentage of hydrogen (11.19) gives 2.016 as the sum of the weight of hydrogen atoms present, or 2 atoms.

Multiplying 18 by 88.81 per cent gives the sum of the weight of oxygen atoms 15.99 or almost exactly 16, or 1 atom. Thus, the formula is H_2O.

Equations.—With the use of symbols and formulas we can now represent chemical changes (reactions) very simply and clearly. For example, the equation

$$2H + O \rightarrow H_2O$$

which is sometimes written with an equals sign instead of an arrow:

$$2H + O = H_2O$$

This equation reads qualitatively that the union of hydrogen and oxygen forms water, and quantitatively that 2 gram-atomic weights of hydrogen (2.016 g. or lb.) combine with 1 gram-atomic weight of oxygen (16 g. or lb.) to form 1 gram-molecular weight of water (18.016 g. or lb.).

We know, however, that the molecules of oxygen and hydrogen contain two atoms each so that the formulas for these gases are written O_2 and H_2 rather than 2O or 2H which would represent two atoms uncombined. To state these facts our equation will have to read

$$2H_2 + O_2 = 2H_2O$$

This type of equation, known as the molecular equation, will ordinarily be used in future studies.

The equality sign, more definitely than the arrow, indicates that the sum of the weights of the reactants is always equal to the sum of the weight of the resultants (law of conservation of weight). It also states that the total number of atoms of each kind in the left-hand part of the equation (left of the arrow or equality sign) must equal the total number in the right-hand portion. When this condition is true, the equation is said to be balanced.

A great amount of practice is necessary before equations can be balanced easily. For example, in the reasoning necessary, let us suppose that by laboratory observation we know that hydrogen reacts with hot iron oxide to form iron and steam. This equation then can be tentatively written as follows:

$$H_2 + Fe_3O_4 \rightarrow Fe + H_2O \text{ (trial)}$$

but on observation we see that all the atoms in the reacting substances are not found in the products. We know that in the formation of any new combinations of elements all the atoms must be accounted for, hence there must be an equal number of H atoms, of O atoms, and of Fe atoms on both sides of the equation. First of all let us try one molecule of Fe_3O_4. In equations we do not prefix "1" to molecules; it is understood if no number is given. As a result of the decision to use one molecule of Fe_3O_4, we must account for 3 atoms of Fe on the right side of the equation. With this change the equation will read

$$H_2 + Fe_3O_4 \rightarrow 3Fe + H_2O \text{ (trial)}$$

We see immediately that the 4 oxygen atoms in Fe_3O_4 are not found in a single molecule of H_2O. It is, therefore, necessary to have 4 molecules of H_2O to dispose of the 4 oxygen atoms because each molecule of H_2O uses only one atom of oxygen. This change will bring a further improvement.

$$H_2 + Fe_3O_4 \rightarrow 3Fe + 4H_2O \text{ (trial)}$$

With 4 molecules of H_2O on the right side there are required 8 atoms of hydrogen, found in 4 molecules of H_2, on the left side for proper balance:

$$4H_2 + Fe_3O_4 \rightarrow 3Fe + 4H_2O \text{ (balanced)}$$

Every atom is now accounted for on both sides of the equation which is, therefore, properly balanced.

A chemical equation, then, must represent the reacting substances, the products formed, and the relative weights involved. It does not, however, name the conditions—temperature, etc.,—necessary to cause the reactions to take place nor does it tell how rapidly or to what extent the reaction occurs.

From our previous observations we can set up a system for making an equation. This is as follows:

1. Write on the left of the arrow (→) the formulas (or symbols) of the substances entering into the reaction, and on the right the formulas (or symbols) of the substances formed.

2. Balance the equation or modify it, if necessary, so that there will be just as many atoms of each element on one side of the equation as on the other.

Type of Reactions.—After a study of many reactions, the chemist has found that equations may represent processes of decomposition, direct combination, simple replacement, and double replacement. We shall find almost all the reactions that we have met and shall meet can be assigned to one of these processes. Many of the equations used to illustrate these processes will not be familiar; however, they are used here to aid the student in formulating completed equations.

Decomposition is the separation of one compound into other compounds or elements. The equations that describe the preparation of oxygen by applying heat to certain substances will serve to illustrate this process. They are

From mercuric oxide:

$$2HgO \rightarrow 2Hg + O_2 \qquad (1)$$

From potassium chlorate → potassium chloride + oxygen:

$$2KClO_3 \rightarrow 2KCl + 3O_2 \qquad (2)$$

Direct combination is the formation of one compound from two or more elements. This is illustrated by the combustion of elements in oxygen and by the action of hydrogen on different elements.

Combustion of phosphorus → phosphorus pentoxide:

$$4P + 5O_2 \rightarrow 2P_2O_5 \qquad (3)$$

Combustion of iron → magnetic iron oxide:

$$3Fe + 2O_2 \rightarrow Fe_3O_4 \qquad (4)$$

Hydrogen + chlorine → hydrochloric acid:

$$H_2 + Cl_2 \rightarrow 2HCl \qquad (5)$$

Hydrogen + nitrogen → ammonia:

$$3H_2 + N_2 \rightarrow 2NH_3 \qquad (6)$$

Hydrogen + oxygen → water:

$$2H_2 + O_2 \rightarrow 2H_2O \qquad (7)$$

Simple replacement, or simple displacement, means that one element may take the place of another in a compound, the

substituted element being set free. This is illustrated by the following reactions:

Preparation of hydrogen from acids by the action of metals:

Iron + hydrochloric acid → ferrous chloride + hydrogen:

$$Fe + 2HCl \rightarrow FeCl_2 + H_2 \qquad (8)$$

Iron + sulfuric acid → ferrous sulfate + hydrogen:

$$Fe + H_2SO_4 \rightarrow FeSO_4 + H_2 \qquad (9)$$

Preparation of hydrogen from water by the reaction as follows:

Water + sodium → sodium hydroxide + hydrogen:

$$2H_2O + 2Na \rightarrow 2NaOH + H_2 \qquad (10)$$

Water + iron → magnetic iron oxide + hydrogen:

$$4H_2O + 3Fe \rightarrow Fe_3O_4 + 4H_2 \qquad (11)$$

Double replacement, or double decomposition, probably the most common type of reaction, consists in the interchange of two elements present in two different compounds, thus resulting in the formation of two new compounds. This may be illustrated by another equation showing the formation of hydrochloric acid. This involves

Sodium chloride (salt) + sulfuric acid → sodium sulfate + hydrochloric acid:

$$2NaCl + H_2SO_4 \rightarrow Na_2SO_4 + 2HCl \qquad (12)$$

In this case the sodium of the sodium chloride and the hydrogen of the acid change places to form two new compounds.

Application of Equations.—The balanced equation of a reaction, in which molecular formulas are used, tells us a great deal regarding the reaction besides the mere statement of the substances entering into and resulting from it. For example, from the equation below, the succeeding quantitative data can be deduced:

	$2H_2$	+ O_2	→	$2H_2O$
Weights:	2×2.016 g.	32 g.		2×18.016 (= 36.032 g.)
Molecules:	2	1		2

Given the formula for a chemical compound, we can easily calculate the percentages of the constituents in it. A sample

calculation to discover the percentage composition of potassium chlorate ($KClO_3$) follows. The first step is to look up the atomic weights of the elements involved and calculate the formula weight, the weight of substance represented by the molecular formula. The atomic weight of potassium is 39.1, that of chlorine 35.46, and that of oxygen 16. The formula weight of the substance is therefore

$$39.1 + 35.46 + 3 \times 16 = 122.56$$

The percentage of potassium is $\frac{39.1}{122.56} \times 100 = 31.9+$ per cent

The percentage of chlorine is $\frac{35.46 \times 100}{122.56} = 28.9+$ per cent

The percentage of oxygen is $\frac{48}{122.56} \times 100 = 39.1+$ per cent

Another way of stating the above is as follows: If 39.1 parts of potassium are contained in 122.56 parts of $KClO_3$, X parts will be contained in 100 parts of $KClO_3$. The proportion is

$$39.1 : 122.56 :: X : 100$$

$$X = \frac{39.1}{122.56} \times 100$$

and the result is the same as the first statement.

It is often necessary or desirable to know the amount of a product that can be obtained from a chemical reaction when the weight of the original material is known. For example, let us determine the weight of ferrous sulfide that can be produced from 100 g. of iron, assuming that the necessary sulfur is at hand. The necessary steps in the solution are as follows:

1. Write the balanced equation:

$$Fe + S \rightarrow FeS$$

2. Place under each formula the weight it represents.

$$\begin{array}{ccccc} Fe & + & S & \rightarrow & FeS \\ 55.84 & & 32.06 & & 87.90 \end{array}$$

3. Read the expanded equation. In this case: 55.84 parts of iron combine with 32.06 parts of sulfur to give 87.90 parts of ferrous sulfide.

4. Reread the original problem: "What weight of ferrous sulfide can be made from 100 g. of iron?" Then place the amount given in the problem (100 g. of iron) under the formula of the substance in question and an X under the formula of the substance, the amount of which is desired in the answer (FeS).

$$\begin{array}{ccccc} \text{Fe} & + & \text{S} & \rightarrow & \text{FeS} \\ 55.84 & & 32.06 & & 87.90 \\ 100\text{ g.} & & & & X \end{array}$$

5. Read the problem as now written: 55.84 g. of iron give 87.90 g. of ferrous sulfide. Therefore, 100 g. of iron will produce X g. of FeS.

6. State the proportion and solve:

$$55.84 : 87.90 :: 100 : X$$

$$X = \frac{87.90}{55.84} \times 100$$

$$X = 157.4 \text{ g. of FeS}$$

In such a simple problem, some parts of this procedure seem unnecessary. In more intricate problems, however, such a procedure is necessary in order to arrive at the correct result without error and the student is advised to get into the habit of using the above method in detail in order to avoid trouble in more complex cases.

Another type of problem is one involving both weights and volumes. For example, to find the weight of lime and the volume of carbon dioxide gas resulting from the burning of 1 ton of pure limestone.

1. The equation:

$$\begin{array}{ccccc} \text{CaCO}_3 & \rightarrow & \text{CaO} & + & \text{CO}_2 \\ 100.0 & & 56.0 & & 44.0 \end{array}$$

2. The weight of lime produced:

$$\begin{array}{ccccc} \text{CaCO}_3 & \rightarrow & \text{CaO} & + & \text{CO}_2 \\ 100.0 & & 56.0 & & \\ 2{,}000\text{ lb.} & & X & & \end{array}$$

$$100 : 56 :: 2{,}000 : X$$

$$X = \frac{56 \times 2{,}000}{100}$$

$$X = 1{,}120 \text{ lb. of lime}$$

3. The volume of CO_2 produced: The pound-molecular volume of any gas equals 359 cu. ft.

$$\begin{array}{ccc} CaCO_3 & \rightarrow CaO + & CO_2 \\ 100.0 & & 44.0 \\ 2{,}000 \text{ lb.} & & X \end{array}$$

$$100:44::2{,}000:X$$

$$X = \frac{2{,}000 \times 44}{100}$$

$$X = 880 \text{ lb. of } CO_2$$

$$880 \text{ lb. } CO_2 = \frac{880}{44} = 20 \text{ lb. molecules}$$

$$20 \text{ lb. molecules} \times 359 = 7{,}180 \text{ cu. ft.}$$

Volume of CO_2 = 7,180 cu. ft. at standard conditions

Problems Involving Calculations of Gas Volume.—It is often necessary to calculate the volume of a gas that can be obtained in a given reaction when measured under ordinary laboratory conditions or the weight of materials that are required to produce a given volume. Equations, as we know, deal with weights, so it is necessary to determine first the weight of the gas and from this calculate the volume. Since it is always necessary to reduce a measured volume of gas to standard conditions before its weight can be calculated, for convenience the weights and volumes of a few of the more common gases are as follows:

TABLE 5-I.—VOLUMES AND WEIGHTS OF COMMON GASES AT 32°F. (0°C.) AND 1 ATM. PRESSURE

Gas	Weight of 1 cu. ft., in lb.	Volume of 1 lb., in cu. ft.	Weight of 1 liter, in g.	Volume of 1 g., in liters	Molecular weight
Oxygen	0.089	11.2	1.43	0.70	32.0
Hydrogen	0.0056	178.0	0.09	11.10	2.016
Nitrogen	0.078	12.8	1.25	0.80	28.0
Air	0.081	12.4	1.29	0.78	29.0
Carbon dioxide	0.123	8.15	1.98	0.50	44.0
Carbon monoxide	0.078	12.8	1.25	0.80	28.0
Ammonia	0.047	21.1	0.77	1.30	17.0
Methane	0.045	22.4	0.72	1.39	16.0
Ethane	0.084	12.0	1.36	0.73	30.0

Problem: What volume of oxygen, measured under ordinary laboratory conditions (say, 750 mm. and 20°C.), may be obtained by heating 100 g. of mercuric oxide?

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

$$433.22\ (2 \times \text{mol. wt. HgO}):32\ (\text{mol. wt. of } O_2) = 100:X$$

$$X = 7.38 \text{ g. of oxygen}$$

1 liter of oxygen (standard) weighs 1.429 g.

$$7.38 \div 1.429 = 5.16 \text{ liters (standard)}$$

The determination of the volume that this will occupy under laboratory conditions necessitates the use of the gas laws. Therefore,

$$V \text{ (standard)} = \frac{P \times V_1 \times 273}{760 \times T}$$

Substituting,

$$5.16 = \frac{750 \times V_1 \times 273}{760 \times 283}$$

$$V \text{ (laboratory)} = 5.63 \text{ liters}$$

If we were asked to determine the number of grams of mercuric oxide to yield 10 liters of oxygen measured at 750 mm. pressure and 20°C., we would proceed as follows:

$$V_s = \frac{P \times V \times 273}{760 \times T} = \frac{750 \times 10 \times 273}{760 \times 293} = 9.19 \text{ liters (standard)}$$

$$9.19 \times 1.429 = 13.13 \text{ g. oxygen}$$

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

$$32:433.22 = 13.13 \times x$$

$$x = 177.75 \text{ g. mercuric oxide}$$

Problem: What volume (in cubic feet) of carbon dioxide is produced by the burning of 1,300 lb. of pure carbon with oxygen under standard conditions?

$$\begin{array}{ccccc} C & + & O_2 & \rightarrow & CO_2 \\ 12 & & 32 & & 44 \\ 1{,}300 & & & & X \end{array}$$

$$12:44::1{,}300:X$$

$$X = \frac{1{,}300 \times 44}{12}$$

$$X = 4{,}766 \times 8.15 = 38{,}843 \text{ cu. ft.}$$

PERIODIC TABLE

In the previous studies it was found that each element has certain peculiar properties that distinguish it from all other elements. However, if all the elements are considered together, it is found that there are certain groups that have very similar chemical properties. Mendelyeev, a Russian chemist, was the first to discover this relationship between the elements and in

1869 he proposed a system of classification in which the elements are arranged according to their properties. This system is known as the periodic system and is shown in Table 6-I.

In this chart the symbols of the elements are given with the atomic weight of each directly below it. A study of the chart reveals that the elements are arranged in horizontal rows of nine in the order of increasing atomic weight. There are nine regular groups marked Groups 0 to VIII, and the elements contained in each of these groups have similar chemical properties. The formulas R_2O, RO, etc., placed above each group represent the general type of combination of elements in that group which will combine with oxygen. Similarly H_4R, H_3R, H_2R, etc., represent the general type of combination of elements in that group which will combine with hydrogen. The groups are further divided into (a) and (b) columns. The elements in column (a) have some properties in common that differentiate them from the elements in column (b). However, all the elements in the vertical group have one important chemical property in common. This chemical property is known as valence.

Valence.—Valence may be defined as that property of an atom which enables it to combine with a certain number of atoms of another element, the number of other atoms being the valence of the atom in question. The elements in group 0 do not have the power of combining with other elements, hence their valence is zero. The elements of group I have a valence of one, the elements of group II a valence of two, etc. Elements may have positive valence (+) or negative valence (−). The elements enclosed in the heavy-lined area are known as the nonmetals and usually have negative valence; those elements outside the heavy line are the metals with the exception of hydrogen and the elements of group 0 and usually have positive valence. Although hydrogen does not have metallic properties, its chemical properties are similar to those of the metals and it has a valence of +1. As a general rule, elements having a positive valence combine with those having a negative valence. Thus the metals usually combine with the nonmetals to form compounds. The elements in group VII have a valence of −1, those in group VI a valence of −2. Thus, we see that positive valence increases as we go from left to right in the periodic table while negative valence increases as we go from right to left.

TABLE 6-I.—PERIODIC TABLE—GROUPS

0	I R_2O (a)	I R_2O (b)	II RO (a)	II RO (b)	III R_2O_3 (a)	III R_2O_3 (b)	IV RO_2 H_4R (a)	IV RO_2 H_4R (b)	V R_2O_5 H_3R (a)	V R_2O_5 H_3R (b)	VI RO_3 H_2R (a)	VI RO_3 H_2R (b)	VII R_2O_7 HR (a)	VII R_2O_7 HR (b)	VIII RO_4-RO-R_2O_3		
	1 H 1.008																
2 He 4.0	3 Li 6.94		4 Be 9.1			5 B 10.9		6 C 12.00		7 N 14.00		8 O 16.00		9 F 19.00			
10 Ne 20.2	11 Na 23.00		12 Mg 24.32			13 Al 27.10		14 Si 28.30		15 P 31.02		16 S 32.06		17 Cl 35.46			
18 A 39.94	19 K 39.10		20 Ca 40.07		21 Sc 44.10		22 Ti 48.1		23 V 50.00		24 Cr 52.00		25 Mn 54.93		26 Fe 55.8	27 Co 58.9	28 Ni 58.6
		29 Cu 63.57		30 Zn 65.37		31 Ga 70.10		32 Ge 72.50		33 As 74.96		34 Se 79.20		35 Br 79.92			
36 Kr 82.92	37 Rb 85.45		38 Sr 87.63		39 Yt 89.33		40 Zr 90.60		41 Cb 93.10		42 Mo 96.00		43 Ma 99 ±		44 Ru 101	45 Rh 102	46 Pd 106
		47 Ag 107.9		48 Cd 112.4		49 In 114.8		50 Sn 118.7		51 Sb 120.2		52 Te 127.5		53 I 126.9			
54 Xe 130.2	55 Cs 132.8		56 Ba 137.4		57—71 Rare Earths		72 Hf 178.6		73 Ta 181.5		74 W 184.0		75 Re 188±		76 Os 190	77 Ir 193	78 Pt 195
		79 Au 197.2		80 Hg 200.6		81 Tl 204.0		82 Pb 207.2		83 Bi 208.0		84 Po 210 ±		85 Ab 221 ±			
86 Rn 222.4	87 Vi 224. ±		88 Ra 226.0		89 Ac 230.0		90 Th 232.4		91 Pa 234.0		92 U 238.2		No. Symbol At. Wt.				

A few examples will help to clarify the concept of valence. The chemical formula of common salt, sodium chloride, is written NaCl. Sodium falls in group I and is a metal; therefore, it has a valence of +1. Thus one atom of a metal with a valence of +1 can combine with only one atom of a nonmetal having a valence of −1. The one atom of chlorine fulfills this requirement.

In writing the formula for aluminum chloride, we find that aluminum has a valence of +3 and that of chlorine is −1. The molecule of aluminum chloride must have such a combination of atoms that the sum of all the valences of the aluminum atoms equals the sum of all the valences of the chlorine atoms. Therefore, the aluminum atom with a valence of +3 requires three atoms of chlorine with a valence of −1, to make the combination. The formula of this compound is $AlCl_3$. As another example, suppose we wish to write the formula for aluminum oxide. According to the table, aluminum has a valence of +3 and oxygen −2. Again we must make the combination of atoms of aluminum oxide so that the sum of all the valences of the aluminum atoms equals the sum of all the valences of the oxygen atoms. The number 6 is divisible by both 3 and 2. Therefore it takes two aluminum atoms and three oxygen atoms to make the combination. The formula of aluminum oxide is Al_2O_3. The formulas of chemical compounds must obey the rule of valence which states that in every formula the algebraic sum of all the units of valence, both positive and negative, is equal to zero. The units of valence are obtained by multiplying the valence of an element by the number of atoms of that element present in the compound. Applying the rule to Al_2O_3 we get:

$$(+3 \times 2) + (-2 \times 3) = 6 - 6 = 0.$$

Thus, Al_2O_3 is the correct formula for aluminum oxide.

Some of the elements have more than one valence. Sulfur is a very common element exhibiting this property. In hydrogen sulfide, H_2S, it has a valence of −2, in sulfurous acid, H_2SO_3, it has a valence of +4, and in sulfuric acid, H_2SO_4, it shows a valence of +6. The ending *-ous* is always used in compounds in which the element has the lower positive valence and *-ic* when it has the higher positive valence. Table 7-I shows the valences exhibited by the common elements and radicals. When trying to determine the valence of an element in a compound, we

should remember that hydrogen always has a valence of +1 and oxygen always has a valence of −2.

The two acids, H_2SO_3 and H_2SO_4, each contain what is known in chemistry as a radical. A radical is a group of atoms, usually two or three, which are combined chemically so that they act the same as the atom of a single element and the radical has a valence of its own which is different from the valence of any of its constituent atoms. In H_2SO_3 the radical is SO_3, known as the sulfite radical. It has a valence of −2 because it combines with two atoms of hydrogen. The valence of a radical may be obtained from the algebraic sum of the valences of its constituent elements, if their valences are known. We know that in H_2SO_3 sulfur has a valence of +4 and the valence of oxygen is always −2. Applying the rule of valence we get $+4 + 3(-2) = +4 - 6 = -2$ as the valence of the sulfite radical. In H_2SO_4 the radical SO_4 has a valence of −2 since the SO_4 radical combines with two atoms of hydrogen. The valence of sulfur in the SO_4 radical may be found as follows:

$$S + O_4 = -2 \qquad \text{or} \qquad S + 4(-2) = -2$$
$$S + (-8) = -2 \qquad\qquad S = +6$$

The valence of sulfur in H_2SO_4 is, therefore, +6. SO_4 is known as the sulfate radical. The ending *-ite* on the name of a radical indicates the lower valence of the element from which the radical takes its name and *-ate* the higher valence state of the element. Radicals may have either positive or negative valences. The radicals having positive valence have chemical properties similar to metals and those having negative valence act like nonmetals. The ammonium radical NH_4 has a valence of +1, the formula for ammonium sulfate being written $(NH_4)_2SO_4$. When more than one molecule of a radical combines in a compound it is written inside the parentheses with the subscript outside; the subscript is used as if the radical were one element.

In compounds having only two elements present, the ending *-ide* is generally used on the name of the negative element. In this class are the oxides (ferrous oxide, FeO; ferric oxide, Fe_2O_3; zinc oxide, ZnO, etc.), the chlorides such as sodium chloride, NaCl, and stannous (tin) chloride, $SnCl_2$, also the sulfides, carbides, nitrides, bromides, iodides, etc.

Before we leave the discussion of the periodic table there are two exceptions to the general classification that have not as yet been mentioned. The first is group VIII of the table containing nine metallic elements. This group is known as the transition group and its elements, as the transition elements. Their properties do not conform to the regular periods of the table and so they

TABLE 7-I.—VALENCES OF COMMON ELEMENTS AND RADICALS

	Valence of I	Valence of II	Valence of III
Metals (positive elements)	+ Sodium, Na Potassium, K Silver, Ag Mercury, Hg (mercurous) Copper, Cu (cuprous)	++ Magnesium, Mg Calcium, Ca Iron, Fe (ferrous) Copper, Cu (cupric) Zinc, Zn Barium, Ba Mercury, Hg (mercuric) Lead, Pb	+++ Aluminum, Al Iron, Fe (ferric) Chromium, Cr
Metallic radical (positive)	Ammonium, NH_4		
Nonmetals (negative elements)	− Chlorine, Cl Bromine, Br Iodine, I	−− Oxygen, O Sulfur, S	−−−
Nonmetallic radicals (negative)	Hydroxyl, OH Nitrate, NO_3 Bicarbonate, HCO_3	Sulfate, SO_4 Carbonate, CO_3	Phosphate, PO_4

are placed in a separate group. There are three horizontal rows in this vertical group and the elements of each horizontal row have similar chemical properties. For example, in the top row, iron, cobalt, and nickel all have properties very nearly alike and show the same valences in compounds.

The second exception to the general rule of the table is a group of 15 elements known as the *rare-earth elements.* They have a valence of +3 and their properties are almost identical. They are placed together in one position in group III-A. Their

atomic weights run from 139 to 174. These elements are not as yet of great practical importance and will not be considered further.

WATER AND ITS CONSTITUENT ELEMENTS

The methods of obtaining chemical elements and their compounds, as well as the means used in determining their properties, can best be illustrated by a brief study of the most important compound substance known to man—the compound called water. Water is the most plentiful of all compound substances because it covers about three-fourths of the surface of the earth. It is always present in the atmosphere and is necessary for the continuance of all kinds of life. It is composed, as we have seen, of the elements oxygen and hydrogen, both gases at ordinary temperatures and pressures. These two elements will be studied first.

Oxygen.—Oxygen is an element of utmost importance to us as all living things would die without it. Nearly 50 per cent of the matter composing the earth and its atmosphere is oxygen. Water contains about 89 per cent oxygen and about one-fifth by volume of the air is free oxygen. Air is a mixture of oxygen and nitrogen with less than 1 per cent total of several rare and inert gases.

Commercial oxygen is prepared from liquefied air, which consists essentially of a mixture of liquid oxygen and liquid nitrogen. Since oxygen boils (changes from the liquid to the gaseous state) at a higher temperature (−182.5°C., −297°F., under 1 atm. of pressure) than nitrogen (−194°C., −317°F.) about 96 per cent oxygen can be obtained by allowing liquid air to evaporate slowly under controlled conditions. Oxygen can be liberated from natural substances only with difficulty. Saltpeter (potassium nitrate) can be made to give up some of its oxygen by heating it. In the laboratory, oxygen can best be prepared by heating potassium chlorate, a white crystalline substance used in the manufacture of fireworks. This reaction may be expressed in the following way:

$$\underset{\text{Potassium chlorate}}{2KClO_3} \rightarrow \underset{\text{Potassium chloride}}{2KCl} + \underset{\text{Oxygen}}{3O_2}$$

If manganese dioxide is mixed with the potassium chlorate, evolution of the oxygen occurs at a much lower temperature

(below 200°C.). The manganese dioxide is said to catalyze the reaction as it does not enter into the reaction at all but remains unchanged throughout the experiment. Substances that hasten a chemical action without themselves undergoing any permanent change are called *catalytic agents* or *catalysts* and the process is called *catalysis*. Still another method of preparing oxygen is by the reaction of sodium peroxide and water. The peroxide reacts with the water to form sodium hydroxide and oxygen as follows:

$$\underset{\text{Sodium peroxide}}{2Na_2O_2} + \underset{\text{Water}}{2H_2O} \rightarrow \underset{\text{Sodium hydroxide}}{4NaOH} + \underset{\text{Oxygen}}{O_2}$$

Oxygen has neither color, taste, nor odor. It is slightly heavier than air and much heavier than hydrogen. It can be liquefied by pressure if cooled below −118°C., −180°F. Oxygen is only slightly soluble in water (3.1 volumes of the gas in 100 volumes of water at 20°C.) but this is a very important property as fish obtain oxygen from that dissolved in water. These are all specific physical properties of oxygen.

Oxidation.—By means of certain experiments it is possible to show that the action of oxygen upon another element consists in the union of the two elements to form a compound. Thus, when sulfur burns in oxygen, a new gaseous compound is formed, known as sulfur dioxide. Likewise, when phosphorus, iron, carbon, and hydrogen burn in oxygen, there are formed compounds of these elements with oxygen. In general, oxygen combines with most of the metallic elements (metals), particularly when heated. The action of oxygen upon compounds is similar to its action upon elements and usually consists in the union of oxygen with one or more of the elements present in the compound. Thus, when hydrocarbons (compounds of carbon and hydrogen) burn in the presence of oxygen, both the carbon and the hydrogen combine with the oxygen to form carbon dioxide, CO_2, and water vapor, H_2O. In some cases the compound as a whole unites with the oxygen.

Thus, when any substance or any of its constituent parts combines with oxygen, the substance is said to be oxidized, and the process or change that takes place is called *oxidation*. It should be noted that this term oxidation is not confined to such changes as just mentioned but has a much broader application

in a large group of reactions, in many of which oxygen takes no part.

Oxides.—When an element combines with oxygen, the resulting compound is known as an oxide of that element. Some of the oxides are gases, others are liquids, and others are solids at ordinary temperatures.

The following are a few worth remembering:

Colorless Gases	
Carbon monoxide	CO
Carbon dioxide	CO_2
Sulfur dioxide	SO_2
White Solids	
Sodium peroxide	Na_2O_2
Magnesium oxide	MgO
Zinc oxide	ZnO
Phosphorus pentoxide	P_2O_5
Sulfur trioxide	SO_3
Silicon dioxide	SiO_2
Colorless Liquids	
Hydrogen oxide (water)	H_2O
Hydrogen peroxide	H_2O_2
Colored Solids	
Mercuric oxide (red)	HgO
Silver oxide (brown)	Ag_2O
Magnetic iron oxide (black)	Fe_3O_4
Ferric oxide (steel gray, reddish brown, or black)	Fe_2O_3
Copper oxide (black)	CuO
Lead monoxide—litharge (yellow)	PbO
Manganese dioxide (black)	MnO_2

The prefixes, *mono-*, *di-*, *per-*, refer to the relative amounts of oxygen combined with the other elements.

Conditions Affecting the Rate of Oxidation.—The rate at which oxidation takes place is dependent upon several factors:

1. The nature of the substance. Other things being equal, iron will oxidize more readily than mercury or silver.

2. The temperature. Temperature is probably the most obvious influence affecting the speed of oxidation. At high temperature oxidation takes place rapidly; at lower temperatures the speed decreases until at ordinary temperatures it may be impossible to detect any action. For example, the higher the temperature of a piece of charcoal the faster it will burn. Iron rusts more rapidly in hot water than in cold, provided the water is equally aerated in the two cases.

3. The concentration of oxygen per unit volume and the surface exposed. Anything that tends to increase the quantity of oxygen in contact with the surface of the burning substance will also tend to hasten the reaction. The rapidity of the burning is also governed by the surface exposed. One reason why substances burn more rapidly in oxygen than they do in air is that the concentration of oxygen in pure oxygen is about five times its concentration in air. Thus, union with oxygen goes on about five times as rapidly in pure oxygen as in air, other things being equal. Instead of increasing the concentration of oxygen, we may often hasten the oxidation by increasing the surface of the solid substance. A log of wood burns much more slowly than if it had been whittled into shavings. A lump of coal burns rather slowly, but when it is finely powdered and suspended in the air as dust and ignited by a spark, it will burn instantaneously with explosive violence.

4. A catalyst. The speed of oxidation may sometimes be increased by the action of some suitable catalytic agent. Thus the reaction

$$2SO_2 + O_2 \rightarrow 2SO_3$$

has a very slow rate, but in the presence of finely divided platinum the speed is greatly increased. The sulfur trioxide formed then reacts with water to form sulfuric acid, H_2SO_4.

Importance of Oxygen.—A considerable amount of the decomposition of rocks (weathering) is due to natural oxidation. The process is extremely slow in dry climates, but in moist humid areas oxidation takes place at a relatively rapid rate. The oxidation of rock is aided by the presence of water.

Pyrite (iron pyrites or fool's gold) is a common constituent found in the coal measures and in sedimentary rocks. The oxidation of pyrite (iron sulfide, FeS_2) leads to the formation of sulfuric acid which in turn is an active agent in rock weathering. Ugly stains and pits on building stones are generally accounted for by the oxidation of pyrite. The reaction is as follows:

$$\underset{\text{Pyrite}}{2FeS_2} + \underset{\text{Water}}{2H_2O} + \underset{\text{Oxygen}}{7O_2} = \underset{\text{Iron sulphate}}{2FeSO_4} + \underset{\text{Sulfuric acid}}{2H_2SO_4}$$

It can be shown how oxides react with oxides in nature to form oxidation products. If water is added in the reaction, the

process is called *hydration.* If carbon dioxide, CO_2, is added, the process is known as *carbonation.* Both reactions are common in nature and may take place in the same reaction.

Igneous rocks (granite, lava flows, etc.) are composed of minerals that combine with oxygen under proper conditions. One of the minerals is potash feldspar (orthoclase K Al Si_3 O_8 or $K_2O \cdot Al_2O_3 \cdot 6SiO_2$).

Clays, sand, rocks or stone, abrasives, refractories, mortar, cement, fluxes, and metallic ores represent only a small number of the compounds in the great list of oxides of commercial importance.

Hydrogen.—Free hydrogen is found in the gases issuing from some volcanoes and in pockets in certain rock salt deposits while only a trace of it is present in the air. In its combined forms, it makes up about 11 per cent by weight of water, is an essential constituent of all acids, and is a part of natural gas, petroleum, and all animal and vegetable bodies.

Hydrogen can be liberated from cold water by the action of metals that combine with oxygen more readily than does hydrogen. These metals are calcium, sodium, and potassium, and the action involves the formation of compounds known as hydroxides of these metals. For example, the reaction that takes place when water is decomposed by sodium is as follows:

$$\underset{\text{Sodium}}{2Na} + \underset{\text{Water}}{2H_2O} \rightarrow \underset{\text{Sodium hydroxide}}{2NaOH} + \underset{\text{Hydrogen}}{H_2}$$

Hydrogen is also evolved when steam reacts with metals at high temperatures, producing an oxide of the metal and hydrogen. The reaction is as follows:

$$\underset{\text{Iron}}{3Fe} + \underset{\text{Water}}{4H_2O} \rightarrow \underset{\text{Iron oxide}}{Fe_3O_4} + \underset{\text{Hydrogen}}{4H_2}$$

Hydrogen can be prepared by the action of dilute acids (of which hydrogen is a necessary constituent) on most of the common metals. The metals are arranged in the accompanying list in the order of their activity as referred to hydrogen. This list is also referred to as the electromotive series. Metals above hydrogen in this list will displace hydrogen from dilute acids and from water, although much more slowly. Those below hydrogen in this series will not react to evolve hydrogen. Potassium is the most active metal and gold the least active.

The reaction using zinc, for example, may be stated as follows:

Zinc (65.37) + hydrochloric acid (72.936) → hydrogen (2.016) + zinc chloride (136.29)

Hydrogen—2.016
Chloride —70.92

Zinc—65.37
Chlorine—70.92

$$Zn + 2HCl \rightarrow 2H + ZnCl_2$$

It can be seen that 65.37 parts by weight of zinc liberate 2.016 parts by weight of hydrogen. This is true regardless of whether hydrochloric or some other acid is used. 65.37 parts of zinc and 2.016 parts of hydrogen are an example of *chemically equivalent quantities.* Chemically equivalent quantities or *equivalents* of two substances are *exact* quantities that enter into or result from a chemical reaction.

ORDER OF ACTIVITY OF THE METALS

Potassium
Sodium
Barium
Calcium
Magnesium
Aluminum
Manganese
Zinc
Chromium
Iron
Cadmium
Cobalt
Nickel
Tin
Lead
Hydrogen
Antimony
Bismuth
Arsenic
Copper
Mercury
Silver
Platinum
Gold

Finally, hydrogen may be prepared by a process known as *electrolysis,* which means the decomposition of a compound by the use of electric energy. If the dilute solution of an acid

is subjected to the passage of direct current, bubbles of hydrogen appear on the *negative* pole (the cathode). All the other constituents are attracted to the *positive* pole (the anode), the exact constituents depending upon what acid is used. Electrolysis of hydrochloric acid produces chlorine gas and of sulfuric acid produces oxygen at the anode.

Hydrogen is a colorless, tasteless, odorless gas. Since it is over fourteen times lighter than air, it is used to inflate balloons. It can be liquefied by pressure if cooled below −234°C. (−389°F.). It is only slightly soluble in water. At 20°C. (68°F.) the solubility is 1.8 volumes of gas in 100 volumes of water. The gas burns in air or pure oxygen with an almost invisible blue flame which is so hot that a temperature of 2500°C. (4532°F.) can be produced in a closed space. Hydrogen and oxygen combine so slowly at ordinary temperatures that no change is noticed even after several years. At higher temperatures, however, the reaction proceeds faster until at 700°C. (1292°F.) the reaction is almost instantaneous. Finely divided platinum will catalyze the reaction at room temperature.

Hydrogen acts upon the oxides and chlorides of iron and the metals below iron in the order of activity of the metals. For example,

$$Fe_3O_4 + 4H_2 \rightarrow 4H_2O + 3Fe$$

Magnetic oxide of iron (231.52) + hydrogen (8.064) → iron (167.52) + water (72.064)

This reaction is an example of a process known as *reduction* and is the exact opposite of oxidation. The removal of oxygen from a compound by its union with some other substance (in this case, hydrogen) is called *reduction* and the substance is called a *reducing agent.* In iron metallurgy, carbon is more often used as a reducing agent than hydrogen.

Water.—Water is formed by the union of hydrogen and oxygen in the ratio of 1.008 parts by weight of hydrogen and 8 parts by weight of oxygen. On a *volumetric* basis, it is found that one volume of oxygen reacts with two volumes of hydrogen to produce 2 volumes of steam—a shrinkage of one volume. In other words,

1 volume oxygen + 2 volumes hydrogen → 2 volumes steam

One volume may represent a liter, quart, cubic centimeter, or any unit or fraction of a unit as long as the experimenter is consistent. This fact leads to the *law of combining volumes* which states that "in *every* case, the volumes of the gases used and produced in a chemical change can always be represented by the ratio of *small whole numbers.*"

Water, in thin layers, is transparent and colorless but a thick layer has a blue or greenish-blue color. Its density (grams per cubic centimeter) at 4°C. (39.2°F.) is 1 by definition. It is a poor conductor of electricity. It is a widely used solvent and the role of water solutions in chemistry will be taken up later.

Water is a relatively stable chemical compound. It will decompose into its constituent elements at high temperatures to a slight degree but the amount of decomposition or *dissociation*, as it is called in this case, is less than 2 per cent at 2000°C. (3632°F.). A decomposition which is *reversible* in character is called a dissociation. By reversible is meant that the chemical change can take place in either direction. For example, let us take the equation:

$$\text{Water vapor} \rightleftarrows \text{hydrogen} + \text{oxygen}^1$$

If water vapor is placed in a closed vessel and heated, decomposition into hydrogen and oxygen takes place, increases with rise in temperature, and, at any one temperature, reaches a stable value quite rapidly. If allowed to cool, the elements recombine to form water vapor again. A reversible reaction, therefore, cannot complete itself if the products of the action are kept together and not allowed to separate. It is equally true that a reversible action will go to completion if one of the products escapes. At high temperatures, if the hydrogen is allowed to escape through a membrane that will not allow the passage of oxygen, the reaction will complete itself and the water vapor will entirely decompose in time.

Oxides of some substances, such as calcium oxide, unite violently with water to form hydroxides. Calcium oxide (quicklime) unites with water to form slaked lime.

$$\underset{\text{Calcium oxide}}{CaO} + \underset{\text{Water}}{H_2O} \rightarrow \underset{\text{Calcium hydroxide}}{Ca(OH)_2}$$

[1] The double arrows indicate that the reaction can proceed in either direction.

The product of a reaction of this type is known as hydroxide or a base and, as bases have certain typical properties, will be considered more fully later. The oxides that produce bases on reaction with water are called basic oxides. Other oxides unite with water to form acids, which differ from bases in many important respects and will also be discussed later. This class is represented by such oxides as sulfur dioxide and phosphorus pentoxide. Oxides that have these properties are known as acidic anhydrides or acidic oxides. We may classify the chemical elements on this basis. The elements, like iron, nickel, and sodium, whose oxides react with water to form bases, are known as *metallic elements* while those, like phosphorus and sulfur, whose oxides react with water to form acids are called *non-metallic elements.*

Many substances unite with water when placed in contact with it, the resulting substances being known as *hydrates.* The water picked up by the substances is rather loosely held in combination in most cases and can be driven off in the form of vapor by the application of heat. Hydrates are true compounds because they contain definite proportions by weight of water and the anhydrous (water-free) substance. They differ from both water and the anhydrous substance in physical properties. Some substances are called *deliquescent* because they are able to pick up water vapor from the atmosphere. For example, anhydrous calcium chloride picks up enough water vapor to dissolve itself and is sprinkled on roads to lay the dust. Some hydrates are so unstable that the water passes off in vapor form at room temperature when the hydrate is left in an open vessel and are said to *effloresce.* For example, common washing soda (a hydrate of sodium carbonate, $Na_2CO_3 \cdot 10H_2O$) is efflorescent, decomposing into monohydrated sodium carbonate, $Na_2CO_3 \cdot H_2O$, and water at room temperature.

SOLUTIONS

In a previous section a distinction was made between a mixture and a compound. In mixtures we found that the particles of different properties could be readily distinguished so it was not perfectly uniform. In a compound we found that every portion was identical in composition to every other portion.

Between these there is a large class of substances called solutions, the most familiar of which are the solutions of solids in liquids. Solutions differ most noticeably from mixtures in that they are perfectly uniform in character, or are homogeneous. Mixtures are termed heterogeneous in character. They differ from definite chemical compounds in that their composition can be varied within wide limits. A *solution*, therefore, may be defined as "a substance of homogeneous character whose composition may be varied continuously between certain limits." As a further limitation, solutions are nonsettling. Thus, an intimate mixture of salt and water may be termed a true solution. If a given mixture is less intimate so that the particles of the solid can be seen under a microscope, we may call it a *suspension*. If two liquids are mixed, they may combine to form a true solution but, if they are less thoroughly mixed, minute droplets of one liquid may be found to be suspended in the other. Such a mixture is called an *emulsion*. Milk is an example. Suspensions and emulsions are found to settle, sooner or later, and are not homogeneous under severe tests. A true solution is one, then, in which the particles of the dissolved substance are single molecules or, at the most, groups of a few molecules.

Types of Solutions.—The most familiar type of solution is the solid in liquid. We also have solutions of gases in liquids. For example, we find that a beaker of tap water when warmed will give off bubbles of dissolved air. Furthermore, solids dissolve in solids and liquids dissolve in liquids. For an example of the former, some alloys are mixtures of metals which are so intimate that they deserve the name solution. An example of the latter is alcohol dissolved in water. We also have the case of gases dissolved in solids. Thus we find that iron has a definite solubility for oxygen and nitrogen.

Most of the substances will dissolve quite simply. However, in some cases the substance may first form a soluble compound, which then dissolves. Iron does not really dissolve in nitric acid but is converted to iron nitrate, which dissolves.

Water is probably the most universal solvent, but alcohol, ether, benzene, carbon disulfide, and thousands of other liquids are solvents for various substances.

The liquid in which a solid or gas has been dispersed to form a solution is called the *solvent*, while the substance that is being

dissolved is called the *solute*. If we are dealing with two liquids or two solids, we can say that each one is dissolved in the other; however, the one that is present in the larger quantity is usually termed the solvent.

The concentration of a solution is a frequent term. By this we mean the amount of solute dissolved by a definite quantity of the solvent, often referred to as so many grams per 100 cc. of solvent or per 100 cc. of solution. If this solution contains relatively a small quantity of the solute, it is termed a *dilute solution*. Solutions may be made more concentrated, up to a certain point, by adding more solute and shaking and stirring for some time or by evaporating a dilute solution to remove part of the volatile solvent. If we evaporate to the extreme or to dryness in the case of solids in liquids, we recover the solute as a dry solid.

If we were to place a lump of sugar in a beaker and cover it with water, the lump of sugar would gradually diminish in size and pass into solution and diffuse through the solvent water. If we add sufficient sugar and allow sufficient time for solution, the concentration of the sugar will reach a definite limiting value where the sugar ceases to dissolve and the solution is said to be *saturated*. At this point, it appears that an equilibrium has been reached. In other words, the rate at which the sugar molecules in solution deposit on the lumps of solid sugar just equals the rate at which the solid throws molecules into the solution. A saturated solution is defined as one that is in equilibrium with the undissolved solute.

Temperature Effect.—The solubility of a substance in a given solvent is dependent upon the temperature. In most cases the solubility increases with a rise in temperature, but the reverse is true in some others. For example, 100 g. of water will dissolve 13 g. of KNO_3 at 0°C. (32°F.) and 150 g. at 73°C. (163°F.). On the other hand, the solubility of Na_2SO_4 decreases from 55 g. at 32°C. (90°F.) to 42 g. (per 100 g. of water) at 100°C. (212°F.). The solubilities of other substances vary continuously with temperature, most of them between these extremes. The concentration of a saturated solution of a gas has been found to be proportional to the pressure at which the gas is supplied.

If the saturated solution of a substance whose solubility decreases with decrease in temperature is slowly cooled, excess

solute will be rejected from the solution in the form of solid crystals. With further decrease in temperature these crystals grow in size, corresponding to the amount of solute material thrown out of the solution. In this process, there is commonly some delay in the appearance of the crystals if no undissolved solid is present, *i.e.*, the solution may be slowly cooled several degrees below its saturation value without the appearance of the crystals, a condition known as *supersaturation*. If the supersaturated solution is stirred, shaken, or inoculated by the introduction of a solid crystal of the solute substance, crystallization of the excess solid takes place rapidly. Such a condition also occurs when pure substances and metallic alloys are cooled through their freezing points. For example, pure water can be cooled carefully several degrees below 0°C. before the formation of ice begins to occur. The freezing point of a substance, then, is the temperature at which the solid and liquid forms can exist in equilibrium and not necessarily the temperature at which the liquid freezes on cooling. Only under carefully controlled conditions are these temperatures identical.

Molar and Normal Solutions.—A molar solution contains a molecular weight in grams (one mol) of solute in a liter of solution. For example, the molecular weight of sulfuric acid, H_2SO_4, is 98 and a molar solution of this acid, therefore, contains 98 g. per liter. The student should note particularly that we did not refer to 1,000 cc. of solvent, but to 1,000 cc. of solution.

A normal solution of an acid, base, or salt contains 1 gram-equivalent weight of the solute in 1 liter of solution. In an earlier discussion we learned that the equivalent weight of hydrogen is 1.008, of oxygen 8, of sodium 23, but these are all elements. Now in the following equation we see that 36.468 g. of hydrogen chloride (in water solution) are equivalent to 23 g. of sodium.

$$\underset{23\text{ g.}}{Na} + \underset{36.468\text{ g.}}{HCl} \rightarrow \underset{1.008\text{ g.}}{H} + \underset{58.46\text{ g.}}{NaCl}$$

We have already noted that 23 is the equivalent weight of sodium so we can now say that 36.468 is the equivalent weight of HCl. In fact, the equivalent weight of a compound is that weight which reacts exactly with one equivalent weight of any element.

A normal solution of an acid contains 1.008 g. of replaceable hydrogen in 1 liter of solution. A normal solution of a base must, consequently, contain 17.008 g. of hydroxyl (−OH groups) per liter of solution. The following equation demonstrates this statement:

$$\underset{40.008\text{ g.}}{NaOH} + \underset{36.468\text{ g.}}{HCl} \rightarrow \underset{18.016\text{ g.}}{H_2O} + \underset{58.46\text{ g.}}{NaCl}$$

The symbol for a normal solution is N. A twice normal solution would then be $2N$ and a tenth normal, $0.1N$, or $N/10$.

When it is desirable to convert molar and normal solutions to English units, use may be made of the following factors.

1 g. solute in 1,000 cc. of solution = 0.132 oz. solute in 1 gal. solution.

1 g. solute in 1,000 cc. of solution = 0.00029 lb. solute in 1 gal. solution.

Problem: How many pounds of Na_2SiO_3 are there in 5 gal. of a $10N$ solution of sodiumsilicate?

Molecular weight of Na_2SiO_3	= 122
Equivalent weight of Na_2SiO_3	= 61
$10N$ solution contains 61×10	= 610 g. Na_2SiO_3 per liter
1 g. per liter	= 0.00029 lb. per gal.
$610 \times 0.00029 \times 5$	= 0.885 lb. Na_2SiO_3 in 5 gal. $10N$ solution

ACIDS, BASES, AND SALTS

In general, solutions of compound substances in water may be classified as acids, bases, or salts. For this reason, it is necessary to study in some detail the properties of these three classes of compounds in solution. It should be remembered that the properties discussed in this section refer to the substances dissolved in water *only*. For example, hydrogen chloride gas has entirely different properties from the same compound dissolved in water.

The substances known as *acids* have the following properties in common:

1. The solutions are *sour* in taste.

2. They change the color of *litmus*, a vegetable coloring matter, from blue to red.

3. The solutions are conductors of electricity and are decomposed by the current, hydrogen being liberated at the negative

4. When the metals preceding hydrogen in the "order of activity" are introduced into acids, hydrogen is displaced and liberated.

We have mentioned some acids previously but the common ones are listed below:

Hydrochloric acid	HCl	Nitric acid	HNO_3
Sulfuric acid	H_2SO_4	Hypochlorous acid	$HOCl$
Phosphoric acid	H_3PO_4	Acetic acid	$HC_2H_3O_2$

The substances known as *bases* have the following properties in common:

1. Their solutions have an *acrid* or *bitter* taste.
2. They change the color of litmus from red to blue.
3. Their solutions are conductors of electricity and are decomposed by the current, oxygen being liberated at the positive pole of the circuit.

The common bases are listed below:

Sodium hydroxide	$NaOH$	Calcium hydroxide	$Ca(OH)_2$
Potassium hydroxide	KOH	Cupric hydroxide	$Cu(OH)_2$
Ammonium hydroxide	NH_4OH	Zinc hydroxide	$Zn(OH)_2$

Sodium and potassium hydroxides possess the foregoing properties to a very high degree and are specifically known as *caustic alkalies.* The other bases exhibit the properties given above but not to such a high degree.

When hydrochloric acid and sodium hydroxide react, sodium chloride (common table salt) is one product.

$$HCl + NaOH \rightleftarrows NaCl + H_2O$$

In general, when an acid reacts with a base, one of the products is a substance having properties much like sodium chloride, this product, therefore, being known as a *salt.* The other product of the reaction is water. This process is known as *neutralization.*

Some typical salts are given in the following list:

Sodium chloride	$NaCl$	Potassium chlorate	$KClO_3$
Sodium sulfate	Na_2SO_4	Zinc sulfide	ZnS
Potassium nitrate	KNO_3	Potassium iodide	KI
Ammonium chloride	NH_4Cl	Sodium carbonate	Na_2CO_3
Cupric sulfate	$CuSO_4$	Lead sulfide	PbS

It will be instructive for the student to write the reactions involved in producing these salts.

By comparing the formula of the acids, bases, and salts listed above, several important facts can be discovered. The important ones are as follows:

1. Every acid contains hydrogen combined with one or more other atoms. The H atom is the necessary constituent of all acids.
2. The same atoms or radicals that are combined with hydrogen as acids also appear in salts, such as the radicals SO_4 and NO_3.
3. Every base contains the hydroxyl (OH) radical and usually one other atom but sometimes more than one, for example, (NH_4).
4. The atoms or radicals that are combined with OH in bases are present in salts.

When an aqueous (water) solution of hydrochloric acid is subjected to the passage of an electric current, the acid is decomposed and hydrogen is liberated at the negative pole. Since this pole or electrode attracts only positively charged particles, hydrogen is called a positive atom. This is true because, in electricity, unlike charges attract each other while like charges repel each other. Similarly, the rest of the acid molecule, Cl, is attracted to the positive electrode and is known as a negative atom. When a current is passed through the solution of a base, oxygen is always liberated at the positive pole because the negative radical OH is attracted to it and decomposes at the electrode:

$$4\ (OH) \rightarrow O_2 + 2H_2O$$

The rest of the molecule of the base (K, Na, etc.) is attracted to the negative pole and is therefore a positive atom. In the same way, every salt consists of a positive atom other than H, and a negative atom other than OH. In general, all positive atoms combine with the hydroxyl radical to form bases and all negative atoms combine with H to give acids. Also, each positive atom can theoretically combine with any negative atom to form a salt. In a few cases, the compound cannot be formed because it is unstable under ordinary conditions.

There are several chemical properties common to acids, bases, and salts that are worthy of mention. Most of them have been encountered before and need be only touched upon here. One of these is *electrical conductivity*. Whereas pure water is practically a nonconductor, solutions of acids, bases, and salts

are all conductors of electricity and hence are known as *electrolytes.* The solutions are always *decomposed* by the current. Substances that give solutions of high electrical conductivity are known as *strong* electrolytes, while those which give poor conducting solutions are called *weak* electrolytes.

A *simple* atom belonging to an acid, base, or salt *in solution* can be displaced by another element and obtained in the free state. Examples of this are given below:

Acid:

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

Salt:

$$Zn + CuSO_4 \rightarrow ZnSO_4 + Cu$$

It should be remembered that zinc could not displace copper from $CuSO_4$ if zinc were not above copper in the order of activity of the metals. Similarly, a simple negative atom can be displaced by a more active element. Thus,

$$2KI + Cl_2 \rightarrow 2KCl + I_2$$

Another property common to acids, bases, and salts is that of undergoing *double decomposition.* This property can best be illustrated by the following examples:

Salt and acid:

$$AgNO_3 + HCl \rightarrow AgCl\downarrow + HNO_3$$

Salt and base:

$$CuCl_2 + 2NaOH \rightarrow Cu(OH)_2\downarrow + 2NaCl$$

Acid and base:

$$H_2SO_4 + Ca(OH)_2 \rightarrow CaSO_4\downarrow + 2H_2O$$

Salt and salt:

$$NaNO_3 + KCl \rightleftarrows NaCl + KNO_3$$

It will be noticed that in these equations, the radicals simply exchange partners, the process being known as double decomposition. Double decompositions are all reversible in theory but in many cases one of the products is removed from the sphere of action, thus destroying the reverse reaction. In the

first three reactions, for example, AgCl, $CaSO_4$ and $Cu(OH)_2$ are practically insoluble in water and separate out as a solid from the solution as soon as they form. They are called *precipitates* and are indicated by the downward pointing arrows. The fourth reaction is reversible and results in an equilibrium mixture because all the salts are highly soluble in water and are good conductors of electricity in solution. The same equilibrium mixture results at any one temperature, regardless of whether we start with $NaNO_3$ and KCl or with NaCl and KNO_3.

We see from this that every acid, base, and salt in solution behaves, in double decomposition, as if it consists of two distinct radicals. Furthermore, it can be shown that these substances in solution possess two independent sets of properties, one referring to each radical. For example, a solution of cupric chloride, $CuCl_2$, in water, a salt, exhibits one set of properties that can be referred directly to the cupric atom, to wit: (1) the solution has a blue color and (2) the addition of a base gives a blue precipitate of cupric hydroxide. These properties, among others, are common to all solutions containing the cupric atom. On the other hand, the same solution exhibits properties that can be referred to the chloride atom, to wit: (1) when the solution is heated with H_2SO_4, HCl gas is evolved and (2) the addition of a silver salt produces a precipitate of silver chloride, AgCl. These properties, among others, are also common to chlorides in solution. Incidentally, the properties common to acids are properties of *hydrogen* whereas the properties common to bases are the properties of the *hydroxyl* radical.

IONIZATION

The facts about acids, bases, and salts discussed in the preceding section can all be explained on the basis of the *ionic hypothesis*. According to this hypothesis, the molecules of an electrolyte such as hydrochloric acid are largely dissociated in solution into their constituent atoms or radicals, each being *electrically charged*. These charged particles are known as *ions*. Thus, a solution of hydrogen chloride in water consists of (1) an undissociated part, made up of hydrogen chloride molecules (HCl), and (2) a dissociated or *ionized* part, made up of equal numbers of hydrogen atoms carrying a positive charge (H^+) and chlorine atoms carrying a negative charge (Cl^-). The undissociated HCl

molecules are inactive, play no part in electrical conduction, and exert only normal effects on boiling point rise, freezing point, and vapor pressure lowering. They also play no part in double decomposition and do not convey to the solution any of the properties of an acid. The only active portion of the solution is the ions (H^+ and Cl^-) and all the special properties of solutions of acids, bases, and salts may be referred directly to the ions in the solutions.

An equation showing the dissociation of an acid, base, or salt into its ions is known as an *ionic equation*, several typical examples of which are

Acid:

$$HCl \rightleftarrows H^+ + Cl^-$$

Base:

$$KOH \rightleftarrows K^+ + OH^-$$

Salt:

$$Na_2SO_4 \rightleftarrows 2Na^+ + SO_4^=$$

Salt:

$$FeCl_3 \rightleftarrows Fe^{+++} + 3Cl^-$$

The plus and minus signs represent the electrical charges on the ions. Since the solution itself has no charge, equal quantities of positive and negative electricity must be produced and, therefore, the *total* charge on the ions in the foregoing equations must exactly balance. This leads to the conclusion that univalent ions all possess equal quantities of electricity and other ions bear quantities greater than this in proportion to their valence. An *ion* may be specifically defined as an atom or a group of atoms bearing an electric charge or a number of such charges. Positive ions are called *cations* and negative ions *anions* because positively charged ions are attracted to the negative pole or *cathode* whereas negatively charged ions are attracted to the positive pole or *anode*.

We are now in a position to explain the mechanism of *electrolysis*. We already know that when a solution of HCl in water is placed in a nonconducting container and the two wires that are connected to the poles of a direct battery current are introduced into the solution, bubbles of hydrogen gas are evolved at the cathode and bubbles of chlorine gas at the anode. We also know from the foregoing discussion on ionization that the solution

contains a small number of undissociated HCl molecules and equal numbers of H^+ and Cl^- ions. Equilibrium is maintained between the dissociated and undissociated portions by continual dissociation and recombination. When the current is passed through the solution, all the ions in the solution begin to migrate toward their proper electrodes. The cations (H^+) move toward the cathode and the anions (Cl^-) toward the anode. Two orderly processions of ions, moving in opposite directions, proceed through the solution. It should be emphasized that the *whole* of the products of dissociation of the solute is set in motion.

When a positive ion reaches and touches the negative electrode, its positive charge of electricity is neutralized and the result is an ordinary atom of hydrogen. The atoms combine to form molecules of H_2 which, in turn, form bubbles of the gas. At the same time, the negative ions are discharged at the positive electrode and atoms of chlorine combine to form bubbles of Cl_2 gas. Meanwhile, in the body of the solution, the equilibrium $HCl \rightleftarrows H^+ + Cl^-$ is disturbed. The undissociated part, HCl, continues to dissociate in an attempt to reestablish equilibrium until the electrolysis is complete. The current in the solution is carried by the moving streams of ions.

In many cases of electrolysis, the interaction is not so simple, as in the case of the electrolysis of a substance containing a compound radical. Thus, in the case of cupric sulfate, which dissociates as follows:

$$CuSO_4 \rightleftarrows Cu^{++} + SO_4^{--}$$

metallic copper collects on the cathode while the ion SO_4^{--} gathers at the positive pole. Since this latter radical cannot exist in the free state, it reacts with water to produce oxygen according to the equation:

$$2SO_4 + 2H_2O \rightarrow 2H_2SO_4 + O_2 \uparrow$$

When a metal acts upon a dilute acid, liberating hydrogen, the ions alone are concerned in the mechanism of the action. When zinc acts on hydrochloric acid, the equation may be written in ionic form in this way:

$$Zn + 2H^+ \rightarrow Zn^{++} + H_2 \uparrow$$

The Cl^- ions are not concerned in this substitution reaction, the

zinc merely entering the solution and replacing the hydrogen. All the metals can be set down in an order such that each metal displaces those following it in the list and is displaced by those preceding it, *i.e.*, listed in their order of diminishing tendency to enter the ionic form from the free or elementary condition. Thus, zinc will replace copper in solution according to the ionic equation:

$$Zn + Cu^{++} \rightarrow Zn^{++} + Cu \downarrow$$

The equation may be written in this way because it is immaterial what the negative ion previously associated with the Cu^{++} ion happens to be. The metallic elements arranged in this order correspond exactly to the "order of activity" given on page 55 and will henceforth be known as the *electromotive series.*

It is found that some acids, bases, and salts ionize much more completely than others. Acids and bases that do ionize to a high degree—*i.e.*, most of the substance is in ionic form in solution —are called *strong* acids and bases because they are highly active while those which ionized only to a small degree are called *weak.* The reason for this is obvious because the only active part of the substance in solution is the ionized portion. From the ionic theory we can also see that the more highly ionized a substance is, the better a conductor of electricity it is and the more above normal it raises the boiling point of its solutions, lowers the freezing point, and lowers the vapor pressure.

Based on their ability to ionize, acids, bases, and salts may be classified as to their chemical activity as follows:

1. *Salts,* with the exception of some mercuric salts, are all extensively ionized in a 0.1*N* solution. The salts that dissociate into univalent ions show the greatest degree of ionization.

2. *Acids* show large differences in their degree of ionization and hence in their activities. The strong acids are HCl, H_2SO_4 and HNO_3; the moderate or *transition* acids are H_3PO_4, HF, etc.; the weak acids are H_2CO_3, H_3BO_3, $HC_2H_3O_2$, etc. The weak acids ionize hardly at all.

3. *Bases* also show extreme differences in their degrees of ionization. Strong bases are NaOH and KOH; transition bases are AgOH, etc.; a weak base is NH_4OH.

4. *Water,* which may be written HOH (hydrogen hydroxide), is both a very weak base and an equally weak acid. It dissociates

into H^+ and OH^- ions to an extremely small extent. In fact, the fraction ionized at ordinary temperatures is less than 0.000000002. However, even this small amount of ionization is of considerable importance in some reactions.

We have seen that the number of positive and negative charges on an ion corresponds to the valence of the atom. For this reason, Table 8-I presents the common ions as well as the

TABLE 8-I.—VALENCE AND IONIZATION TABLE

Univalent	Bivalent	Trivalent	Quadrivalent
Na^+	Ca^{++}	Al^{+++}	Sn^{++++} (stannic)
K^+	Ba^{++}	Fe^{+++} (ferric)	$(SiO_4)^{----}$
H^+	Mg^{++}	Cr^{+++}	$C(CH_4, CO_2)$
$(NH_4)^+$	Zn^{++}	Sb^{+++}	
Ag^+	Pb^{++}	Bi^{+++}	Quinquivalent
Cl^-	Ni^{++}	$(PO_4)^{---}$	
Br^-	Co^{++}	$As(AsH_3)$	$N(N_2O_5)$
I^-	Mn^{++}	$B(B_2O_3)$	$P(P_2O_5)$
F^-	Cu^{++} (cupric)	$N(NH_3, N_2O_3)$	$As(As_2O_5)$
$(OH)^-$	Fe^{++} (ferrous)	$P(PH_3)$	
$(NO_3)^-$	Hg^{++} (mercuric)		Sexivalent
$(ClO_3)^-$	Sn^{++} (stannous)		
$(MnO_4)^-$	O^{--}		$S(SO_3)$
	$(SO_4)^{--}$		
	S^{--}		
	$(CO_3)^{--}$		
	O_2^{--} (peroxide)		
	$(CrO_4)^{--}$		
	$(Cr_2O_7)^{--}$		

valence of some elements that do not ionize. The compounds in parentheses are typical examples of radicals having the indicated valence. Such cases, without exception, do not form ions in solution.

CHEMICAL EQUILIBRIUM

The general idea of equilibrium as a balance between two changes opposing each other has been developed in a number of instances in the foregoing pages. Since the principle of equilibrium is so vital from a practical viewpoint, it is highly desirable that we discuss the general subject somewhat in detail in order

that we gain a somewhat better view of the underlying causes effecting equilibrium.

Previously we have had occasion to study in detail some fundamentals of physical equilibrium. In these studies we found that, if we heated a liquid to a definite temperature in a closed space, a condition of equilibrium is soon reached in which there is set up a constant pressure called the vapor pressure. This unchanging pressure at a constant temperature is due to the fact that the rate at which the molecules leave the liquid is just balanced by the rate of their return to it. In this case it must be stressed again that the condition is not one of rest but one of motion.

When there is a chemical reaction between two substances, it is often found that the action is incomplete, some of the materials apparently failing to take part in the reaction. A study of these cases has shown that there has been an equilibrium set up that is very similar to the physical equilibrium just described. The conditions producing this equilibrium, known as chemical equilibrium, will now be studied first by considering the factors influencing the speed of reactions.

Speed of Reactions.—By the speed of a reaction is meant the rate at which the mass of material is transformed. This can be expressed as so many grams, mols, or equivalents in a second, minute, or hour of time. The speed of reactions is in general determined by

1. *The Nature of the Reagents.*—This involves the specific attraction of the reacting substances. Some of the elements, such as fluorine and oxygen, will not react with each other, while others, such as hydrogen and oxygen, under certain conditions will react with great rapidity.

2. *Their State of Subdivision.*—Chemical reactions between two substances can take place only at the surfaces of contact of the reactants. Thus, if the materials are finely ground and mixed, they will present more contact surface and will react more rapidly than if they were coarse. If we carry the process of subdivision until we are considering the individual molecule that would exist if the substances were in solution, the reaction would be even more rapid.

3. *Temperature.*—A rise in temperature, almost without exception, greatly increases the speed of a reaction. Thus, we have

some reactions whose speed at ordinary temperatures is imperceptible, for example, the oxidation of coal, but which become very rapid at the temperature of the Bunsen burner. On the other hand we can greatly retard a reaction by keeping the material cold, as for example, the refrigeration of foodstuffs.

As a rough approximation it has been found that reactions are doubled in velocity by each rise of 10°C. in temperature.

4. *Catalyzers.*—In earlier studies we have observed the effect of catalyzers in bringing about a change in the speed of a reaction. It has been found that the speed of a great majority of reactions can be modified by some suitable catalyst and that it may be either hastened or retarded. Thus, if the catalyst hastens the reaction, it is producing an effect that is the same as would be produced by a temperature increase. It is often more economical to employ a catalyst than to incur the expense of maintaining high temperature. However, it should be emphasized that since a catalyzer merely changes the speed of a reaction and does not add any energy to the reactants, it will not bring about a reaction that does not take place by itself.

5. *The Concentration of the Reactants.*—Since it is known that reactions take place between individual molecules, it can be seen that any condition that will increase the frequency with which the molecules collide will promote the speed of the reaction. Thus, by increasing the number of molecules in a given space (increased molecular concentration), we can greatly increase the speed of the reaction. In cases where the reactants are gases the pressure under any given condition will have considerable influence because the pressure determines the concentration of the gas.

Law of Mass Action.—Of the five factors just discussed, we shall first consider the effect of varying only the concentration (proportions) of the reacting substances. If we consider a mixture of hydrogen and chlorine gases contained in a closed glass vessel and subjected to diffused sunlight, the two gases will slowly combine to form hydrogen chloride.

$$H_2 + Cl_2 \rightarrow 2HCl$$

Considering this reaction from the molecular theory, we think of the molecules of hydrogen and chlorine as being in rapid motion, in all conceivable directions, with all conceivable velocities throughout the vessel occupied by the gases. At the temper-

ature under the above conditions we can assume that a definite percentage of all the collisions of the two gases will result in a chemical union. Anything, then, that increases the number of collisions will increase the reaction velocity in proportion. Thus, if there is an increase in the proportion of hydrogen molecules to the total number present (an increase in hydrogen concentration), the result will be an increase in the frequency of hydrogen contacts with chlorine. It is clear that increasing the concentration of chlorine atoms will bring about the same result. In actual practice the speed of the reaction is also dependent upon the temperature, the presence of catalysts, and the properties of the reacting substances.

The general law that states the above facts is known as the law of mass action: In every chemical change the activity and, therefore, the speed of the reaction are proportional to the molecular concentration of each interacting substance. The molecular concentration is expressed, numerically, in terms of the number of mols (gram-molecular weights) of the substance in a liter of the whole substance.

Equilibrium.—The law of mass action gives us through proper mathematical calculation the reaction rate only at the particular instant at which the concentrations have the stated values. If we should bring two substances together and measure the speed of the reaction over a period of time, we should find that the concentration of the reactants will be less and less and the reaction rate will fall off considerably. The reaction may stop before all the available material has been used.

What actually happens is that there is a reverse action starting which gradually increases in speed until it is going at a rate equal to the original reaction. When this condition exists, there is no further change in the concentrations of the reacting substances and the reaction apparently has ceased. In reality both reactions are continuing but at equal speeds. This condition is known as equilibrium. An equation

$$4H_2O + 3Fe \rightleftarrows Fe_3O_4 + 4H_2$$

represents this condition and is known as an equilibrium equation or reversible reaction. Since many other reactions are of this type, a generalization may be made to the effect that a chemical action must remain more or less incomplete when the reverse

action also takes place to an appreciable extent under the same conditions. Fundamentally, all reactions are probably reversible, but the conditions have never been established that would favor the reversibility of some reactions.

The principle of equilibrium being a balancing of reaction velocities may be illustrated by considering the reaction

$$A + B \rightleftarrows C + D$$

in which substances A and B react to give two other substances, C and D, the reaction, being incomplete because it is reversible. If we first let A and B be present each in a concentration of one mol per liter, the action will proceed, over a period of time, as is shown in Fig. 4-I. The reaction will start from left to right with a velocity that is represented by the length of the line OM. As the reaction proceeds, however, the concentration of the reactants becomes less and less, and hence the speed will drop. The descending curve, MS, shows this decreasing velocity as more and more A and B are transformed.

As soon as the forward reaction has proceeded for a short time, a measurable amount of C and D will have been formed. A reverse action will start immediately, very slowly at first because of the very small concentrations, to form A and B. With more and more time additional amounts of C and D will be formed. The increased concentrations of C and D will result in increased velocity of this reverse action, as shown by the rising curve OSN. After a period of time the velocities of the forward and reverse actions will become equal. This condition of equilibrium is represented by the point S where the two curves intersect.

If we had started with a mixture of C and D instead of A and B, the action would have started with a velocity represented by PN. The velocity would have dropped over a period of time, as represented by the descending curve NVS. The reverse action of A and B would meanwhile be increasing in velocity, as shown by the rising curve PSM. The two curves would cross at the same point S as before.

This diagram shows that regardless of which direction we approach the equilibrium point of a reversible reaction we always arrive at the same concentration of the substance, the equilibrium mixture. Attention should be called here to the fact that the addition of a catalyzer never causes a reaction to become more

complete; it merely increases the speed at which the equilibrium point is reached.

Now if the substances *A* and *B* are mixed as before, but with double the concentration of *A*, we find that the reaction starts with a velocity from left to right as indicated by the length of the line *OR*. This distance is double the length of *OM*; hence the original velocity has been doubled. As the reaction proceeds, the concentrations of *A* and *B* decrease and the velocity decreases as shown by the descending curve *RVP*.

The reverse action, however, is not changed by the increased concentration of *A*. Its value as the reaction proceeds is again

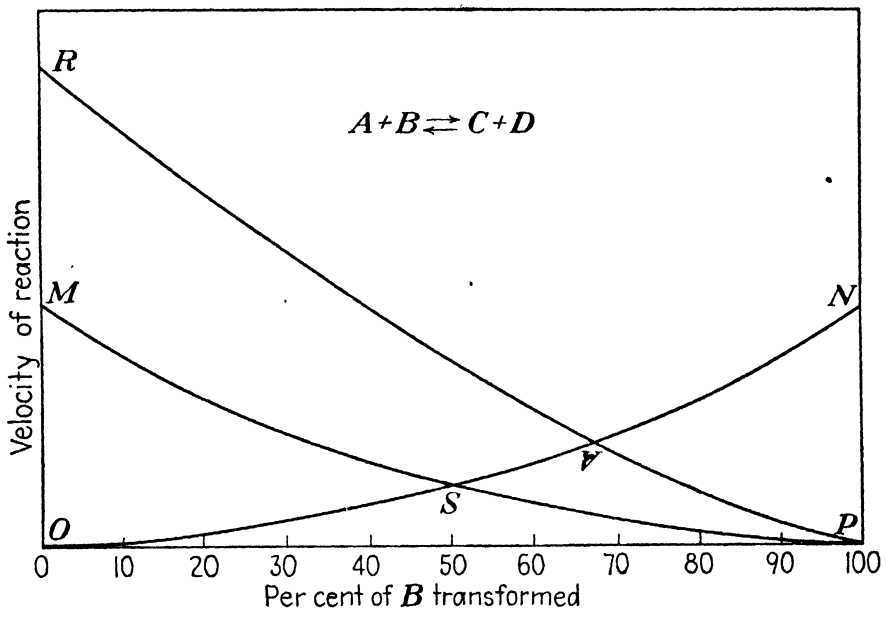


FIG. 4-I.—Velocity of reaction versus concentration. (*From H. G. Deming, "General Chemistry."*)

represented by *OSVN*. The two curves now cross at point *V*, which represents a new point of equilibrium.

This illustrates a principle that follows the law of mass action: If there is an excess of any one of the reactants in an incomplete reaction, the final action will tend to become more complete. When this action occurs, we commonly say that the equilibrium has been shifted toward the right (the right side of the equation).

Influence of Temperature on Equilibrium.—If we increase the temperature at which the reversible reaction is taking place, both the forward and the reverse reactions will be increased in velocity. The increase in temperature, however, is usually more favorable

to one of the opposing reactions than to the other and as a result the proportions of the substances at equilibrium are changed. If the two opposing reactions have reached equilibrium, the reaction that absorbs heat is made more complete by raising the temperature; the reaction that liberates heat is made more nearly complete by lowering the temperature. This is van't Hoff's principle. Otherwise expressed, when the temperature of a system in equilibrium is raised, the equilibrium point is shifted in the direction that absorbs heat. The greater the quantity of heat evolved or absorbed in a reaction, the greater is the effect of temperature on its degree of completeness. Reactions that absorb or evolve very little heat, however, are not measurably affected one way or another by moderate temperature changes.

The Principle of Le Châtelier.—The effects of the various factors just discussed on chemical equilibrium are illustrations of a broad generalization known as the principle of Le Châtelier. This principle deals with changes in an equilibrium of any sort produced by forces of any kind brought to bear on an existing equilibrium. This governing principle states that, if some stress (change in temperature, pressure, or concentration) is brought to bear on a system in equilibrium, a reaction occurs, displacing the equilibrium in the direction that tends to relieve the stress.

Illustration of the Combined Effects.—In the manufacture of sulfuric acid the process depends upon the following equilibrium equation:

$$2SO_2 + O_2 \rightleftarrows 2SO_3 + 45{,}200 \text{ cal.}$$

Industrially the problem is to obtain maximum yield of SO_3 and at a low cost. To accomplish this objective it is necessary to take into account the following considerations: (1) If we consider the law of mass action, the evident suggestion is to increase the O_2 beyond the quantity required by the equation, because the excess oxygen thus used is furnished by the air and is cheap. (2) Since the reaction is one that has a definite decrease in volume, three molecules of reactants forming two molecules of resultant, we should apply pressure to the system if at all economical. This consideration is made since it is found that in a reversible chemical reaction between gases, an increase in pressure will cause a reaction to proceed in the direction that will decrease the number of molecules in unit volume. Thus, the above reaction will, under

pressure, proceed from left to right. Conversely, a decrease in pressure will favor the dissociation of SO_3, for this reaction takes place with an increase in the total number of molecules and the consequent tendency to restore the original pressure. (3) This reaction is one that evolves heat and, if the reaction is proceeding at all rapidly, this rise in temperature will decrease the yield because the reverse action will be stimulated. It is necessary, therefore, that the reaction be cooled by some suitable means. (4) Cooling the reaction mixture, however, would make the rate of the reaction too slow. It is necessary, then, to find an efficient catalyzer to enable the reaction to proceed at an acceptable rate at a reasonably low temperature.

ENERGY AND CHEMICAL CHANGE

A chemical action is accompanied by some change in energy and this change may be in several different forms. For example, the burning of hydrogen in oxygen develops a great deal of heat while the decomposition of mercuric oxide into mercury and oxygen takes place with an absorption of heat. Also, light may be emitted or consumed in a chemical change. When magnesium ribbon is ignited in oxygen, a brilliant white light is emitted while silver chloride is decomposed by light. Again, a current of electricity may be necessary to the furtherance of a chemical change such as in the plating of zinc while, in other cases, electric current may be the result of the action occurring in storage batteries. Finally, mechanical energy produced by friction may result in the decomposition of a substance. Silver chloride may be decomposed into silver and chlorine by violent rubbing in a mortar. All these accompaniments of chemical change—heat, light, electric current, and mechanical work—are forms of energy and one of these forms is consumed or produced whenever a change in the composition of a substance takes place.

We define *energy* as being work and everything that can arise from work or be converted into work. It has been found that in any action involving the change of one form of energy into another or the transfer of energy, *no gain or loss in total energy* takes place. This statement of fact is called the *law of conservation of energy.* Applied to chemistry, this means that in any chemical change there is no gain or loss of energy. Further, we consider substances as containing energy, the amount of which

we cannot measure and, for lack of a better term, we call it *internal energy*. Although we cannot measure the absolute value of the internal energy of a substance, we can measure the *change* in internal energy produced by a chemical action. We may, therefore, say that it is an important characteristic of chemical changes that there is always an alteration in the amount of internal energy in the system. This alteration involves the production of internal energy from, or the transformation of internal energy into, some other form of energy. For example, we consider the heat absorbed in decomposing mercuric oxide as passing into and being stored in the products of the decomposition. We must consider, as a result of this, that all materials, whether elements or compounds, are storehouses of energy as well as being composed of matter. As an illustration, we must think of a piece of iron as consisting of matter known as "iron" and of internal energy. The energy that can be made available as the result of a chemical reaction and converted into work—through heat or electrical energy, for example—is called the *free energy* of the reaction.

The unit of heat used to measure the amount of heat evolved or absorbed in a chemical reaction is known as the *calorie* (cal.). It represents the amount of heat necessary to raise the temperature of 1 g. of pure water from 14.5 to 15.5°C. This exact temperature range is fixed because the amount of heat necessary to raise 1 g. of water 1°C. varies slightly at different temperatures. In practice, the total amount of heat is measured by causing the reaction to take place in a closed container surrounded by a known volume of water. The rise or fall in temperature of the water produced by the reaction is noted and the change in heat energy calculated. The English unit of quantity of heat is the B.t.u. which is the amount of heat necessary to raise 1 lb. of water 1°F. at its maximum density and is equal to 252 cal.

In order to represent the changes in energy that accompany chemical reactions, an additional meaning has been assigned to the chemical formulas. In a *thermochemical* or energy equation the formulas represent, in addition to the weight in grams expressed by the formula weights of the substances, the amount of heat energy contained in the formula weight in one state as compared to the energy contained in the *standard* state. Since we cannot measure the absolute value of the internal energy con-

tained in a substance, we select one set of conditions as the *standard state* at which the substance is referred to as having zero energy and determine changes in energy from that basis. For example, the energy equation

$$C + O_2 \rightarrow CO_2 + 96{,}960 \text{ cal.}$$

means that the energy contained in 12 g. of carbon and 32 g. of oxygen exceeds the energy contained in 44 g. of CO_2 by 96,960 cal. at the same temperature. This also means that the union of 12 g. of carbon and 32 g. of oxygen *evolves* 96,960 cal. of heat. When the action is one that absorbs heat, this fact is indicated by a negative sign preceding the number of calories, thus,

$$2H_2O \rightarrow 2H_2 + O_2 - 116{,}000 \text{ cal.}$$

If the reaction is reversible, as this one is, the heat absorbed when it proceeds in one direction is exactly equal to that liberated when it goes in the other direction.

$$2H_2 + O_2 \rightarrow 2H_2O + 116{,}000 \text{ cal.}$$

A reaction that evolves heat is known as an *exothermic* reaction, while one which absorbs heat is called an *endothermic* reaction.

When working with thermochemical equations in the English system, the molecular weights are given in pounds and the energy values in *British thermal units* (*B.t.u.*). When an equation given in the metric system is to be changed to the English system, it is only necessary to write the molecular weights of the reactants and products in pounds rather than grams and then multiply the number of calories by 453.6/252 or 1.80. The result will be the number of B.t.u. produced (or used) by the reaction when the formulas are expressed in pounds. For example,

$$C + O_2 \rightarrow CO_2 + 174{,}528 \text{ B.t.u.}$$

means that when 12 lb. of carbon reacts with 32 lb. of oxygen, it produces 44 lb. of carbon dioxide and 174,528 B.t.u. of heat.

The heat evolved or absorbed in forming chemical compounds from their elements is known as the *heat of formation* of that substance. Since we do not know the absolute internal energies of the elements and have no known method of determining them,

the convention has been established of placing the *intrinsic* internal energies of the elements equal to zero. If the heats of formation of the substances involved in a reaction are known, the heat of the reaction can be calculated by the use of the following rule:

To find the quantity of heat evolved or absorbed in a chemical reaction, subtract the sum of the heats of formation of the substances initially present from the sum of the heats of formation of the products of the reaction, placing the heat of formation of all elements equal to zero.

As an example of this we can write the equation for the heat of formation of CO_2 as follows:

$$0 + 0 = CO_2 + 174{,}500 \text{ B.t.u.}$$

or

$$CO_2 = -174{,}500 \text{ B.t.u.}$$

Therefore, in writing a thermochemical equation we use the following rule: Replace the formula of each compound in the reaction equation by the negative value of its heat of formation and solve for the unknown term.

The heats of formation of one formula weight of some important compounds are given in Table 9-I. By using the values in this table, the heats of reaction of most of the chemical changes that we shall desire to study can be calculated. As an example, suppose it is desired to calculate the heat of reaction involved in the reaction of magnesium chloride and sodium to form sodium chloride and magnesium. The equation is written as follows:

$$MgCl_2 + 2Na \rightarrow 2NaCl + Mg + X \text{ B.t.u.}$$

X being the required value of the heat of the reaction.

From Table 9-I, the heat of formation of $MgCl_2$ is 272,000 B.t.u. and NaCl is 176,000 B.t.u. Substituting these values in the equation as follows:

$$-272{,}000 + 0 = -(2 \times 176{,}000) + 0 + X$$
$$X = 80{,}000$$

and the complete thermochemical equation is

$$MgCl_2 + 2Na \rightarrow 2NaCl + Mg + 80{,}000 \text{ B.t.u.}$$

TABLE 9-I.—HEATS OF FORMATION

Chemical formula	B.t.u. per pound mol.	Calories per gram mol.
Oxides		
SiO_2	362,000	201,400
Na_2O	175,000	97,100
K_2O	164,000	91,000
CaO	261,000	145,000
MgO	258,000	143,000
BaO	240,000	133,000
ZnO	152,000	84,400
FeO	118,000	65,700
Fe_2O_3	355,000	197,000
Al_2O_3	718,000	399,000
PbO	90,500	50,300
B_2O_3	505,000	280,000
Nonmetallic compounds		
HCl	39,600	22,000
H_2O (liq.)	123,000	68,400
H_2O (gas)	104,500	58,000
NH_3	27,000	11,900
SO_2	128,000	71,100
H_2SO_4	348,000	193,000
HNO_3	73,800	41,600
CO	52,200	29,000
CO_2	174,500	96,960
CH_4	39,200	21,750
C_2H_2	−86,000	−47,800
$Ca(OH)_2$	425,000	236,000
Salts		
Na_2S	161,000	89,300
CaS	162,000	90,800
$NaCl$	176,000	97,900
KCl	190,000	105,600
$CaCl_2$	344,000	191,000
$MgCl_2$	272,000	151,000
$NaNO_3$	200,000	111,000
KNO_3	214,000	119,000
Na_2SO_4	593,000	329,000
K_2SO_4	620,000	344,000
$BaSO_4$	612,000	340,000
$CaSO_4$	605,000	336,000
$MgSO_4$	544,000	302,000
$ZnSO_4$	413,000	229,600
$PbSO_4$	389,000	216,000
Na_2CO_3	488,000	271,000
K_2CO_3	495,000	275,000
Na_2SiO_3	665,000	369,000
$CaSiO_3$	675,000	375,000
$MgSiO_3$	623,000	346,000
$CaCO_3$	520,000	289,000
$MgCO_3$	481,000	267,000

The heat of formation of one compound can be determined if the heat of a reaction in which the compound is involved is known as well as the heats of formation of the other reacting substances. For example, the heat of combustion of one molecular weight of carbon disulfide is 265,100 cal. and the heats of formation of CO_2 and sulfur dioxide are 96,960 and 71,000 cal., respectively. The heat of formation of carbon disulfide, CS_2, can be calculated as follows:

$$CS_2 + 3O_2 = CO_2 + 2SO_2 + 265{,}100 \text{ cal.}$$
$$-X + 0 = -96{,}960 - (2 \times 71{,}000) + 265{,}100$$
$$X = -26{,}140 \text{ cal., the heat of formation of } CS_2$$

Several physical changes that take place are accompanied by heat effects and will be briefly mentioned at this time. They are not to be confused with the foregoing chemical changes and are given here merely for the purpose of definition.

The thermal change accompanying the solution of one molecular weight of a substance, in so large a volume of solvent that subsequent dilution of the solution causes no further change in temperature, is called the *heat of solution at infinite dilution.* Some substances, when they dissolve, cause an absorption of heat while others cause an evolution of heat. An example of the latter type is sulfuric acid, H_2SO_4. Its heat of solution is so great that, when it is poured into a small volume of water, the solution actually boils.

The heat of *dilution* of a solution is the quantity of heat evolved or absorbed per molecular weight of solute when the solution is greatly diluted. Beyond a certain dilution, further addition of solvent produces no thermal change. The heat of dilution of a solution is an indefinite quantity because it depends upon the concentration of the solution. It is used only in describing a specific solution.

When a pure substance undergoes a change of state—for example, from liquids to solid—heat is either evolved or absorbed. The heat evolved or absorbed in changing from the liquid to the solid state (or the reverse) is known as the *heat of fusion* and is a fixed and distinct quantity for each substance. Likewise, the heat evolved or absorbed when a substance changes from the gaseous to the liquid state (or the reverse) is known as the *heat of vaporization* and is also a fixed quantity for each substance

When most substances freeze (pass from the liquid to the solid state), heat is evolved and, when this change takes place in the reverse direction, the same amount of heat is absorbed. It should be remembered that this amount of heat is evolved or absorbed when the change in state takes place at *constant temperature.* Most gases evolve or liberate heat when they condense and absorb the same amount of heat when vaporized. For example, 1 g. of water evolves 80 cal. in passing from the liquid to the solid state and absorbs 80 cal. in melting (constant temperature). In condensing from the gaseous state at a constant temperature of 100°C., 1 gr. of steam evolves 540 cal. The reason why live steam burns so badly is that each gram gives up this large amount of heat in condensing in addition to the heat evolved in cooling. The pressure must be taken into account in determining the heat of vaporization.

ELEMENTS OF COMMERCIAL IMPORTANCE

Silicon.—This element derives its name from the Latin word *silex,* meaning flint.

Silicon is classed as a nonmetallic element and is somewhat similar to graphite in appearance. It is a dull grayish-black material having a melting point of 1415°C. (2580°F.). Elemental silicon is not found in nature inasmuch as silicon oxidizes readily, the mineral quartz (rock crystals, SiO_2) being a typical example. Its most common occurrence (over 12 per cent of the minerals on the earth's surface) is quartz. Silicon dioxide is a constituent of the important minerals of a granite, namely, orthoclase, feldspar, quartz, mica, hornblende, augite, and olivine. Agate, sand, onyx, amethyst, chalcedony, flint, and opal are common natural oxides of silicon. Quartz sand is composed of fragments of quartz weathered from granites. These particles are deposited in low areas, such as shallow seas, and are later encountered by the driller as he drills through sandstone strata which were laid down millions of years before and later covered by other formations.

Sandstone formations are natural resources. They act as hosts to oil and gases and, if they are pure and accessible, are used for making glass and refractories. SiO_2 in the form of pure sand is known as *silica.* Silica is a very stable compound having a

melting point of 1728°C. (3142°F.). Melted silica has the property of cooling as a glass, but the high melting point makes pure silica glass a rather difficult product to make. Varying amounts of sodium oxide, Na_2O, and calcium oxide (lime, CaO) when added to silica reduce the melting point to a practical commercial limit, common glass being the resulting product. All ceramic bodies, which have been fired, contain a certain amount of glass depending upon the amount of silica present and the temperature at which they were fired.

Silicon dioxide is widely used as a refractory in the linings of metallurgical furnaces because of its high melting point.

Iron ores contain silica which must be removed during metallurgical operations. Small amounts of elemental silicon are added to special steels to improve their acid-resisting properties.

Aluminum.—Aluminum is the most abundant metal on earth but its great affinity for oxygen in almost any form is responsible for the fact that no native (metallic) aluminum is found in nature. This metal always occurs in a combined state with other elements and it forms such stable compounds that it is very difficult to extract. In nature the minerals bauxite, $Al_2O_3 \cdot 2H_2O$ and cryolite, Na_3AlF_6 constitute the most important source of aluminum ore. Bauxite is a weathering product of aluminum-bearing rocks and is formed most rapidly under tropical climatic conditions.

Corundum, Al_2O_3, is an extremely hard mineral which, if pure, is a source of gem stones. Ruby (red) and sapphire (blue, yellow, green, and purple) are two well-known varieties of corundum. The impure variety, emery, has found wide application in the field of abrasives.

Bauxite clay contains from 50 to 75 per cent aluminum oxide with varying amounts of silica, ferric oxide, and water. Pure aluminum oxide (alumina) is necessary in the metallurgical process in the preparation of metallic aluminum.

The pure aluminum oxide is dissolved in molten cryolite and metallic aluminum is precipitated in the bottom of a high-temperature electrolytic cell. Carbon anodes suspended in the molten bath of alumina and cryolite, contained in a thick carbon-lined cell, discharge current through the fluxed material causing oxygen to be given off at the anodes and metallic aluminum precipitated.

The metal is a silver-white substance capable of taking a high polish. Dullness soon results, however, because of a thin oxidized coating which forms in the presence of air. It is lighter than any other common metal and has about the same density as glass.

The property of having a strong affinity for oxygen makes aluminum useful as a commercial material. The thermit process of welding is sometimes used in welding large iron masses such as machines. Aluminum powder is mixed with pure iron oxide. The reaction is started by ignition and the rapid combustion that follows produces a high temperature (3000°F.) when the iron oxide is reduced and the resulting iron is deposited between the metallic pieces being welded. The reaction is as follows:

$$\underset{\text{Iron oxide}}{Fe_2O_3} + \underset{\text{Aluminum}}{2Al} = \underset{\text{Iron}}{2Fe} + \underset{\text{Alumina}}{Al_2O_3}$$

Since metallic aluminum has a tremendous affinity for oxygen in any form, it is used to remove oxygen from liquid steel. This is known as the deoxidation process. As an oxide, alumina, Al_2O_3, has a very high melting point 2050°C. (3722°F.) and unless its concentration is controlled in the blast furnace, a thick slag will result.

Artificial corundum is prepared by melting alumina in an electric furnace and, with certain control, synthetic rubies and sapphires may be produced. Bauxite fused in an electric furnace yields a fused alumina that has found wide application as an abrasive and refractory under the trade name of Alundum.

Alloys of metallic aluminum and copper, magnesium, and other metals offer a vast number of metals extremely strong in proportion to their weight. Bridges, airplanes, locomotives, car bodies, and many other types of construction are more durable and lighter because of their alloy construction.

Iron.—Iron is without question the most useful of all metals to our present civilization. Without it our great industrial feats would be impossible.

Pure or native iron does not exist in nature except when found in a meteorite (falling star). Even then it more often occurs as an alloy with nickel and other metals. For the most part the bulk of the ore from which iron is obtained occurs as the mineral *hematite*, Fe_2O_3; however, absolutely pure hematite is rather

difficult to find. Generally the ore is a mixture of hematite (red to brown), limonite, $2Fe_2O_3 \cdot 3H_2O$ (yellow), and often magnetite, $FeO \cdot Fe_2O_3$. Iron ore has much the same appearance as red or yellow earth.

Pure iron is gray white in color and is relatively soft. It can be cut easily by a knife and works with not much more difficulty than lead. It is so malleable and ductile that it bends and can be pulled out with relative ease. A cubic centimeter weighs 7.83 g. (density) and the metal melts at a temperature of 1530°C. (2786°F.). Pure iron can be prepared electrolytically from ore or impure iron.

The commercial forms of iron are known as pig iron, which is hard, brittle, and contains C, Si, S, Mn, etc., as impurities; wrought iron, which is much purer than pig iron and is consequently more ductile and malleable; and steel, which is iron combined with C, Mn, and Si. It is frequently alloyed (combined) with such other elements as nickel, chromium, molybdenum, vanadium, or tungsten, either individually or in certain combinations to impart certain definite desirable properties. This last commercial form of iron (steel) is by far the most important as it possesses the best properties. These forms of iron can all be obtained by the reduction of the oxides with carbon, although this is not always the most economical method.

Iron is considered generally as an impurity by the ceramic industry. At 1200°C. (2200°F.) the oxides of iron form powerful fluxes with respect to clays and silica. Thus, clays containing more than a few per cent of iron oxides are worthless as refractories. Iron oxides also impart color to white china so that more than 0.25 per cent Fe_2O_3 in a clay makes it unsuitable for whiteware. Greenish glass is the result of using a sand containing over 0.05 per cent Fe_2O_3. If the amounts of iron oxide increase, a brown and possibly black glass will result.

The petroleum and natural gas industry is interested in alloy steels because of their resistance to heat and erosion. Drill pipe, sucker rods, machines, derricks, tools, and other items must all be made of the proper steel to give maximum and satisfactory service.

Calcium.—Calcium is an element found in practically every rock on the earth's surface. It is named from the Latin word *calx*, meaning lime. Calcium is dissolved from rocks during rock

weathering and is carried to sedimentary basins in solution as a bicarbonate $Ca(HCO_3)_2$.

The organic functions of shelled animals deposit calcium carbonate, $CaCO_3$, in the form of shell, the water and CO_2 in the calcium bicarbonate being given off. Chemical action within the shelled animal yields the following:

$$\underset{\text{Calcium bicarbonate}}{Ca(HCO_3)_2} \rightarrow \underset{\substack{\text{Calcium carbonate}\\ \text{(limestone)}}}{CaCO_3} + CO_2 + H_2O$$

Accumulation of a large number of shells is responsible for the production of limestone, and later geological processes recrystallize the limestone into marble.

Metallic calcium is prepared electrolytically by depositing pure calcium upon an iron rod (the cathode) suspended in a fusion of calcium chloride, $CaCl_2$, contained in a graphite crucible (the anode). The short iron cathode is raised mechanically as a rod of solid calcium is gradually built up on its end. Calcium metal becomes the cathode after the process is once started.

Pure calcium is a bright silver-white metal which is between lead and zinc in hardness.

Calcium carbonate (pure limestone) is one of the most abundant compounds of nature. Limestone decomposes upon being heated to a red heat (1000°C. or 1832°F.) into calcium oxide, CaO, or quicklime (unslaked lime) and carbon dioxide as follows:

$$\underset{\text{Limestone}}{CaCO_3} \rightarrow \underset{\text{Calcium oxide}}{CaO} + CO_2$$

CaO is used in purifying steel; it combines with both sulfur and phosphorus as well as some silicon and manganese.

Calcium oxide, CaO, combines with water to form calcium hydroxide, $Ca(OH)_2$, or slaked lime.

$$\underset{\text{Unslaked lime}}{CaO} + \underset{\text{Water}}{H_2O} \rightarrow \underset{\text{Slaked lime}}{Ca(OH)_2}$$

If calcium oxide is left exposed to air, it will absorb moisture and carbon dioxide to form a mixture of calcium carbonate and calcium hydroxide. Upon standing, the calcium hydroxide also becomes calcium carbonate.

Mortar is a mixture of slaked lime, sand, and water. A paste is made and applied between bricks or stones in a building. The

water evaporates leaving a hard mass of calcium hydroxide with sand embedded in it for added strength. After long setting the reaction mentioned above between slaked lime and air takes place and the entire calcium hydroxide is converted into calcium carbonate.

$$\underset{\text{Slaked lime}}{Ca(OH)_2} + \underset{\text{Carbon dioxide}}{CO_2} \rightarrow \underset{\text{Calcium carbonate}}{CaCO_3} + \underset{\text{Water}}{H_2O}$$

Good mortar consequently improves with age.

Commercial glass contains about 10 per cent CaO and Portland cement contains about 65 per cent. CaO has a very high melting point, 2570°C. (4650°F.), but it cannot be used as a refractory material because it is unstable when exposed to moisture.

Magnesium.—The element magnesium is very similar to calcium and often occurs in combination with it. The element itself is of small commercial importance but its compounds, like those of calcium, are very useful. The oxide, MgO, known as *magnesia* may be prepared by heating the carbonate, the reaction being of the same type as the limestone decomposition. MgO has an even higher melting point 5072°F. (2800°C.) than lime. On prolonged heating at high temperatures, MgO converts to a form that does not combine with moisture. This form is known as dead burned magnesite and is used to line the bottoms of open-hearth steel furnaces. It is also made into bricks for refractory purposes. If the magnesia is not dead burned, it may be united with water to form magnesium hydroxide, $(MgOH)_2$. Milk of magnesia, used for medicinal purposes, is a mixture of $Mg(OH)_2$ and water. MgO like CaO is present in most silicate rocks. It is used in glass as a substitute for lime and is a primary constituent of such minerals as asbestos, talc, and dolomite.

Sodium.—This element belongs to the group known as the alkali metals. They occupy group I in the periodic table. The metals of this group react violently with water to form the hydroxides, which are commonly known as the caustic alkalies or lye. Sodium hydroxide, also known as caustic soda, is the most important of the alkali hydroxides. It is a strong base which reacts readily with acids to form sodium salts. *Sodium oxide,* Na_2O, is so unstable under ordinary conditions that there is considerable doubt that it has ever been prepared and none of its properties in the uncombined state are known. However,

Na_2O in the combined state is a constituent of a very large number of rocks and minerals, especially the feldspars which comprise over one-half of the rocks of the earth. Na_2O is the most important fluxing material used in ceramics. By adding it to the high-melting silicates it is possible to form combinations that melt at a relatively low temperature. A good example of this fluxing power is the lowering of the melting point of silica. Pure SiO_2 melts at 3142°F. (1728°C.) but, when one-fourth of the SiO_2 is replaced by Na_2O, the melting point of this mixture is only 1459°F. (793°C.), a lowering of almost 1000°C. Since Na_2O is not available as such, it must be used in some combined form. The most common source of the oxide is sodium carbonate, Na_2CO_3, known as *soda ash*. This compound reacts with the SiO_2 in silicates according to the equation:

$$Na_2CO_3(Na_2O{\cdot}CO_2) + SiO_2 = Na_2SiO_3(Na_2O{\cdot}SiO_2) + CO_2.$$

The CO_2 may be considered to be replaced by SiO_2 and it passes off as the gas.

Potassium.—Potassium belongs to the same group of elements as sodium and it is the only other commercially important element of this group. The chemical properties of potassium are much the same as sodium and its oxide is not known with certainty. The hydroxide, caustic potash, KOH, has about the same usage as NaOH. K_2O is not so strong as flux, weight for weight, as is Na_2O but it has other desirable properties not possessed by sodium oxide. One of these desirable properties is resonance or the ability to emit a musical sound when struck. Fine glass and china that contain potash, K_2O, possess this property to a marked extent. K_2O finds a rather large use in glassmaking and in whitewares, the chief sources of the oxide being the carbonate, K_2CO_3, for glass, and potash feldspar, $K_2O{\cdot}Al_2O_3{\cdot}6SiO_2$, for whiteware bodies. The feldspar is a relatively cheap material but potassium carbonate is more expensive than sodium carbonate and consequently is not used so much in making glass.

Phosphorus.—This element is named from the Greek word meaning light bearing.

Phosphorus is never found free in nature but is widely distributed in limited amounts in soils and in all iron ores. It occurs in commercial deposits in the form of apatite and phos-

phorite (names of the minerals). The element can be prepared by the reduction of phosphoric acid, H_3PO_4, by carbon at high temperatures and in the free form has a melting point of 42°C. It burns in air to form P_2O_5 and is very poisonous. It forms a compound with iron, Fe_3P.

Phosphorus is a detrimental impurity in iron and steel in most cases and considerable time and money are expended in removing it as completely as possible from steel during its manufacture. It is completely reduced in the blast furnace and is present in pig iron. It can be removed from steel by oxidation to P_2O_5 and combination of this oxide with calcium oxide, principally in the form of $3CaO \cdot P_2O_5$ or $Ca_3(PO_4)_2$.

Sulfur.—This element is found free in nature and in the combined state in the form of FeS_2, $FeCuS_2$, ZnS, PbS, $CaSO_4$, and $PbSO_4$. Compounds of sulfur occur in iron ores, in limestone, and in coal. Sulfur, itself, is pale yellow in color, has a melting point of about 113°C., and burns in air to SO_2. It is a necessary constituent of sulfuric acid, the most important commercial acid.

Since the compounds of sulfur present in iron ore, coal, and limestone are largely reduced in the blast furnace and some of it finds its way into the pig iron in the form of FeS and MnS, sulfur is an ever-present constituent in steel. It is a detrimental constituent in all but a very few cases and is eliminated as completely as possible. This can be done by causing the conditions to be such that the sulfur reacts with CaO to form CaS.

Chromium.—This is a rather rare element, the existing commercial deposits being composed of chromite, $Cr_2O_3 \cdot FeO$. This double oxide, when pure, is an excellent refractory, having a melting point of nearly 2200°C. The pure metal can be made by reducing the oxide (Cr_2O_3) with metallic aluminum; the product looks like iron but is harder and has a melting point of 1615°C. The most important chemical compounds are the chromates (K_2CrO_4) and the dichromates ($K_2Cr_2O_7$). Chromium forms carbides with iron and carbon in some steels.

Chromium is principally used in metallurgy as an alloying element in steels, the function of the chromium being greatly to increase the strength of the steel and its resistance to oxidation. In pure form, it is often electroplated on metal objects to produce a surface luster as well as a very hard and wear-resistant covering.

Manganese.—This metal occurs in nature as the dioxide MnO_2 in deposits that are very limited in this country. It is present in small amounts in nearly all the raw materials of iron manufacture and, as 75 per cent of it is reduced in the blast furnace, manganese is present in all pig iron. As it aids in purifying steel of harmful impurities, such as oxygen and sulfur, it is nearly always present in steel, although in small amounts (under 1 per cent) except when the element is deliberately alloyed with iron.

Pure manganese may be prepared by the reduction of the dioxide with sodium, magnesium, aluminum, or by electrolysis. In the pure form it is a gray-white metal resembling iron but harder and more brittle. It has a density of 7.42 and a melting point of 1230°C. Its most important compounds besides MnO_2 are the chloride ($MnCl_2$), sulfate ($MnSO_4$), oxide (MnO), permanganate ($KMnO_4$), the sulfide (MnS), and, at high temperatures, double oxides, such as $MnO{\cdot}SiO_2$.

Nickel.—This element is found principally in the form of a hydrated silicate with iron and is prepared by a special process in which a purified oxide of nickel is reduced by CO gas or by carbon. The metal itself is almost white in color, is hard, malleable, and tough, is a good conductor of electricity, and is somewhat magnetic at ordinary temperatures. It has a melting point of 1450°C. Its important compounds are the sulphate ($NiSO_4$) and the oxides (NiO) and (Ni_2O_3). Nickel is soluble in iron in the solid state.

Nickel is the most used alloying element added to steel. It increases the strength of steel greatly without increasing brittleness. When used in conjunction with fairly large amounts of chromium, the steels are very resistant to oxidizing influences.

Lead.—Metallic lead is a heavy, soft, low-melting at 621°F. (327°C.), bluish-grey metal. Although lead is not one of the most common elements, it has numerous uses both in the metallic form and in the combined form. Basic lead carbonate, $2PbCO_3{\cdot}Pb(OH)_2$ known as *white lead* is an important paint pigment. It is also used to a small extent in making glazes for pottery. The lead compound of importance in ceramics is the oxide, *PbO*, known as *litharge*. PbO does not occur in any natural minerals of importance but is obtained by the oxidation of metallic lead. It is an orange-yellow powder having a melting point of

1630°F. (880°C.). PbO may also be obtained from Pb_3O_4 by its decomposition, on heating, according to the reaction:

$$2Pb_3O_4 \rightarrow 6PbO + O_2$$

PbO is a very strong fluxing oxide which combines readily with all of the other ceramic oxides. It forms low-melting liquids such as are required in glazes and enamels. Glasses containing lead oxide are very brilliant and pleasing to the eye and much of the expensive glass tableware is lead glass.

Boron.—Boron is a nonmetallic element having a valence of three, and although it is rightly placed in group III of the periodic table, the properties of its compounds resemble those of silicon more than aluminum. Boron forms two common compounds which are commercially important, borax, $Na_2O{\cdot}2B_2O_3{\cdot}10H_2O$, and boric acid, H_3PO_3 ($B_2O_3{\cdot}3H_2O$). *Boric oxide, B_2O_3,* combines with the other oxides to form borates which have properties somewhat similar to the silicates. B_2O_3 possesses the glass-forming tendency the same as SiO_2 and confers this property on most of the borates. Borax may be obtained in the glassy form by heating it to a sufficiently high temperature to drive off the 10 molecules of water and melt the dehydrated borate. Boric acid, if heated to about 930°F. (500°C.), will lose its water of hydration and form liquid boric oxide. On cooling, this liquid will always form a clear glass which becomes soft when heated above 570°F. (300°C.). At room temperature this glass reacts slowly with the moisture in the air forming boric acid again. The low melting point of B_2O_3 as compared with most of the silicates makes it an important fluxing material, although it is not so good a flux as the alkalies. Borax containing both soda and boric oxide is an excellent fluxing material and is used extensively in glasses and enamels.

Carbon.—The element carbon, a nonmetal, is widely distributed in nature, occurring in the uncombined or free form as graphite and diamond, and in an impure form as coal; in combination it is found in carbon dioxide of the atmosphere, and very abundantly in the carbonates of certain metals, especially calcium and magnesium. It is also a constituent of all living things in the form of organic compounds. The discussion of the more important organic compounds will be generally treated.

Carbon and carbon monoxide, the product of the combination of carbon with an insufficient supply of oxygen, are the principal chemical agents used in the reduction of metals from their ores. An outstanding example is their use in the reduction of iron ore in the blast furnace. CO is usually the most powerful reducing agent under normal operating conditions. Carbon also forms a compound with iron known as iron carbide, Fe_3C. This compound is quite important as most of the valuable properties of steels can be traced directly to its presence.

Questions and Practice Problems

1. Define (*a*) substance, (*b*) element, (*c*) compound, (*d*) mixture. Give examples of each.

2. Define and illustrate the four laws of chemical combination.

3. Define the atomic weight of an element.

4. Calculate the molecular weights of

$$FeO;\ Fe_2O_3;\ SiO_2;\ MgCO_3;\ P_2O_5;\ NaCl$$

5. Calculate the empirical formula for the compounds having the following percentage composition:

		Per Cent
(*a*)	Chromium	35.390
	Oxygen	38.025
	Potassium	26.585
(*b*)	Aluminum	53.03
	Oxygen	46.96

6. Calculate the percentage of Mn in MnO.

7. Calculate the percentage of Al in $Ca(AlO_2)_2$.

8. Balance the following equations:

$$Fe + O_2 = Fe_3O_4$$
$$Fe + O_2 = Fe_2O_3$$
$$Si + O_2 = SiO_2$$
$$H_2 + Cl_2 = HCl$$
$$H_2 + O_2 = H_2O$$
$$KClO_3 = KCl + O_2$$
$$Na_2O_2 + H_2O = NaOH + O_2$$
$$Fe_3O_4 + H_2 = Fe + H_2O$$
$$P + O_2 = P_2O_5$$
$$CH_4 + O_2 = CO_2 + H_2O$$
$$HCl + O_2 = H_2O + Cl_2$$
$$H_2SO_4 + Ca(OH)_2 = CaSO_4 + H_2O$$
$$Fe_2O_3 + Al = Al_2O_3 + Fe$$
$$C + O_2 = CO$$
$$C_2H_4 + O_2 = CO_2 + H_2O$$

9. The formula of a compound cannot be written unless the valences of the elements composing it are known. Using the correct formulas given below to determine the valences, write the correct formulas for the compounds given in the incomplete form.

Correct: HCl; $FeCl_3$; H_2O; H_2S; $AlCl_3$; H_2SO_4; $CaCl_2$; H_3PO_4; H_2SiO_3.

Incomplete: FeO; FeS; $Al(SO_4)$; $Ca(PO_4)$; $Ca(SiO_3)$; $Fe(SO_4)$; $Ca(OH)$.

10. Aluminum displaces hydrogen from sulfuric acid according to the following equation:

$$2Al + 3H_2SO_4 = Al_2(SO_4)_3 + 3H_2$$

How much sulfuric acid is required to react completely with 100 g. of aluminum? *Ans.:* 547 g.

11. Natural gas is largely methane (CH_4). The products of its combustion are CO_2 and H_2O. If all the gases are measured under the same conditions, what volume of oxygen will be required to burn 100 cu. ft. of pure CH_4? What volume of CO_2 and H_2O will be formed?

Ans.: 200, 100, and 200 cu. ft., respectively.

12. The City Gas Company maintains gas tanks with adjustable tops so that constant pressure can be maintained. On Dec. 1 at 8 A.M. the temperature at one tank was 17°C., and the volume was 50,000 cu. ft. At 2 P.M. the temperature was 23°C. What was the volume at that time?

Ans.: 51,034.5 cu. ft.

13. Are the following compounds acids, bases, or salts?

$Ni(OH)_3$; $PbSO_4$; KNO_3; $Ca(OH)_2$; H_2CO_3; H_3PO_4;
NH_4OH; HNO_3; $Al(OH)_3$; $CaSO_4$.

14. Explain the mechanism of the electrolysis of a solution of hydrochloric acid, HCl, in water on the basis of the ionic hypothesis.

15. Calculate the heat of reaction of the following equations in B.t.u.:

(*a*) $CaO + SiO_2 \rightarrow CaSiO_3$
(*b*) $Na_2O + SiO_2 \rightarrow NaSiO_3$
(*c*) $Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$
(*d*) $CaCO_3 \rightarrow CaO + CO_2$
(*e*) $CaO + H_2O \rightarrow Ca(OH)_2$

Ans.: (*a*) + 52,000 B.t.u.
(*b*) +128,000 B.t.u.
(*c*) + 11,900 B.t.u.
(*d*) − 84,500 B.t.u.
(*e*) + 41,000 B.t.u.

16*a*. The weight of an open-hearth bath is 270,000 lb. The carbon content is 0.62 per cent. If 2,000 lb. of ore (Fe_2O_3) were added, what residual carbon, in per cent, would be present after the ore had all worked through the bath? (Neglect the oxidizing influence of the slag.)

b. What volume of gas, in cubic feet, would be liberated if the furnace temperature were 3000°F. and the pressure 770 mm.?

c. Is heat absorbed or given off in this reaction? Calculate the amount of heat, in B.t.u., absorbed or liberated.

Ans.: a, 0.45 per cent; *b*, 93,600 cu. ft.; *c*, −2,432,800 B.t.u.

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CHAPTER II

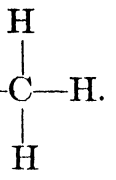
GENERAL ORGANIC CHEMISTRY

Having learned something of the nature of matter from general chemistry, one is prepared to consider the various branches of chemistry in some detail. One of the most important of these is organic chemistry, so designated because many of the materials with which it deals are involved in life processes, both animal and vegetable. It was once thought that these substances could not be synthesized, which means produced artificially, but could be obtained only as they are produced by plants and animals. However, in 1828, a German chemist named Wöhler synthesized urea, a substance occurring naturally in plants and animals, and since then chemists have produced thousands of organic compounds. Such things as fats and waxes, sugars, starches, rubber, soaps, dyes, petroleum which is a mixture of many compounds, gelatin, and drugs are all organic materials, and it will be recognized that they all occur naturally. Many of them can also be produced at will in the laboratory. The study of the nature of these compounds, how they are constituted and how they behave, comprises organic chemistry.

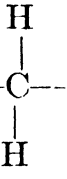
There are a few general facts pertaining to organic chemistry that should be considered in a brief review of the subject. The most significant is that all organic compounds contain carbon. In fact, organic chemistry is often called the chemistry of the carbon compounds. These number more than 250,000, whereas all other compounds made up of the other elements which, it will be recalled, number 91, excluding carbon, combine to make only about 26,000 compounds.

The reason for there being so many compounds of carbon is that this element combines in a way in which few other elements do, and none to such an extent. It has been proved that carbon atoms are linked together, thus C—C—C, and the number of carbons that can link together in this way is almost limitless. However, each one of the C's has four bonds to which some other atom must be linked (except where C joins C) to form a stable

molecule. These bonds are represented by dashes. Since hydrogen is the element most often found in organic compounds in combination with carbon, the simplest organic compound could almost be guessed, it being

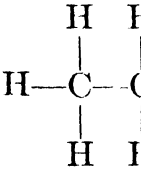


This first compound, then, is the familiar gas methane. When the formula is written as inorganic ones usually are, it is CH_4. The structural method is often used by the organic chemist, however, and we have

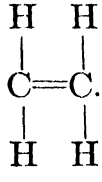


Methane is the principal component of natural gas. It also forms in coal mines, producing an explosive mixture with air. Compounds containing carbon and hydrogen are called *hydrocarbons.*

Instead of a hydrogen atom being linked to the carbon, another carbon may be linked directly to a second like this



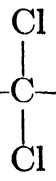
which may be written C_2H_6. This is also a gas called ethane, found in natural gas and petroleum. Bearing in mind that carbon must always have four bonds, represented by dashes, we may have two of these bonds between two carbon atoms



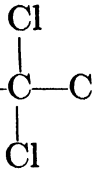
This is a gas called ethylene, which is used as an anesthetic and to ripen fruits. There may be three of the bonds joining two carbon atoms, and the simplest compound of this type is H—C≡C—H, acetylene, a very reactive gas which is used as an illuminating gas and in the oxyacetylene torch since it gives off much heat as well as light when burned.

With carbon and hydrogen as building blocks, a whole series of compounds is built up. They are known as the aliphatic or straight-chain hydrocarbons.

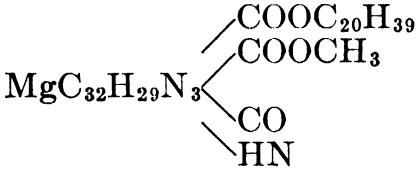
Other elements may be substituted for hydrogen in organic compounds. Chlorine, bromine, and iodine occur in many of them. For instance, carbon tetrachloride, CCl_4, written structurally



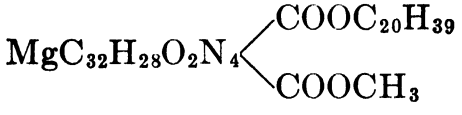
dry cleaning. There is also $CHCl_3$, chloroform, written structurally



compounds, sulfur being responsible for the disagreeable odor of many of them. Metals such as magnesium, copper, arsenic, and iron may also be attached to carbon. Most organic compounds are very complex, containing many atoms to the molecule. For example, the green coloring matter in plants called chlorophyll, is a mixture of

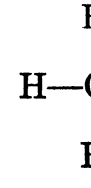


and



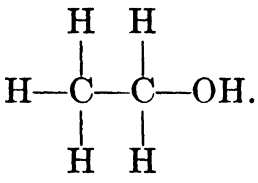
Hemoglobin, the substance that makes the blood red, is similar to chlorophyll, except that it contains iron instead of magnesium.

Certain groups of atoms or "radicals" when attached to an organic molecule form a series of compounds. For instance, the OH group (O = oxygen, H = hydrogen) is remembered from inorganic chemistry where it is part of such compounds as NaOH, sodium hydroxide, a substance which is a base with a soapy feel and a caustic action. In the aliphatic compounds, however, the OH group determines an alcohol. Methyl or wood alcohol is CH_3OH, written structurally



Ethyl or grain

alcohol is C_2H_5OH which may be written structurally, thus



Note that the OH group has simply replaced a hydrogen atom in the compounds previously described as methane and ethane. Besides alcohols, there are also the following types of compounds. It should be borne in mind that each type mentioned represents many compounds, only a couple of which are noted here:

Acids.—Formic acid, HCOOH, the COOH denotes an acid. It is responsible for the "sting" from bees.

Acetic acid, CH_3COOH, the acid in vinegar.

Palmitic acid, $C_{17}H_{35}COOH$. The "ester" of this acid is found in body fats and oils.

Aldehydes.—Formaldehyde, HCHO, is used as a preservative.

Acetaldehyde, CH_3CHO.

Ketones.—Acetone, $CH_3—CO—CH_3$, used as a solvent for fats, gums, etc.

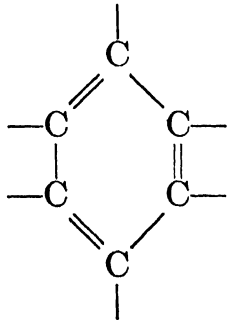
Ethers.—Ethyl ether, $C_2H_5—O—C_2H_5$, used as an anesthetic and also as a solvent for fats, oils, etc.

Salts.—Sodium formate, H—COONa (see the formula for formic acid). The sodium and potassium salts of the more complex acids are familiar, as soaps. Soap is made from fats and alkali and the formula for one soap is $C_{15}H_{31}COONa$, named sodium palmitate.

Esters.—Ethyl acetate, $CH_3COOC_2H_5$.

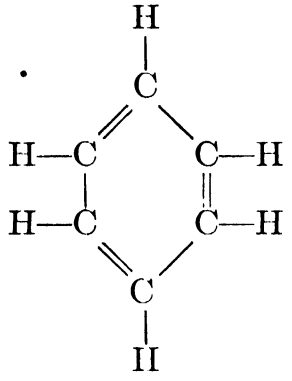
Sugars.—Galactose, maltose, lactose, sucrose, fructose. Fructose as fruit sugar is $C_6H_7(OH)_5$.

Besides occurring in compounds linked in a straight chain, carbon appears in another series of compounds in a closed ring like this



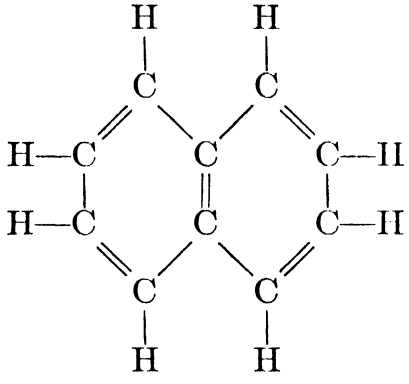
which is known as the benzene ring.

Since the complete formula for benzene is C_6H_6, it is written structurally as



Most of the ring compounds of carbon contain six carbon atoms, though there are some that have only four or five. Different elements or groups of elements may be substituted for the hydrogen atoms attached to the ring and thus thousands of compounds are formed. The ring, or cyclic, compounds are known as the aromatics, since many of them have distinctive odors.

Two benzene rings are attached side by side in the compound naphthalene which is one of the products obtained from the distillation of coal tar. Its formula looks like this:



Three benzene rings are likewise joined together to form anthracene. All these compounds are used by the organic chemist in the synthesis of such things as drugs and dyes which are very large, complicated molecules.

Many industrial processes involve organic chemistry. In the petroleum industry the crude petroleum, which consists essentially of mixtures of many different hydrocarbons, is subjected to a process known as *fractional distillation.* This process consists in distilling the mixture, causing its separation into parts (frac-

tions) differing in their boiling points, and collecting separately the distilled parts. These different fractions are then further refined to obtain such products as gasoline, benzene, kerosene, gas oils, lubricating oils, vaseline, paraffin. These final products, like petroleum itself, are mixtures of hydrocarbons in very variable proportions. When bituminous coal is coked in a by-product oven, the materials evolved from this destructive distillation are collected, treated, and purified to obtain numerous organic compounds. These products include coke, gas, tar, ammonia, benzene, toluene, ethylene, naphthalene, explosives, dyes, etc., to mention only a few of the recovered and refined organic compounds that may be obtained.

This introduction to organic chemistry and to the evidences of its uses has been made necessarily quite brief and has had to omit much that is significant. For a more detailed knowledge of the subject the following books are recommended:

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CHAPTER III

APPLICATIONS OF CHEMISTRY

CERAMICS

Scope of the Ceramic Industry.—Before entering into a discussion of the applications of chemistry in the ceramic industry, we should define the term "ceramics" and explain the scope of the industry. In its broadest sense, ceramics includes the study of all compounds and mixtures of silica, SiO_2, and related materials. The ceramic industries, therefore, consist of the glass, cement, clay products, refractories, whiteware, enamel, and allied industries. Since all these industries use silicate materials for their manufacturing processes, the chemistry concerned is essentially that of silica and its compounds. This branch of chemistry is often called silicate chemistry or ceramic chemistry. For reasons of space only a brief discussion of silicate chemistry and a few of its applications can be given here.

As we have seen previously, oxygen and silicon are the two most abundant elements in the earth's crust. The chemical compound silica, SiO_2, in the form of quartz constitutes about 12 per cent of the rocks in the earth's crust. In addition SiO_2 enters into various chemical combinations with practically every other metallic oxide found in the earth's crust.

Some of the silicate compounds are of very complex composition, containing several different elements. For purposes of simplicity and convenience the ceramic chemist writes the formulas of these compounds in terms of their constituent oxides. For example, the formula of potash feldspar is written $K_2O \cdot Al_2O_3 \cdot 6SiO_2$ rather than $KAlSi_3O_8$. The oxide formula shows at once that the feldspar contains one molecule of potassium oxide, one molecule of aluminum oxide, and six molecules of silicon dioxide. The analysis of a ceramic compound is always expressed in terms of the weight per cent of its constituent oxides because, on complete analysis of the material, it is found that there is always just enough oxygen to satisfy all the other elements when they are in the form of oxides.

Most ceramic raw materials are compounds of the first eight elements of Table 3-I. These eight elements comprise over 95 per cent of the earth's crust. With but few exceptions they occur as oxide compounds and most of these compounds contain silica.

Because of their universal distribution, the ceramic raw materials are relatively cheap. However, large deposits of raw materials having desirable characteristics are on the whole rare and highly prized. In the manufacture of ceramic products the characteristics of the finished product depend upon its ultimate chemical composition. In general, each of the constituent oxides contributes its specific properties to the compound (or mixture) in proportion to the amount of that oxide present in the compound. For example, a mixture of 95 per cent sugar and 5 per cent salt tastes more like sugar than like salt.

With the exception of SiO_2 the oxides of ceramic importance do not occur in the free state but are combined with one or more oxides. These oxide compounds are very stable and cannot be separated into the individual oxides. For this reason, when it is desired to make a product having certain properties, it is necessary to obtain first a raw material containing the oxides that, when properly treated, will produce the desired result. Alumina, Al_2O_3, is an excellent refractory material for certain purposes and although clay, $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$, contains a large amount of Al_2O_3, it is not so refractory as pure Al_2O_3 because of the SiO_2 which it contains. At present there is no cheap chemical or physical means of effecting a separation of alumina from clay and so it must be obtained from some natural material such as bauxite, $Al_2O_3 \cdot 2H_2O$, or diaspore, $Al_2O_3 \cdot H_2O$, from which the water may be removed by simple heating.

The Properties of Silica.—The compound SiO_2 has, in addition to its widespread occurrence, certain characteristic chemical and physical properties that make it the most important compound in the field of ceramic chemistry:

1. Silica has a remarkable chemical affinity for the other oxides and combines readily with them to form a group of over 1,000 silicate compounds.

2. It acts chemically as an acidic oxide. The oxides of the metals in general are basic and combine with the acidic oxides. Silica is by far the most abundant acidic oxide. Therefore, over

95 per cent of the earth's crust is in the form of silicates of the basic oxides.

3. Silica when melted has the property of cooling in the form of a glass. This property of glass formation is possessed by only a few oxides and with the exception of boric oxide, B_2O_3, silica is the only one of sufficient abundance to be commercially important. It confers this glass-forming property on most of the silicates especially those which contain a large proportion of SiO_2. Commercial glass is the best example of a glassy silicate, containing about 70 per cent SiO_2 and varying amounts of Na_2O and CaO. All ceramic bodies that have been properly fired contain a certain amount of glass, depending on the amount of silica present and the temperature to which they have been fired. The glassy part of the body forms the bond that holds the crystalline grains together.

4. Silica is very stable chemically at ordinary temperatures. Pure SiO_2 has a very high melting point, 3142°F. (1728°C.). This is above the temperature encountered in any commercial gas-, oil-, or coal-fired furnace. Consequently, silica makes an excellent refractory material. At room temperature silica is not attacked by any of the common acids or bases. As the temperature is increased, the attack becomes more rapid but at 1000°F. (438°C.) the rate of attack is still slow. At 2732°F. (1500°C.) silica will react almost instantly with any of the other oxides. The resistance to reaction at ordinary temperatures gives ceramic materials their qualities of permanence and durability.

The Properties of the Silicates.—It has been stated previously that silica has the ability of combining with practically all the other oxides. The resulting compounds are known as silicates. There are over 1,000 silicates known but most of them are rare and of no commercial importance. In this brief discussion it will be possible to describe only a few of the more important ones.

Aluminum Silicates.—The most important silicate is the mineral *kaolinite*. It is a hydrated aluminum silicate having the formula

$$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$$

Kaolinite is the principal mineral constituent of all clays and is the compound that gives them their characteristic claylike properties. Clays, in addition to kaolinite, contain various

amounts of other substances that are considered as impurities. The purest types of clays are white in color and consist of almost pure kaolinite with very little impurity. A clay of this type is usually white and is known as a kaolin.

Kaolinite was formed by the gradual decomposition of the feldspar group of minerals. One of the most common of these, the potash feldspar, has the formula

$$K_2O \cdot Al_2O_3 \cdot 6SiO_2$$

The formation of the kaolinite has been explained by the following reaction:

$$K_2O \cdot Al_2O_3 \cdot 6SiO_2 + 2H_2O + CO_2 = Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O + K_2CO_3 + 4SiO_2$$

This reaction is very slow at ordinary temperatures and it takes ages to form a deposit of clay from a feldspar rock. The carbon dioxide is present in the air in small amounts and dissolves in the water. The potassium carbonate formed is soluble in water and is leached away from the kaolinite. The silica formed as a product of this reaction is slightly soluble in water and is also partly leached away. When clay is mined, it always contains some silica in addition to the kaolinite but it never contains K_2CO_3.

When clay is heated, the kaolinite decomposes in the temperature range 900 to 1100°F. or 500 to 600°C. In this temperature range the $2H_2O$ is driven off as water vapor and the Al_2O_3 and $2SiO_2$ are dissociated into the free oxides. As the temperature increases, the alumina and silica react according to the following reaction:

$$3Al_2O_3 + 2SiO_2 = 3Al_2O_3 \cdot 2SiO_2$$

The excess SiO_2 from the kaolinite remains as free silica mixed with the new compound, $3Al_2O_3 \cdot 2SiO_2$, known as *mullite*. Mullite is the only compound of alumina and silica that exists at high temperatures. It is present in almost all ceramic materials containing clay, after they have been fired. Mullite has a very high melting point, 3226°F. (1830°C.) and consequently is a valuable constituent in refractory materials. Any mixture of Al_2O_3 and SiO_2 will form some mullite on heating above 1000°C. (1832°F.).

The foregoing discussion of clay has been confined to very pure clays containing almost 100 per cent kaolinite. However, in

actual practice even the purest clays contain appreciable quantities of other oxides and silicates. The presence of these compounds has an effect on the behavior and properties of the clay. They are regarded as impurities because they tend to destroy the properties of the pure clay. However, in clays used for specific purposes certain impurities are desirable. For example, in the manufacture of common red building brick, a clay containing 4 to 7 per cent Fe_2O_3 is desirable to produce a good red color during firing. On the other hand, a china clay suitable for whitewares will usually contain less than 0.5 per cent of Fe_2O_3.

Many clays contain iron in the form of *pyrite*, the iron sulfide, FeS_2. This compound when heated in air reacts with oxygen to form Fe_2O_3 and SO_2 according to the reaction

$$4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2$$

The SO_2 usually is driven off as a gas and the remaining Fe_2O_3 may react with the SiO_2 of the clay.

The Alkali Silicates.—The most important alkali silicates are those of sodium and potassium. These compounds are not found in nature because of the fact that they are soluble in water and would be leached out of any deposit.

There are only two silicates of sodium of any commercial importance, sodium metasilicate, $Na_2O{\cdot}SiO_2$, and sodium disilicate, $Na_2O{\cdot}2SiO_2$. They may be formed by heating sodium carbonate, Na_2CO_3, with silica according to the following reaction.

$$Na_2CO_3 + SiO_2 = Na_2O{\cdot}SiO_2 + CO_2$$

When two mols of SiO_2 are present, the product is sodium disilicate.

These compounds form glasses on rapid cooling. When the glasses are dissolved in water, the result is a viscous liquid known as "water glass." This material finds wide application as an adhesive and in the manufacture of pasteboard.

The chemistry of the potassium silicates is very similar to that of the sodium compounds. The potassium silicates are of little commercial importance because of the higher price of K_2CO_3.

The Alkaline Earth Silicates.—The oxides of the metals of column (a), group II, in Table 6-I, are known as the alkali earth oxides. Of this group calcium and magnesium are the most

abundant while barium is also of considerable importance. These elements occur in vast quantities as the carbonates. Limestone consists essentially of calcium carbonate, $CaCO_3$. The carbonates when brought to a red heat decompose into carbon dioxide and the oxides of the metal.

$$CaCO_3 = CaO + CO_2$$

This reaction explains the process of lime burning. The product CaO is called *quicklime* or *burnt lime*.

There are four compounds of CaO and SiO_2: tricalcium silicate, $3CaO \cdot SiO_2$; dicalcium silicate, $2CaO \cdot SiO_2$; $3CaO \cdot 2SiO_2$; and calcium metasilicate, $CaO \cdot SiO_2$. The metasilicate occurs in nature as the mineral *wollastonite*. Dicalcium silicate and tricalcium silicate are important constituents of Portland cement. They have the property of combining with water to form hydrates. These hydrates are stable chemical compounds and their formation produces a strong and durable cement.

There are two magnesium silicates: the metasilicate, $MgO \cdot SiO_2$ known as clinoenstatite and the orthosilicate, $2MgO \cdot SiO_2$ known as forsterite. Magnesium compounds are not so widely used in ceramics as are the calcium compounds. MgO has a very high melting point, 5072°F. (2800°C.) and makes an excellent refractory material. It is chemically basic and is used in the basic open-hearth process for steel making. The compounds high in MgO, such as forsterite, also have high melting points and find use as basic refractories. Forsterite melts at 3434°F. (1890°C.).

The Complex Silicates.—For the most part the silicates that occur naturally as minerals are not the simple ones such as wollastonite or forsterite. They consist usually of rather complex combinations of two or more oxides combined with silica. The group of minerals known as the feldspars are a good example of complex silicates.

The feldspars are aluminum silicates of potassium ($K_2O \cdot Al_2O_3 \cdot 6SiO_2$), sodium ($Na_2O \cdot Al_2O_3 \cdot 6SiO_2$) and calcium ($CaO \cdot Al_2O_3 \cdot 2SiO_2$). These three compounds and various mixtures of them make up about 60 per cent of the rocks of the earth's crust. Granite, the most common rock, is composed of feldspar, quartz, and mica. Mica is another aluminum silicate having the formula, $K_2O \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot 2H_2O$.

In certain localities deposits of nearly pure feldspar are found. These are mined and find extensive use in the various ceramic industries. The potassium feldspar is used as a source of Al_2O_3 for glass. The other feldspars are primary constituents of whiteware bodies.

There are numerous other silicates of lesser importance which will be described in connection with the operations in which they are important.

The Ceramic Industries.—For the purpose of this section on the ceramic industries it is convenient to divide the discussion into six parts. Each part contains a brief description of one of the main divisions of the industry. As stated previously, all these divisions have in common the treatment of silicates by the application of heat. However, each division produces a different type of product by a process different from that used by the other divisions.

Glass.—The word "glass" has two general definitions: (1) It designates the condition of a substance which has, for the most part, the properties of a liquid but at the same time possesses the rigidity of a solid. This condition is usually designated as the glassy or vitreous state. It is the result of cooling a liquid so rapidly that it is unable to crystallize, as liquids usually do when they are cooled. (2) It designates a group of commercial products that have the characteristics of the vitreous state. These products are familiar to us all in the form of windowpanes, bottles, and tableware.

The first definition of glass is a technical one and it is important in all branches of the ceramic industry because most of the silicates may be easily obtained in the glassy form. The ceramic materials other than commercial glass contain a certain amount of glass which serves as a bond to hold the structure together. The importance of this glassy bond will be taken up later. In this section the discussion will be limited to glass as a commercial product.

There are several types of commercial glasses depending upon their chemical compositions. The most common type is the soda-lime-silica glass which constitutes over 90 per cent of all the glass manufactured. This type of glass, as the name indicates, consists of sodium oxide (Na_2O), lime (CaO), and silica (SiO_2).

Glass is not a definite compound but rather a solution of several chemical combinations. Since it is not a definite compound, its chemical composition may vary over rather wide limits. Table 1-III gives the approximate compositions of various soda-lime-silica glasses.

TABLE 1-III

	Window glass	Plate glass	Bottle glass
SiO_2	72	73	74
Na_2O	15	13	17
CaO	13	14	9

In regular commercial practice all glasses contain a certain amount of other oxides either as impurities or as minor constituents. The impurities are the result of impure raw materials or solution of part of the refractory walls of the melting furnace. The minor constituents are purposely introduced to obtain for the glass certain properties which the straight soda-lime-silica glass could not have.

Glass is made by taking the desired quantities of suitable raw materials to give the correct glass composition, mixing them thoroughly, and melting this batch of raw materials in a furnace lined with a refractory sufficiently resistant to the hot glass.

Since the soda-lime-silica glass consists of Na_2O, CaO, and SiO_2, these oxides must be introduced into the raw batch in some form that will lend itself readily to mixing and melting and at the same time contain a minimum of impurities. Some oxides may be obtained directly from naturally occurring raw materials while others are the products of complicated chemical processes and naturally are more expensive.

Silica, SiO_2, occurs naturally as the mineral quartz. In certain regions of the country there are large deposits of quartzite rock which when ground and washed yield a sand of a sufficient purity to be used in almost any type of glass. Glass sand of the best quality should contain less than 0.02 per cent of Fe_2O_3. This iron oxide is an undesirable impurity as it gives the glass a greenish color. When a perfectly clear glass is not necessary, sand of a lower quality is often used.

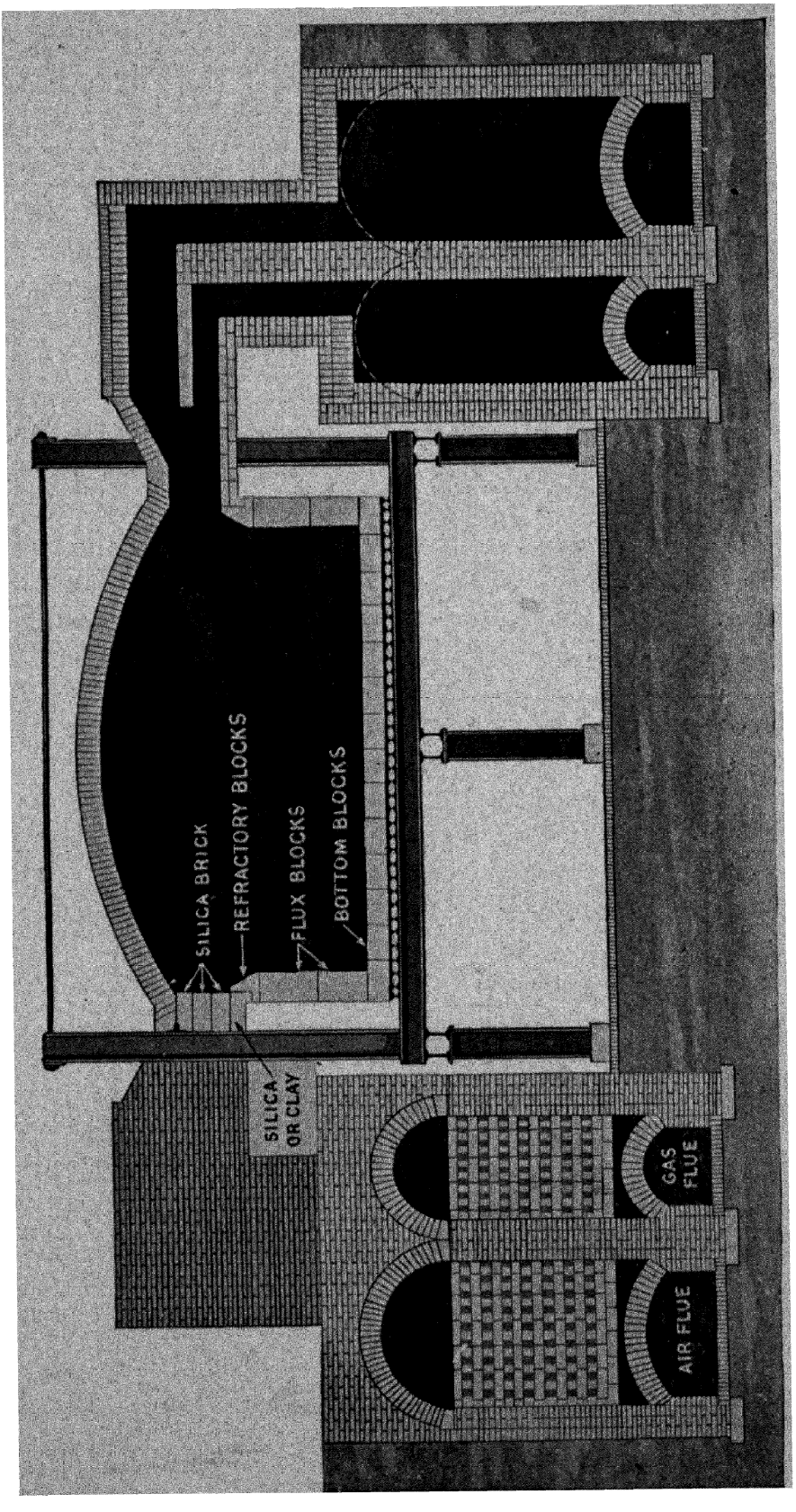


Fig. 1-III.—Detail of construction of a tank in which glass is melted.

Sodium oxide, Na_2O, is not available in the form of the oxide because this compound is not stable under ordinary conditions. The chief source of "soda," as the oxide is usually called, is sodium carbonate, Na_2CO_3, usually known as soda ash. This compound is made from salt by a chemical process and does not contain enough undesirable impurities to affect the glass. Na_2O may also be obtained from sodium sulphate, Na_2SO_4, usually known as salt cake. Sometimes both salt cake and soda ash are used together as this combination aids in the melting of some types of glass.

Lime, CaO, occurs in vast deposits in limestone. Limestone, the carbonate of calcium, $CaCO_3$, may be ground and used directly in glass or it may be calcined to CaO and the oxide used. The iron content of lime used in glassmaking may be several times that of sand because glass contains only 10 to 15 per cent CaO. In this country a large amount of dolomitic lime is used. This lime contains MgO as well as CaO. The MgO acts much the same as CaO and is often preferred for certain types of glass.

Colored glass may be produced by introducing certain coloring oxides into the batch. These oxides are melted and go into solution in the molten glass. Some of the common colorants are as follows: cobalt oxide, CoO, blue; chromium oxide, Cr_2O_3, green; selenium, Se, pink or red; uranium oxide, UO_3, yellow; sulfur and carbon, yellow or brown. Opal or milk glasses are produced by introducing some compound containing fluorine into the glass.

Glass products are shaped from the molten liquid by numerous processes. However, there are three main types of processes: (1) blowing, (2) drawing and rolling, (3) pressing. The individual processes used are all modifications of one of these main types.

All hollow ware, bottles, jars, light bulbs, etc., are produced by a blowing process, either hand or machine. Sheet glass, both plain window glass and plate glass, is made by first drawing or rolling the glass into sheets and then grinding and polishing if necessary. Thick-walled ware such as tableware, baking dishes, and signal lenses is made by pressing the molten glass into molds of the proper size.

After a piece of glass has been shaped into its final form, it must be cooled slowly to room temperature or certain strains will be set up in the glass because of the unequal rates of cooling.

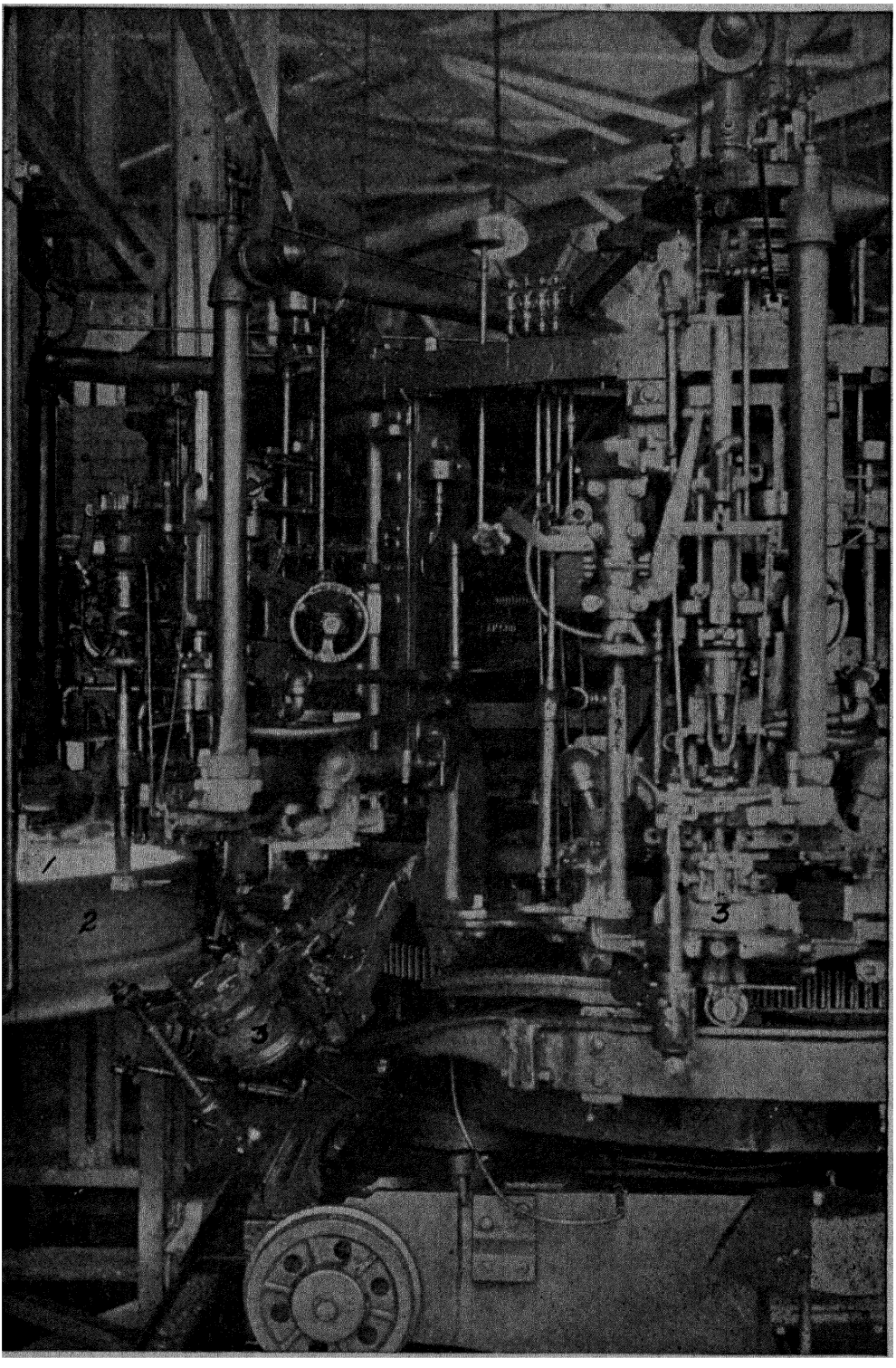


FIG. 2-III.—Owens automatic bottle machine. (1) Melted glass. (2) Revolving pot. (3) Bottle mold.

These strains are especially severe in large or complicated shapes and they will usually result in breakage of the object unless it is properly cooled. This cooling process is known as annealing. It is carried out in a low-temperature furnace through which a continuous chain belt passes. The ware is placed on this belt and as it passes through the furnace, it encounters a gradually decreasing temperature. The maximum temperature in an annealing furnace for a soda-lime-silica glass is approximately 1050°F. (565°C.). The time of annealing depends upon the size of the piece.

Cements.—The field of cements usually covers not only Portland cement but also lime and gypsum products. The discussion of this section will be limited to the Portland cement industry. This particular branch is the second largest of the ceramic group in value of production.

Portland cement derives its name from the fact that it closely resembles a certain building stone quarried on the Isle of Portland in England. It is a synthetic chemical product containing 60 to 65 per cent CaO, 20 to 25 per cent SiO_2, and 5 to 12 per cent Fe_2O_3 and Al_2O_3. Although a cement must be of this approximate composition, the individual constituents vary with the process used and the type of product desired.

The primary property of Portland cement is its ability to form hydrated compounds when mixed with water. Certain compounds of CaO—Al_2O_3 and CaO—SiO_2 have this property to a marked extent. They are tricalcium silicate, $3CaO \cdot SiO_2$; dicalcium silicate, $2CaO \cdot SiO_2$; and tricalcium aluminate, $3CaO \cdot Al_2O_3$. Since these are the desirable compounds, the main problem is to control the heat-treatment of a suitable charge of raw materials to produce a maximum amount of them.

The raw materials are as follows: limestone, marl, or "cement rock" which provides the CaO, and clay or shale which provides the Al_2O_3 and SiO_2. These materials are for the most part quite impure but it is possible, by using a combination of them, to obtain the correct oxide composition in the finished product. White cement is produced from iron-free raw materials.

The raw batch is pulverized in ball or tube mills. This is necessary to obtain intimate contact between the various particles. This fine-grained material is then fed into the upper end of a rotary kiln inclined at a slight angle. As the charge passes

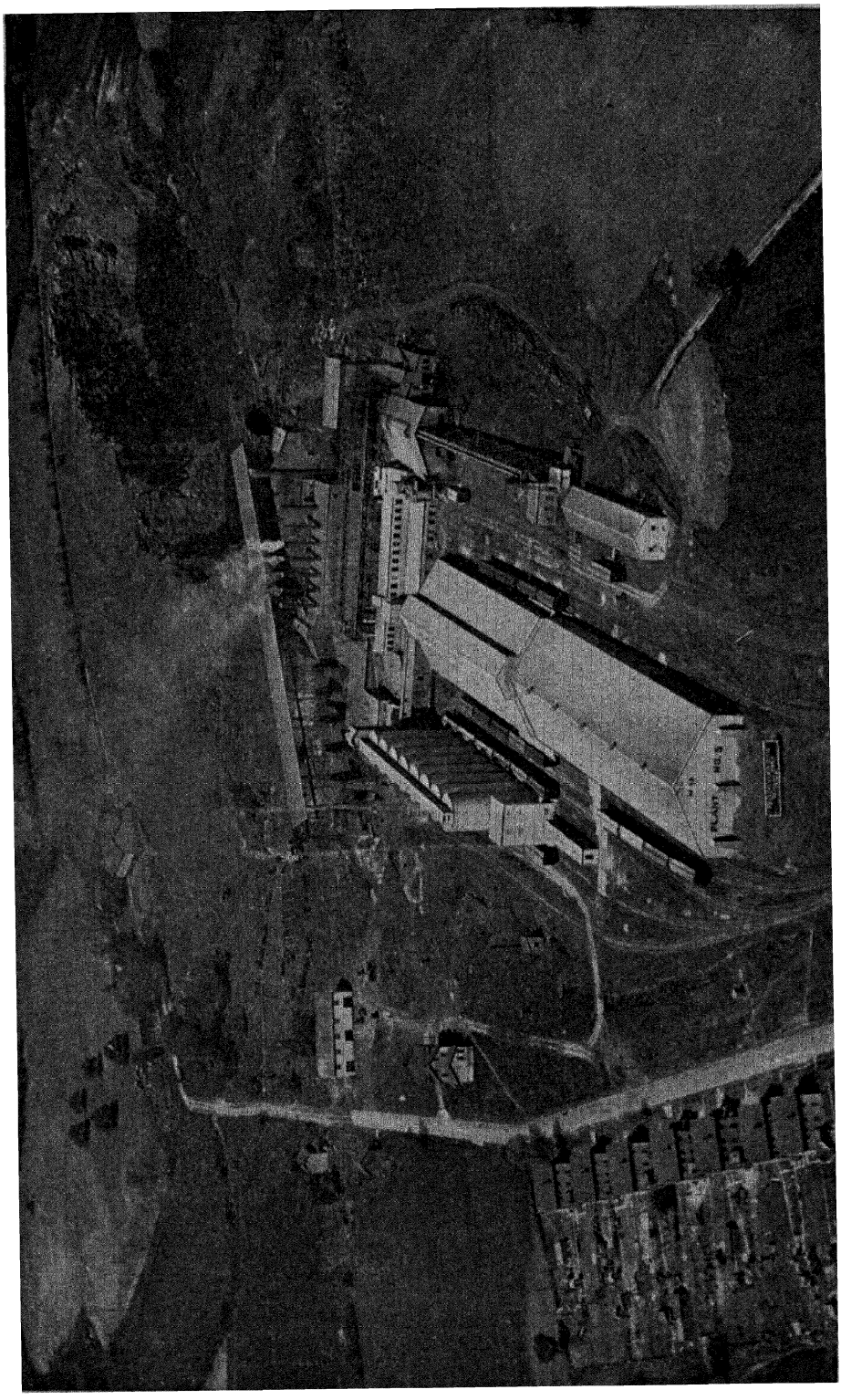


FIG. 3-III.—A modern Portland cement plant.

down through the kiln, it is tumbled through a flame which reaches a maximum temperature of about 2732°F. (1500°C.). As the charge is heated, water and carbon dioxide are given off, and the clay and lime begin to react to form the various compounds. By careful control of both the temperature of the kiln and the time the charge is in the kiln, it is possible to make practically all the oxides react to form the desired compounds.

During the firing operation the powdered material forms small hard clinkers. Before the product can be used, these clinkers must be pulverized so that the cement can be easily mixed with water. This grinding is done in ball or tube mills. After grinding, the powder is mixed with a small amount of plaster of Paris, which regulates the rate of setting of the Portland cement when mixed with water. When the cement sets, the various compounds take up water in chemical combination producing an interlocking structure of insoluble, hydrated, crystalline compounds. This process of hydration and recrystallization takes place slowly and may continue for years. For this reason cement structures grow stronger with age.

Clay Products.—All those ceramic industries which use clay as their principal raw material may be conveniently classed as the clay-products industry. This group includes the producers of all types of brick, tile, sewer pipe, paving blocks, structural clay products, terra cotta, earthenware, and similar products.

Since there is an almost unlimited variety of clays available and individual products that can be produced from them, space will permit only the description of a typical example, the making of facebrick. This product is made principally from shales and low-grade fire clays. A shale is a hardened clay which must be ground before it can be mixed with water. Shales generally produce dark-colored brick while the fire clays give a light-gray or buff-colored product. Facebrick are usually made by what is known as the "stiff-mud" process.

In this process the shale or clay must be ground and mixed thoroughly with water until it has the consistency of putty. Such a mixture may then be fed to an auger machine and forced through a die. A column of clay emerges from the die and may be cut into suitable lengths by passing wires through it. The wire cutter may cut 12 to 14 bricks at a single stroke.

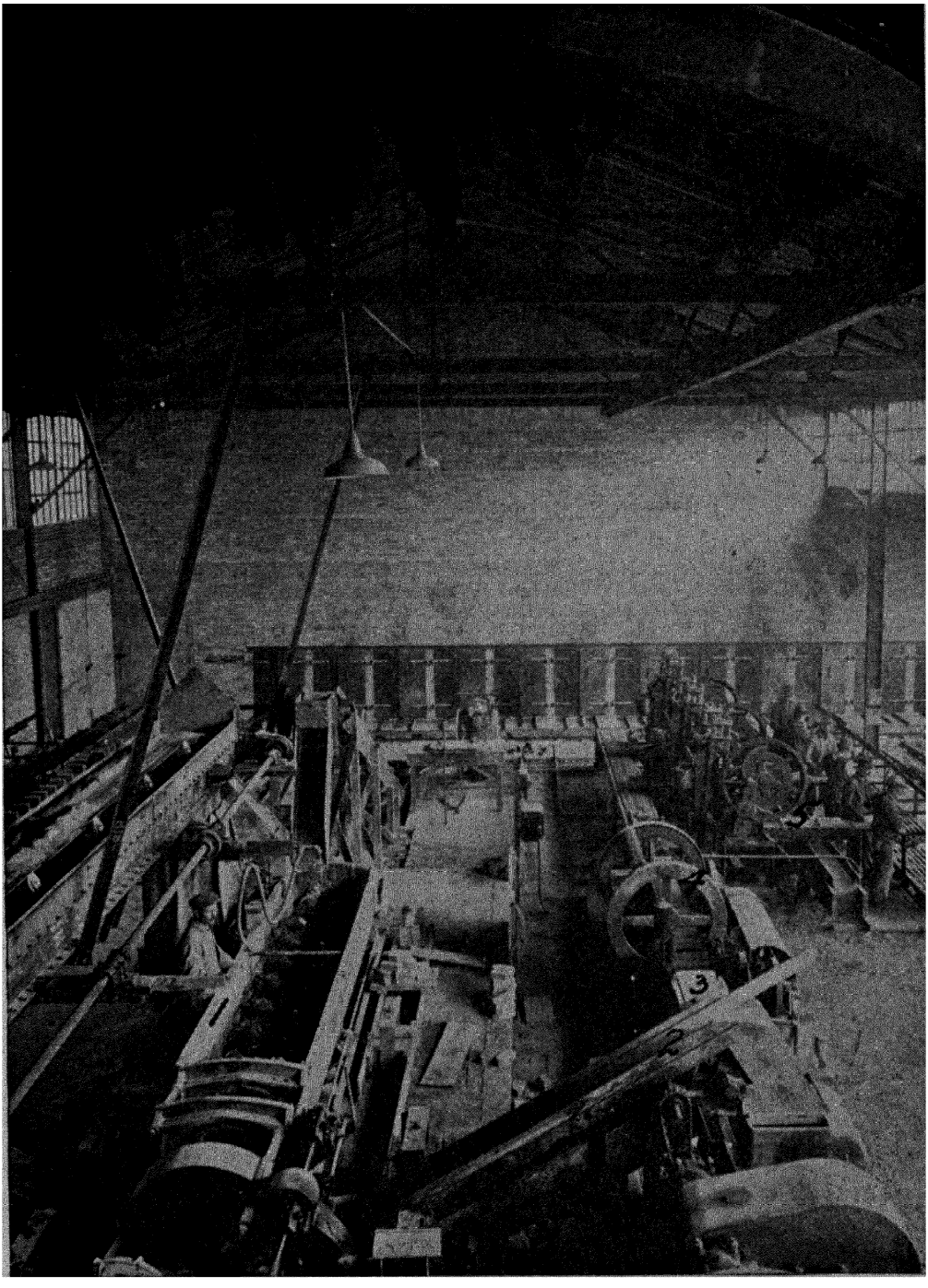


FIG. 4-III.—Interior of a brick plant. (1) Pug mill. (2) Conveyer. (3) Brick machine. (4) Wire cutter. (5) Repress.

After the bricks have been cut they are placed on trays and removed to a drier. Here they are subjected to a temperature that is gradually raised until it is above the boiling point of water. This drying process effectively removes all the water except that which is chemically combined with the clay. The dried bricks are then placed in a kiln. The kiln may be a tunnel kiln through which the bricks are pushed on cars. As they pass along the interior, they encounter a gradually increasing temperature until a maximum is reached, after which the bricks are cooled almost to room temperature before emerging from the kiln. The other type of kiln is the periodic kiln, in which the bricks are stacked while the kiln is cold. When the kiln is full, it is sealed and the temperature gradually raised to the maximum and then allowed to cool.

Regardless of the type of kiln used, the maximum temperature of firing is about 2200°F. (1205°C.). At this temperature part of the clay melts and forms a very viscous silicate liquid which flows around the grains of unmelted clay. When the brick are cooled, this liquid becomes a solid glass and serves as a cementing material, holding the mass of grains together. This process of melting part of the clay to form a glassy bond is known as vitrification (glass formation) and is one of the fundamental processes of the ceramic industry. The amount of liquid formation in a clay is dependent upon its chemical composition.

Refractories.—Any process involving the use of heat must make use of equipment and structures capable of withstanding the temperatures to which the product is subjected. For temperatures up to 1000°F. there is a wide variety of suitable materials but as the temperature is increased these materials are gradually eliminated because their melting points are reached and they become liquid. Any material capable of remaining a solid at a high temperature is known as a refractory. However, because most of these materials are either silicates or related mineral products, the use of the word "refractories" is usually reserved for the nonmetallic materials, such as fire clay, chrome, magnesite, and silica, rather than the high-melting metals such as platinum and tungsten.

The approximate distribution of refractories into various classes is as follows: fire clay, 80 per cent; silica, 18 per cent; and chrome, magnesite, silicon carbide, graphite, and other minor

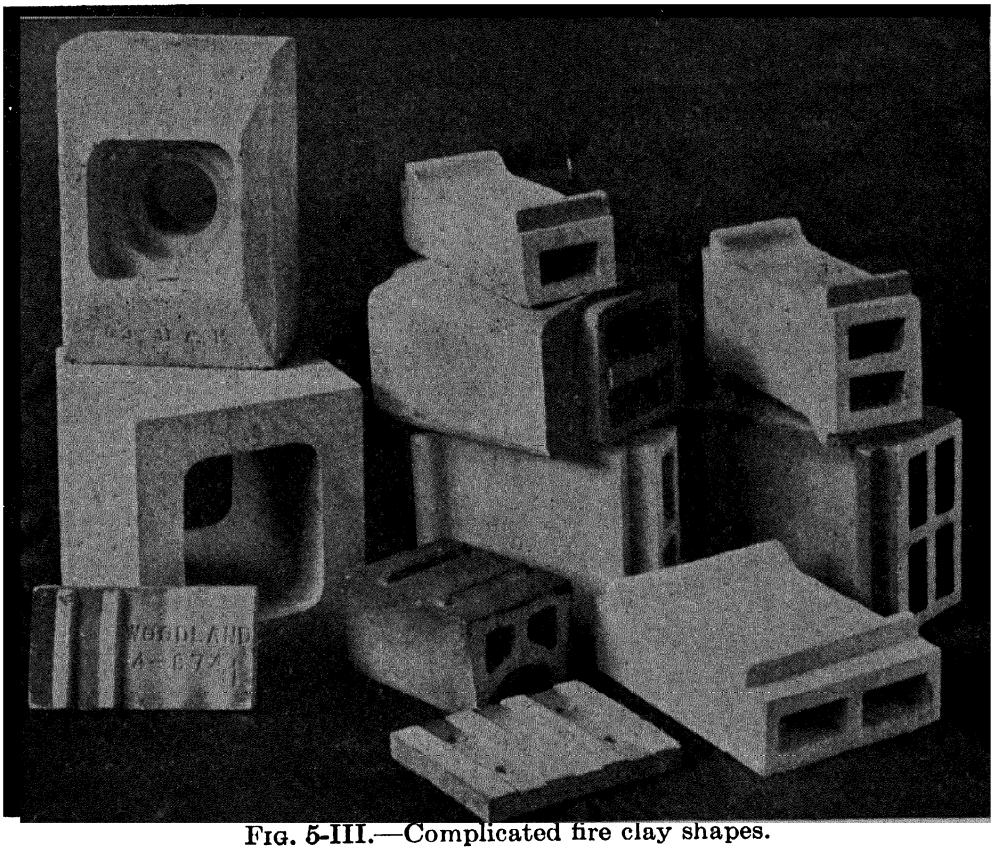


FIG. 5-III.—Complicated fire clay shapes.

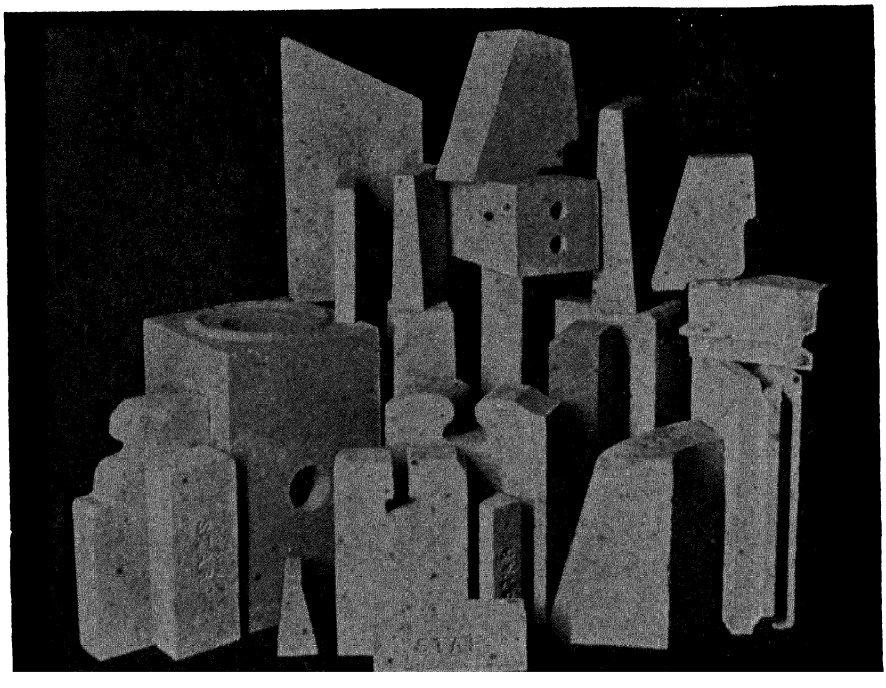


FIG. 6-III.—Silica refractory special shapes.

refractories, 2 per cent. Fire clay is relatively abundant, has a high melting point, and in addition has remarkable chemical stability. The fire clays are very pure clays consisting mostly of kaolinite, $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$. A clay of this type melts at about 3245°F. (1785°C.). Naturally, clays containing impurities have lower melting points. A clay that melts below 2900°F. is not good enough to be classified as a true fire clay. Fire-clay refractories find their greatest use in the metallurgical industries, especially in the iron and steel industry. They are manufactured much the same as other clay products but are fired at higher temperatures.

Silica brick are made by grinding a nearly pure quartzite rock and mixing it with about 2 per cent lime. This mixture is then ground with water, shaped into brick, and fired to about 2750°F. for a period of about 10 days. During the firing the lime reacts with the silica and produces a liquid that forms the bond for the brick. Silica brick find their greatest use in the roofs of open-hearth steel furnaces and in glass tanks.

As mentioned above, there are numerous types of special refractories that have important uses in certain industrial operations. Although their bulk production is not so large as fire clay or silica, their value is great because of their special properties and the high price of their raw materials.

Whitewares.—This branch of the industry is concerned with the production of white burning products composed of clay, silica, and feldspar. The principal products manufactured are chinaware, electrical porcelain, vitreous sanitary ware, and white floor and wall tile.

The raw materials must be as nearly free of iron oxide as possible because of the strong coloring effect it has on this type of body. The raw materials are pulverized, mixed with a large amount of water, and stirred until the entire mass is a homogeneous fluid. It is then pumped through cloth filters which extract most of the water leaving the solids in a plastic condition. This plastic mass is then shaped by pressing it into plaster molds. It is also possible to cast the fluid "slip" into plaster molds to form large or intricate shapes.

After the ware has been formed, it is dried and fired in the same manner as are other clay products. Such products as china, porcelain, and sanitary ware must be glazed before they can be

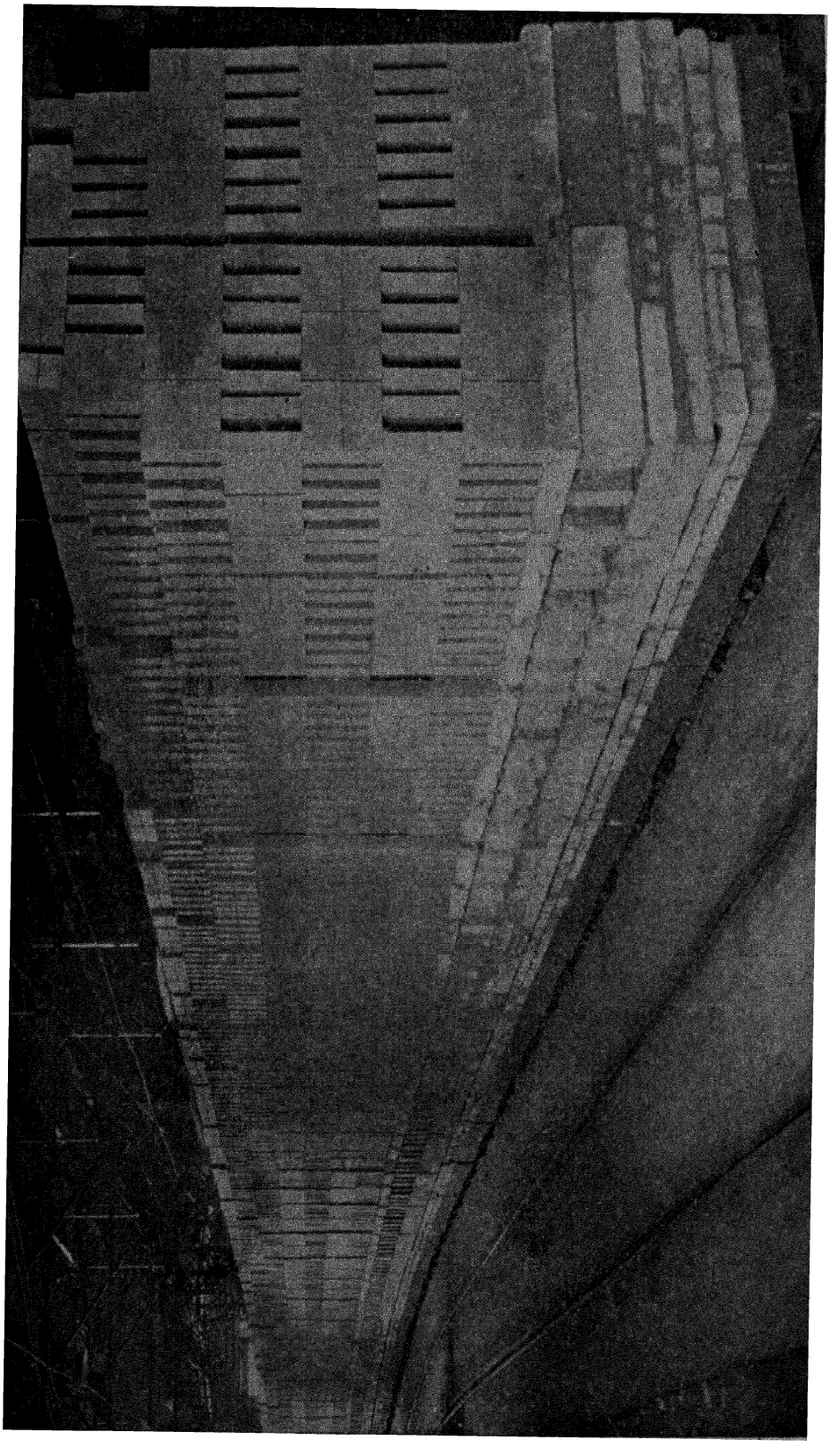


FIG. 7-III.—A trainload of brick ready to enter tunnel kiln for firing.

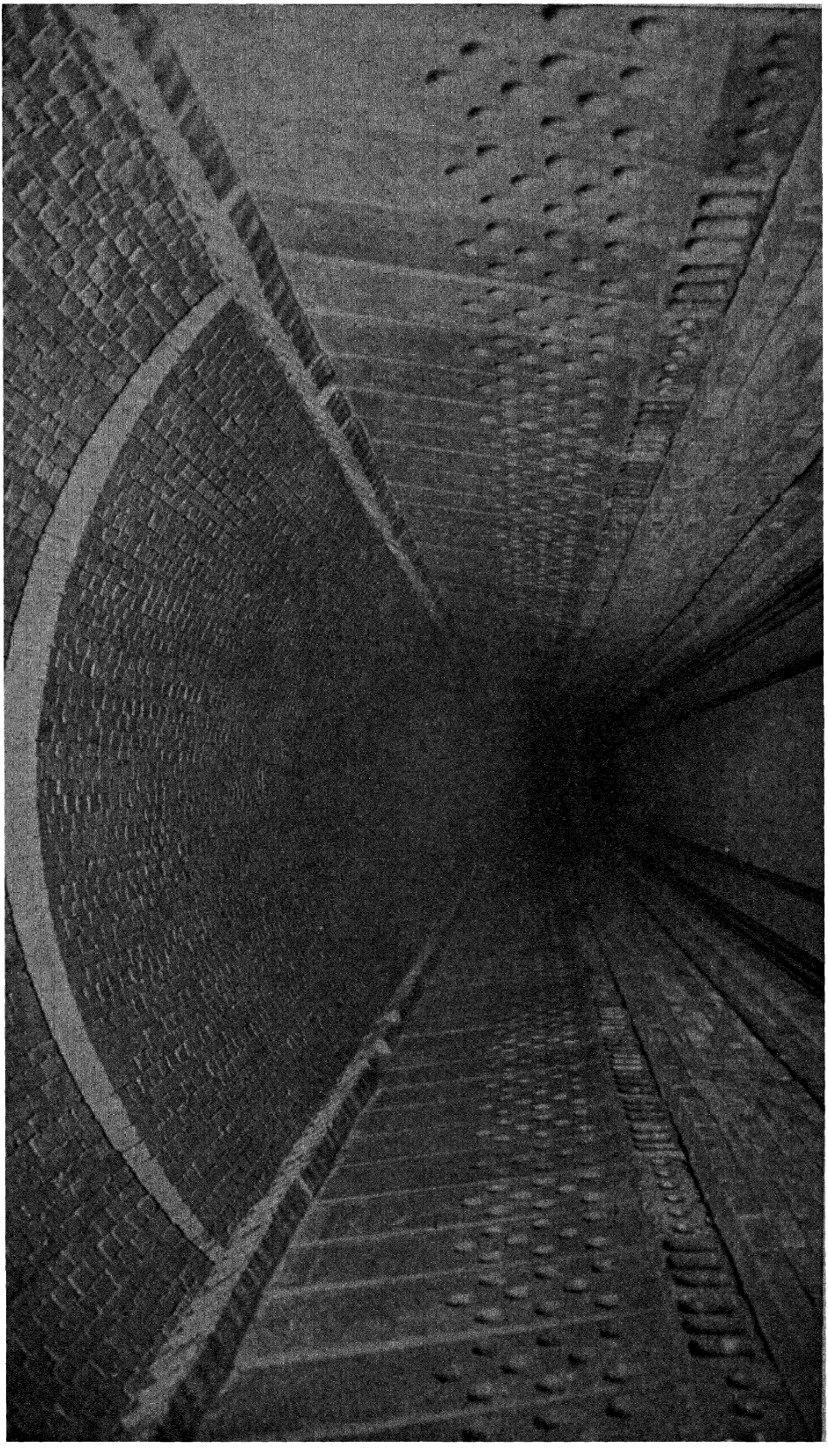


FIG. 8-III.—Interior of a Dressler tunnel kiln.

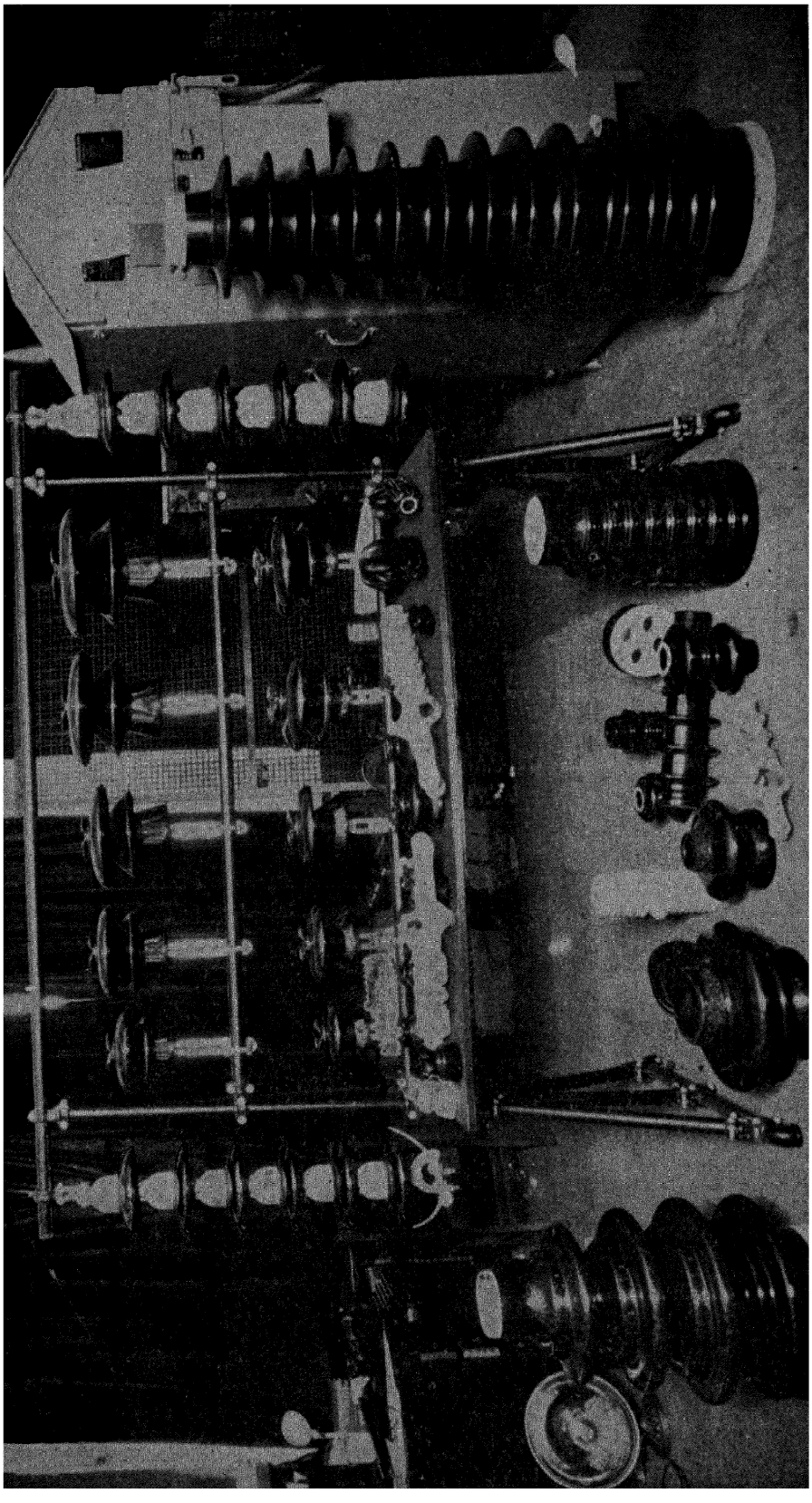


FIG. 9-III.—Electrical porcelain insulators.

used. Glazing is the process of melting a glass on the surface of a clay body. The glass is first melted, then ground to a fine powder, and mixed with water to form a paintlike mixture. This liquid is sprayed or painted on the surface of the body or the body is dipped into the liquid. It is then dried and refired, allowing the glaze to melt and spread over the surface of the ware. When cool, this glaze forms a durable and waterproof finish for the product.

Enamels.—Enameling is the process of fusing a low-melting glass on some metal, usually cast iron or steel. It is in many respects a process similar to the glazing of whiteware but in this case the base is metallic. Common types of enameled ware are kitchen utensils, refrigerators, stoves, plumbing fixtures, and signs.

The enamel, as mentioned above, is a low-melting glass containing a large amount of boric oxide and fluorides which act as fluxes. It also contains a coloring oxide because all enamels are either white or colored. In the case of white and many of the light-colored enamels, the coloring material is mixed with the ground glass before it is applied to the metal. By this procedure the colorant is not dissolved in the glass but rather is mixed as a pigment. It is possible to produce practically any shade or color by a combination of dissolved or mixed colors. The manufacture of ceramic colors for glazes and enamels is one of the most interesting and highly technical processes in the industry. These colors are, of course, based entirely on chemistry.

It is easier to cause enamels to adhere to cast iron than to steel. This is due to the fact that cast iron contains small pores into which the liquid enamel flows and then hardens, when cooled. In the case of steel, however, the metal is so dense that the enamel cannot penetrate the surface to gain a hold. For this reason, it is necessary to resort to a chemical reaction between the enamel and the steel to effect a suitable bond. The chemical reagent used to promote this reaction is cobalt oxide, CoO. The role of CoO is not entirely clear but it has been explained by the following reaction:

$$CoO + Fe = Co + FeO$$

This reaction takes place at the surface between the molten enamel and the steel. The iron goes into solution replacing the

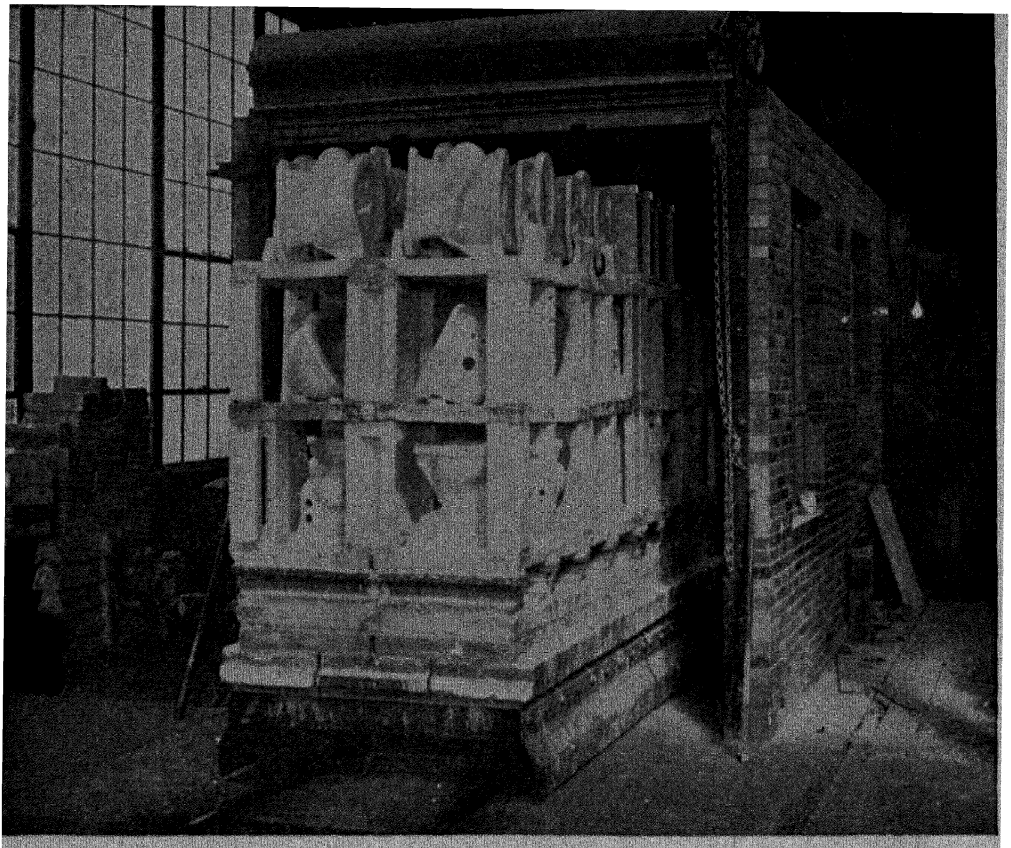


FIG. 10-III.—Vitreous sanitary ware entering tunnel kiln.

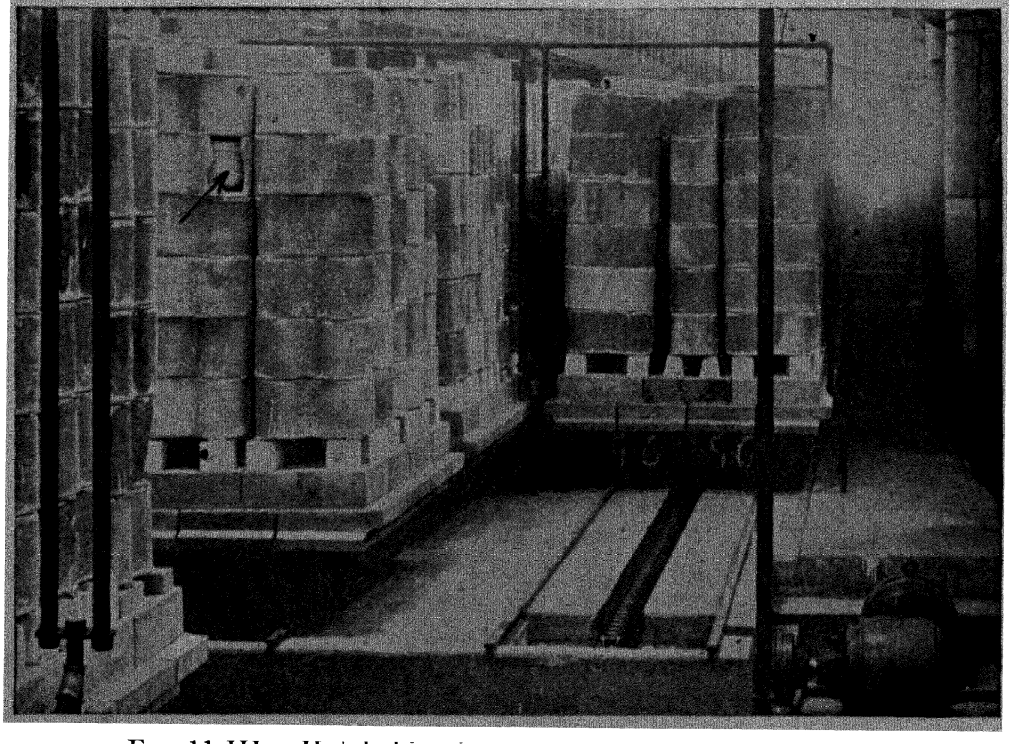


FIG. 11-III.—Hotel china in saggers ready for tunnel kiln.

cobalt which is then plated out on the steel. This condition provides a zone that contains an intimate mixture of both steel and enamel, the condition necessary for suitable adherence.

Enamels are applied to metals by spraying, dipping, or dusting. The first two methods are wet processes in which the enamel is ground and suspended in water. In the dusting process the ground enamel is merely sprinkled on the dry surface. It is necessary to have perfectly clean metal surfaces in order to achieve good results. The metal is usually cleaned by dipping it in hydrochloric acid or by sand blasting. The firing temperatures for enamels vary with the metal used and the composition of the enamel, but in general the temperature is between 1400 and 1700°F.

Since the steel enamels contain CoO, their color is a dark blue. When another color is desired, it is necessary to apply cover coats over this blue "ground coat." Most enameled ware contains three coats: a ground coat for adherence and two cover coats of the color desired.

FERROUS METALLURGY

Metallurgy is the science of extracting metals from their ores and adapting them to the uses for which they are desired. This subject has a wide scope in that it includes all the metals and all the processes applied to them, from the mining of the ore to the working and treating of the finished product. It is very convenient when studying this science to divide it into two parts: (1) the extraction of the metals from their ores, which deals principally with the chemical changes brought about in the material and extends up to the time when the metal is cast into ingot form; (2) the adaption of the metals to their intended service, which deals chiefly with physical changes that are brought about in the properties of the metals after the chemical composition has been fixed. For convenience then, we may call the first part "process" or "chemical metallurgy" and the second "physical metallurgy." This latter part contains such branches of this science as the heat-treatment which has to do with those changes brought about in metals by heating and cooling; metallography, a branch that deals with the study of internal structure; mechanical treatment which deals with the hot and cold working of metals; pyrometry which deals with

the measurement of temperatures; and physical testing which deals with the measurement of the physical properties.

In this brief section, we are concerned chiefly with the applications of the principles of physics and chemistry to iron and steel in each of the two branches of metallurgy. Our interest, however, must be confined, principally because this section is merely an illustration of how these previously studied principles may be applied to this very broad field. In view of this fact, we shall, therefore, confine our studies to those well-known refining methods, the blast furnace, the Bessemer, and the basic open hearth.

Production of Iron and Steel.—The modern methods for making iron alloys may be considered from a fundamental viewpoint as consisting of three successive chemical processes:

1. The reduction or removal of oxygen from the ores by heating in the presence of carbon. The iron produced from the reduction will absorb carbon in large amounts, along with other impurities, and the resultant product is pig iron.

2. The elimination of the carbon and the impurities from the pig iron by heating it with a controlled amount of oxygen. This gives as pure an iron as it is possible to attain.

3. The addition of carbon in desired amounts along with certain other elements, such as manganese, silicon, nickel, and chromium, to act, in some cases, as scavengers for the removal of any remaining oxygen and other impurities, and in other cases to act as alloying elements. In any case these additions are made to give and to improve the physical properties, such as strength and hardness, of the steel.

Process metallurgy in general involves the first process, the blast furnace. The second and third processes are in general combined according to the methods used in the making of steel, such as the Bessemer converter, open-hearth, and electric furnaces.

Blast Furnace—Pig Iron.—The modern blast furnace for the reduction of such ores as hematite, Fe_2O_3,[1] magnetite, Fe_3O_4, and limonite, $Fe_2O_3 \cdot H_2O$, is a tall, cylindrical stack, about 90 ft. high and 15 to 22 ft. in diameter, lined with firebrick. Figure 12-III, a diagrammatic section of a blast furnace, shows some of the essen-

[1] At the present time in the United States only hematite is of much commercial importance.

tial details. The materials used are ore, coke—which serves the double purpose of a fuel to furnish the heat necessary to melt the materials and bring about the heat-absorbing reactions, and as a reducing agent, for combining with the oxygen of the ore—and limestone, which acts to render certain impurities more easily fusible so that they will not clog the furnace, to combine chemi-

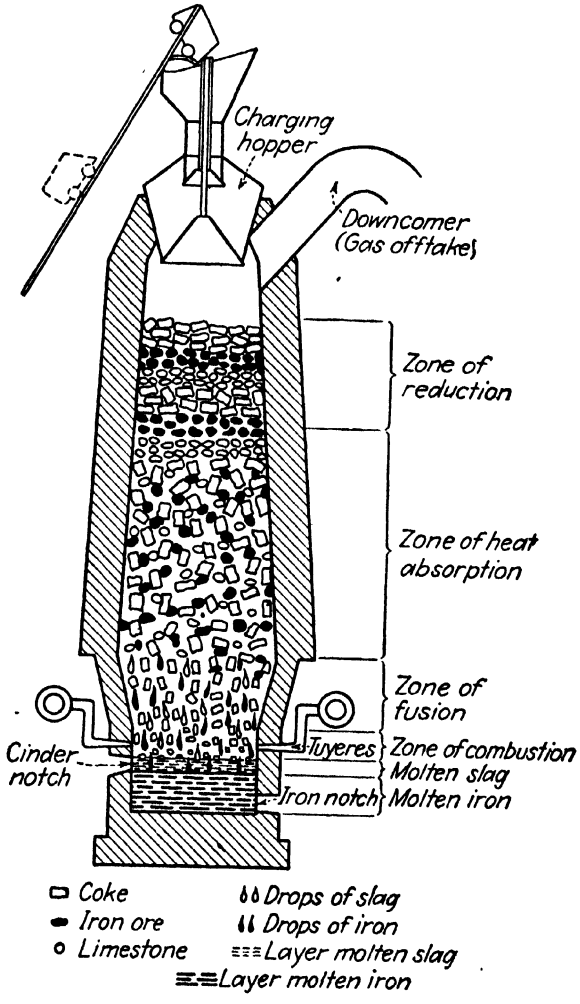


FIG. 12-III.—Diagrammatic section of a blast furnace.

cally and thus remove certain impurities from the metal, and to act as a covering to protect the molten metal from the furnace atmosphere. These materials are carried to the top of the furnace by cars on a "skip hoist" and dumped into the charging hopper at the top of the furnace. They are charged in successive layers into the top of the furnace and gradually work their way down as the smelting progresses.

A powerful blast of air, which has been preheated by passing through a series of stoves, is injected through the tuyères into the base of the charge for combination with the coke which produces a temperature of approximately 3000°F. The iron and flux at this level are melted and drip to the hearth. After a given interval of time, the pool of molten metal and slag is drained from the furnace. The slag is taken from the cinder notch and the iron from the iron notch. This "cast" of iron, according to its composition, is further converted by various refining operations into one or another of the following commercial products: cast iron, malleable iron, wrought iron, Bessemer steel, acid open-hearth steel, basic open-hearth steel, and electric steel.

Elements of Blast-furnace Chemistry.—The function of the blast furnace is to bring about a separation of iron, Fe, from its ore, Fe_2O_3. This separation is brought about through chemical reduction which involves the separation of a metal from its oxide and is accomplished by means of a reducing agent which is a material having a greater attraction for oxygen, under operating conditions, than has the metal to be reduced. This reducing agent must be in a form that is available on a huge scale. Carbon, C, in the form of coke is the only commercial agent available under these conditions.

The chemical reaction between coke and iron oxide is as follows:

$$\underset{\text{Iron oxide}}{Fe_2O_3} + \underset{\text{Coke}}{3C} \rightarrow \underset{\text{Iron}}{2Fe} + \underset{\text{Carbon monoxide}}{3CO\ (gas)} \qquad (1)$$

As carbon monoxide is also a powerful reducing agent with respect to Fe_2O_3, the following equation may also take place:

$$Fe_2O_3 + 3CO \rightarrow 2Fe + \underset{\text{Carbon dioxide}}{3CO_2\ (gas)} \qquad (2)$$

Under operating conditions reaction (2) is found to be more important. The temperature at which these reactions take place is quite important. If the reactions are carried out at comparatively low temperatures (1200 to 1500°F.) the resulting iron is a spongy solid mass. At higher temperatures (2800°F.+) the iron will be a liquid.

Slag Formation.—If the ore that was added to the furnace was entirely iron oxide, there would be relatively little difficulty in bringing about the reduction, but it is found that there is also the problem of eliminating such things as clay ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$)

and sand (SiO_2), which are also contained in the ore. These "gangue" materials are found to be lighter than iron and insoluble in it. Why not raise the temperature to a point where the iron is molten and float off the sand and clay? Certain difficulties, however, are encountered. The melting point of SiO_2 is 3000°F. (approximate) and clay is 3300°F. (approximate) which makes these impurities very difficult to handle at the temperatures commercially attainable in the blast furnace. However, it is found that by adding CaO in the form of limestone ($CaCO_3$) we are able to put the sand and clay into a more fusible and fluid form. A properly proportioned mixture of the three materials Al_2O_3, SiO_2, and CaO will have a melting point lower than the melting point of any one of the individual constituents, which ranges from 2400 to 2800°F. This purposely added limestone is called a *flux*.

The decomposition of limestone occurs at a temperature of about 1800°F., according to the following equation:

$$CaCO_3 + \text{heat} \rightarrow CaO + CO_2 \text{ (gas)} \qquad (3)$$

and the CaO then unites with the gangue materials to form a slag. The control of this slag by proper fluxing is a very important item in the metallurgical control of the furnace operations. It is essential that we keep the proper proportion of the acid oxides, principally SiO_2, to the basic oxides, CaO, MgO, and FeO so that we can control the physical and chemical aspects of the slag. The physical aspects, namely, the melting point and proper fluidity, are important as it is necessary to have slags become liquids of very low viscosity. (The resistance to flow is called viscosity, the opposite term being fluidity.) The chemical aspects are also important when we consider that slags are chemical reagents. Hence, any purification that may be carried out by these means is governed by their chemical composition. This latter control is illustrated by the reaction that eliminates the sulfur (S) present in the iron as the iron sulphide (FeS).

$$FeS + CaO + C \rightarrow CaS + CO + Fe \qquad (4)$$

Two factors are essential for the promotion of this reaction, namely, a very high temperature and a slag high in CaO. This reaction will, therefore, take place in the hottest part of the furnace, which part lies in the area marked the zone of fusion on

Fig. 12-III. The CaS formed in the reaction will be dissolved in a slag which is high in lime, CaO. Such a slag is termed a basic slag and would contain a percentage of basic oxides (CaO + MgO) greater than the acid oxides (SiO_2).

There are other reactions taking place within this fusion zone which are quite important from the viewpoint of the steelmaker but which, through the necessity for brevity, will be only noted here. The following reactions are all reducing:

$$SiO_2 + 2C = Si + 2CO$$
$$MnO_2 + 2C = Mn + 2CO$$
$$P_2O_5 + 5C = 2P + 5CO$$

It is quite apparent that all the reactions thus far considered occur at high temperatures and will, therefore, require a large amount of heat. It is necessary then to charge coke in amounts sufficient to reduce the Fe_2O_3 and produce the heat required. The production of this heat is brought about through the following reactions, which take place between the coke—which goes to the bottom of the furnace—and the incoming preheated air:

$$2C + O_2 \rightarrow 2CO + \text{heat (zone of combustion)} \qquad (5)$$

$$2C + 2O_2 \rightarrow 2CO_2 + \text{heat} \qquad (6)$$

The oxygen that unites with the carbon (coke) is supplied as air which contains 20 per cent of O and 80 per cent of N. The nitrogen being an inert gas does not enter into the chemistry of the blast furnace.

It must be noted that a portion of this carbon also dissolves directly in the melted iron. The amount that dissolves in the iron (about 3 to 4 per cent of the weight of the iron) is not desirable but it cannot be controlled by the blast-furnace operator as can many of the other reactions.

Summing up this operation from a raw material-product standpoint, we can show the average weight of each as follows:

Raw materials per ton of iron (approximate):

	Tons
Ore	2
Coke	1
Limestone	½
Air	4½

and the products per ton of pig iron produced:

Pig iron	1
Slag	½
Gas	6

It is interesting to note that this latter product, gas, which comes from the top of the furnace, is produced in such large quantities. In fact in a 500-ton furnace, there is produced some 80,000,000 cu. ft. per day. This "top gas," which has an approximate composition of

12 per cent CO_2
25 per cent CO
60 per cent N

will, when burned (the 25 per cent CO is the only combustible product), according to the following reaction

$$2CO + O_2 \rightarrow 2CO_2$$

produce sufficient heat to (1) preheat the "blast" to a temperature of from 1000 to 1500°F., (2) produce all the power needed in the blast-furnace plant, and (3) produce a great deal of power for outside consumption.

COMMERCIAL METHODS OF STEELMAKING

Bessemer Converter.—The steel-mill converter is somewhat like a large steel barrel about 10 ft. in diameter and 18 ft. in height, lined with refractory brick, with the top open and the bottom pierced with a number of holes or ports, called "tuyères" (Fig. 13-III). The usual capacity is about 20 tons of pig iron which will form a bath about 20 to 24 in. deep. In America the converter lining is always made of some high-grade siliceous refractory (SiO_2) and is, therefore, metallurgically acid. In use, the converter is tipped on its side, liquid iron from the blast furnace, cupola, or mixer is poured in, and then, with a strong blast of air blowing into the converter through the tuyères in the bottom, it is tipped back to its original upright position. The oxygen of the air, in passing through the liquid iron, burns the carbon, manganese, and silicon out of the liquid and results in a more nearly pure iron containing only small amounts of carbon, manganese, and silicon with some phosphorus and sulfur. The

amounts of the first three elements mentioned which are desired in the final composition are added to the molten metal, which is then cast into ingots to be rolled and forged into commercial products.

Chemistry of the Bessemer Operation.—In the study of blast-furnace chemistry we have seen where coke (C) may be burned (oxidized) at high temperatures to form either carbon monoxide gas, CO, or carbon dioxide gas, CO_2. It is found also that the carbon dissolved in the pig iron may be eliminated by the addition

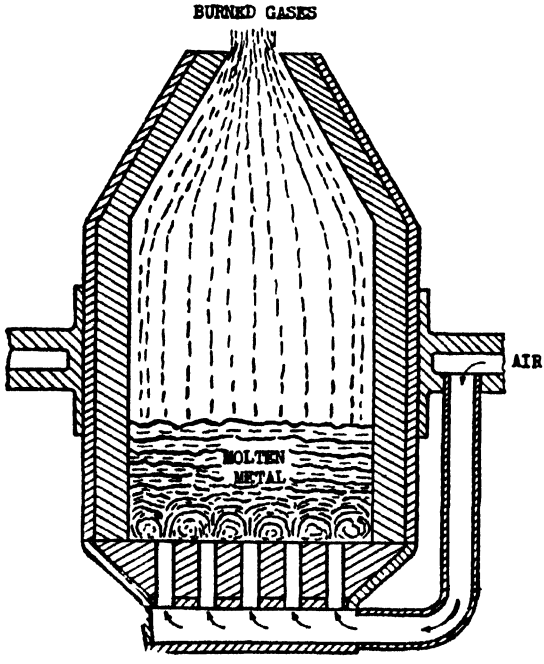


FIG. 13-III.—Diagrammatic section of a Bessemer converter.

of oxygen, O. This process of refinement by oxidation may be carried out in a number of different ways, two of which, Bessemer and open hearth, we shall describe briefly.

In the Bessemer operation, we make use of a raw material that is free, *i.e.*, air. The process then consists essentially of passing air (N + O) through the molten metal. The nitrogen (N) will pass through the iron without effect but the oxygen will attack it to form ferrous oxide (FeO), an oxide that is very stable and exists only in solution in metal or slag. The reaction is

$$O + Fe \rightarrow FeO + \text{heat} \qquad (1)$$

The FeO thus formed will, because of its solubility in the liquid

iron and because of the violent agitation of the bath brought about by the blast of air, evenly distribute itself and oxidize the carbon,

$$FeO + C \rightarrow Fe + CO \qquad (2)$$

the silicon (Si), and the manganese (Mn) of the pig iron.

$$2FeO + Si \rightarrow 2Fe + SiO_2 + \text{heat} \qquad (3)$$
$$FeO + Mn \rightarrow Fe + MnO + \text{heat} \qquad (4)$$

The carbon monoxide (CO) will pass off as a gas and will unite, at the nose of the converter, with the oxygen of the atmosphere and be converted to CO_2 as

$$2CO + O_2 = 2CO_2 + \text{heat}$$

This reaction is also a very high heat producer as we have previously observed, but unfortunately this takes place outside the converter and the heat is lost. It is through this flame, however, that the blower is able to judge the condition of his heat. The SiO_2 (acid oxide) will unite with the MnO and some FeO (both basic oxides) to form a complex silicate slag, $FeO \cdot MnO \cdot SiO_2$, similar to the one produced in the blast furnace.

The other product of the above reactions, heat, is very important since it is this heat which keeps the metal well above its melting point even though the air blown into the converter enters it at atmospheric temperature. The refining reactions can thus be carried to completion with the removal of carbon, silicon, and manganese. It so happens that reaction (3) is probably the most important reaction, (1) because of the fact that it is the chief source of heat and (2) because the formation of SiO_2 helps to protect the acid lining from corrosion by FeO and MnO (basic oxides). If there were not sufficient SiO_2 formed to satisfy chemically the basic oxides, they would immediately attack the acid lining and result in its rapid corrosion.

Under the conditions existing in the acid-lined Bessemer converter, no phosphorus or sulfur is removed from the metal. These two elements are very detrimental to steel for most purposes when they are present in excessive amounts and must therefore be kept low in Bessemer pig iron.

Following the removal or oxidation of all the silicon, manganese, and carbon, there remains dissolved in the metal some ferrous oxide, FeO. If this FeO were allowed to remain in the metal or

steel after solidification, the metal would be very brittle and would tend to crumble when subjected to such forming operations as would be necessary in producing a finished product. To prevent this effect, an operation is carried out which is known as *deoxidation.* This operation consists in adding to the melt, after the removal of the silicon, manganese, and carbon, the proper amount of other elements such as manganese, silicon, aluminum, or carbon which additions will react in two ways: (1) the added metals will react with the FeO and reduce it, *i.e.,* take away the oxygen from the iron, and (2) the other products of the reactions, namely, the oxides of the metals, have very little or no solubility in iron and being lighter than iron will separate from the metal, float upward, and join the slag.

The chemistry of this deoxidation is as follows:

$$2FeO + Si \rightarrow 2Fe + SiO_2$$
$$FeO + Mn \rightarrow Fe + MnO$$
$$3FeO + 2Al \rightarrow 3Fe + Al_2O_3$$

In Bessemer practice sufficient amounts of these deoxidizing materials are added to eliminate the FeO and to have some remaining to alloy with the steel so that the final composition will be within the desired range, which range is dictated by the commercial use of the metal.

THE BASIC OPEN HEARTH

It is rather apparent that the Bessemer operation has certain disadvantages that must be overcome. These disadvantages are overcome by processes that will

1. Remelt a partly cold or all cold charge to any extent necessary.
2. Dephosphorize or desulphurize the metal.
3. Control more closely the extent to which the melt is oxidized.
4. Permit a wider variation in the time limits so as to allow the possibility of control by chemical analysis of the melt.
5. Permit the production of expensive, highly controlled alloy steels.
6. Do all of the above on a tonnage basis.

The methods that are employed in the production of open-hearth and electric furnace steel have most successfully met these

demands. We shall in this discussion study the basic open-hearth only.

Construction.—The open-hearth furnace (Fig. 14-III) consists of an approximately rectangular chamber in which is located a shallow, elliptical hearth. The entire furnace is built of a refractory of suitable nature; the hearth upon which the steel is made is in this case a basic refractory known as magnesite, MgO. At one side of the furnace there are doors for charging, repairing, and operating. From the bottom and center of the hearth a tap hole and spout lead to the pouring pit opposite the charging doors. At either end of the hearth are ports which act as passageways for the fuel and air that pass to and from the checker

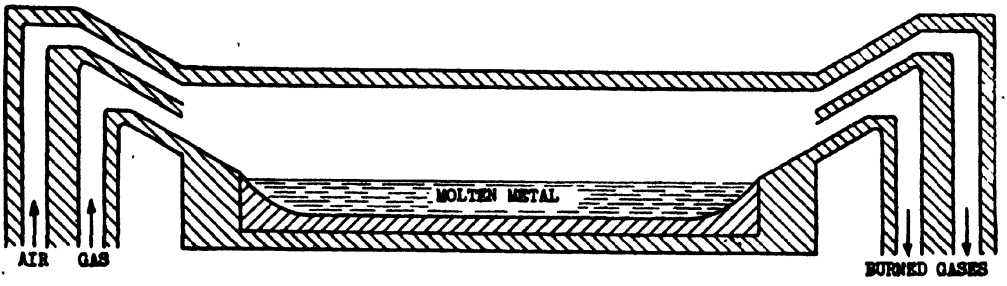


FIG. 14-III.—Diagrammatic section of an open-hearth furnace.

chambers. The checkers, which are open firebrick structures, lie beneath the furnace and are alternately heated by the hot furnace gases which pass through them and serve to preheat the incoming air and gas before they meet over the hearth. It is this regenerative system of preheating which makes it possible to attain the high temperatures desired (3000°F. +) in the hearth.

The Charge.—The largest tonnage of steel in this country is made by using a charge of cold pig iron, scrap, hot metal (molten pig iron), and limestone ($CaCO_3$) so this type of charge will be assumed in the discussion. The scrap, cold pig iron, and limestone are charged first, and after partial melting, the hot metal charge is added.

Melting the Charge.—During the period between the charging of the scrap and the hot metal addition, there are two chemical reactions taking place in the bath: (1) the oxidation of the melting scrap is due to the excess oxygen in the furnace atmosphere

$$O_2 + 2Fe \rightarrow FeO + \text{heat}$$

and (2) the calcination of part of the limestone

$$CaCO_3 \rightarrow CaO + CO_2$$

The FeO thus formed reacts with the silicon, manganese, and some of the carbon of the charge to form the usual oxides SiO_2, MnO, and the evolution of some CO from the reaction

$$FeO + C \rightarrow Fe + CO$$

along with some CO_2 from the limestone reaction. These oxides will react chemically to form a slag high in lime (CaO) and iron oxide (FeO).

With the addition of hot metal (pig iron), there is a very rapid chemical reaction between the silicon, manganese, and carbon of the fresh material and the iron oxide that has been formed during the early melting. During this so-called "boil period," which gets its name from the bubbling and foaming of the bath, the following reactions are occurring:

$$2FeO + Si \rightarrow 2Fe + SiO_2$$
$$FeO + Mn \rightarrow Fe + MnO$$
$$FeO + C \rightarrow Fe + CO$$

The slag volume is, therefore, further increased. The evolution of the CO gas during this period is the principal cause of the boiling appearance of the bath.

During this period another very important reaction takes place

$$2Fe_3P + 8FeO \rightarrow 3FeO \cdot P_2O_5 + 11Fe$$

in which the phosphorus of the metal present as the iron phosphide (Fe_3P) is oxidized and forms an iron phosphate which dissolves in the slag. This reaction takes place in the early part of the boil at the comparatively low temperatures during that time.

This early boil period will after a time become stronger until it becomes a violent bubbling. This intensified action is brought about through the very active calcination of the limestone on the furnace bottom which is now evolving CO_2 gas rapidly. This period in the boil is known as the "lime boil." The total boil period will last from 2 to 4 hr. The lime, CaO, as it is formed then rises through the bath into the slag where it then slowly

replaces the FeO until the FeO has been reduced to the desired value, around 10 per cent.

Several important effects are brought about through the rise of lime into the slag and the very violent mixing action caused by the rise of CO_2 gas. These effects are as follows:

1. The FeO in the iron phosphate is replaced by the lime, CaO, according to the reaction:

$$3CaO + 3FeO \cdot P_2O_5 = 3CaO \cdot P_2O_5 + 3FeO$$

This calcium phosphate dissolves in the slag and because of the fact that it is very stable (more difficult to break down than iron phosphate) gives greater assurance that the phosphorus will remain in the slag and not return to the metal.

2. The sulfur content is the least affected of the major elements in the steel. Some of the sulfur, however, is removed when the basicity of the slag is high (high CaO) according to the following reaction:

$$FeS + CaO + C \rightarrow CaS + Fe + CO$$

3. The iron oxide, FeO, is then free to react with the carbon remaining in the metal. This reaction is quite rapid because of the active boiling in the bath.

4. The slag becomes very basic, *i.e.*, the lime, CaO, content is quite high with respect to the total per cent of acid oxides present.

Working and Finishing the Heat.—When the boil has quieted, *i.e.*, when all the lime has risen to the slag and the FeO has been reduced to a low value, the carbon content of the metal through chemical analysis is still found to be quite high (around 1.00 per cent). It becomes necessary then to adjust the carbon content to the desired value, raise the temperature of the bath to the proper pouring temperature, and regulate the slag, *i.e.*, keep it highly basic, so that the phosphorus will have no chance to revert to the metal and so that the steel will reach the final degree of refinement desired with very little FeO left dissolved in it, and finally, deoxidize the metal.

The carbon content is adjusted by the familiar oxidation reaction:

$$FeO + \underset{\text{High carbon metal}}{[\times Fe + C]} \rightarrow \underset{\text{Pure iron}}{(Fe + \times Fe)} + \underset{\text{Gas}}{CO}$$

It is interesting to note that this reaction is the same one that occurred in the blast furnace, in which case the ore was reduced. It is evident, then, that a reaction may be either oxidizing or reducing, depending upon the conditions. The oxidation, in this case, is brought about by adding iron ore, Fe_2O_3, or mill scale, Fe_3O_4.

During the carbon and slag adjustment, the temperature is regulated but, since this process is oxidizing throughout, the steel inevitably absorbs some oxygen. The metal in this condition will not cast satisfactorily, nor will it—after solidification—have the desired soundness, toughness, ductility, etc., acceptable for most manufacturing processes. Since the deoxidation is the same as that discussed under the Bessemer practice, it will not be discussed here. This deoxidation, according to the practice, may be carried out in the furnace, in the ladle into which the steel is tapped from the furnace, in the mold into which the metal from the ladle is "teemed," or in some balanced proportion between these three.

In concluding this brief discussion of some of the features in the "process metallurgy" of steel, it might be interesting to make a brief comparison between the all-important factors of cost and quality of the three chief refining methods, namely, the open-hearth, Bessemer, and electric furnace. (This latter process was not discussed because of the need for brevity.)

Costs.—This factor will vary widely from one locality to another, but in general, it is found that the electric furnace method is the most expensive, principally because of the high power costs, the open-hearth second, with the Bessemer the cheapest.

Quality of Product.—Each process, it is found, can produce certain grades of steel which are better than those produced by any of the other processes, but in general the best quality engineering steels are produced in the electric furnace, then second the open-hearth, and the poorest grade is the Bessemer.

PETROLEUM AND NATURAL GAS

The principles of physics and chemistry are applied continuously in the present-day production of oil and gas. It is possible to classify certain engineering operations as being strictly physical, such as hoisting, use of pulleys and levers, or the action

of gears; likewise, it is possible to classify certain processes as being strictly chemical, such as the action of acid in the acid treatment of wells, chemical water softening, or acid refining. In many cases, however, engineering principles involve both physics and chemistry, a classification of science known as physical chemistry. Studies involving combustion, heat transfer, chemical action at various temperatures, and the flow of gases and liquids are only a few examples of those included in this branch of science.

The petroleum industry, although not strictly of a chemical nature, is very dependent upon a number of the previously discussed chemical processes. It is only necessary to mention the complete dependence of the petroleum and natural gas industries upon the metallurgical industries to point out this fact for without an ample supply of iron, steel, bronze, copper, and other metals for the fabrication of equipment, the production and refining of oil and gas would be practically impossible.

It is also true that the petroleum and natural gas industries are dependent upon the ceramic industry for bricks, refractories, glass, tile, and other products the manufacture of which involves chemical processes. All the mineral industries are dependent upon each other; one cannot survive without the others, and all the industries are dependent in one form or another upon the application of physics and chemistry.

Several examples may be chosen as demonstrations of the direct application of chemistry to the petroleum and natural gas industries.

Acid Treatment of Wells.—The use of hydrochloric acid, HCl, to treat oil wells to increase production has been in practice for more than forty years, but many difficulties were encountered in the use of raw acid because metallic equipment also was corroded or "eaten" by the action of the acid. In recent years certain organic materials have been found that inhibit or prevent acid action on metallic parts yet do not interfere with reactions in the oil-bearing formation.

"Acidizing" or the acid treatment of oil wells is useful to increase the permeability of limestone or high lime reservoirs. Successful treatment has resulted in an increase in the production of oil, reduction of the gas:oil ratio, increased oil:water ratio in flooding operations, and an increase of water in input water

flooding wells. A number of other claims are made for the process where limestone formations are involved.

Limestone is predominantly calcium carbonate, $CaCO_3$, or dolomite, $CaMg(CO_3)_2$. The latter contains varying amounts of magnesium which retards, to some extent, the reaction speed of hydrochloric acid upon calcium carbonate. Heated acid reacts uninhibited upon dolomitic formations. If the formation contains oxides of iron and aluminum, these also are soluble in acid. Sand, granite, chert, serpentine, clay, shale, gypsum, and anhydrite are insoluble in acid, thus a formation composed predominantly of these materials would not lend itself to successful acid treatment.

The question arises as to what takes place when hydrochloric acid reacts to dissolve limestone. The following equation is written to express this reaction:

$$\begin{array}{rcrcrcrcr} 2HCl & + & CaCO_3 & = & CaCl_2 & + & H_2O & + & CO_2 \\ 73 & + & 100 & = & 111 & + & 18 & + & 44 \end{array}$$

Two molecules of hydrogen chloride react with one molecule of calcium carbonate to yield one molecule of calcium chloride, one molecule of water, and one molecule of carbon dioxide. The numbers represent the reacting weights based on the molecular weights of the reacting compounds: 73 lb. (grams or ounces) of hydrogen chloride will react with 100 lb. (grams or ounces) of calcium carbonate, to produce 111 lb. (grams or ounces) of calcium chloride, 18 lb. (grams or ounces) of water, and 40 lb. (grams or ounces) of carbon dioxide.

The acid acts upon the relatively insoluble (in water) calcium carbonate to produce the water-soluble calcium chloride, water, and the gas, carbon dioxide. The dissolved limestone consequently is completely removed from the well in a water solution.

It is noted that the reaction is written for pure hydrogen chloride, a gas which is dissolved in water to form hydrochloric acid.[1] At ordinary temperatures and pressures, it is possible to dissolve about 15 cu. ft. of hydrogen chloride gas in 1 gal. of water resulting in a solution with a specific gravity of 1.183

[1] Dowell, Inc., The Chemistry of Acidizing, *The Acidizer*, No. 4, November, 1936.

(1.183 times heavier than an equal volume of pure water). By weight the solution will contain about 36 per cent dissolved gas and 64 per cent water.

Fifteen per cent acid is generally used in the treatment of wells. Such an acid has a specific gravity of 1.075. If 15 per cent acid is used, it is necessary to determine the weight of pure HCl available. Since water weighs 8.33 lb. per gal., a solution with a specific gravity of 1.075 will weigh 8.33×1.075 lb. per gal. If 2,000 gal. of 15 per cent acid are used, then $2{,}000 \times 0.15 \times 8.33 \times 1.075 = 2{,}686$ lb. of HCl available in 2,000 gal. of acid.

Referring to the equation:

$$2HCl + CaCO_3 = CaCl_2 + H_2O + CO_2$$
$$2{,}686 + 3{,}680^1 = 4{,}084 + 662 + 1{,}620$$

To find the volume represented in the reaction, we find that ordinary limestone in nature has a density of 170 lb. per cu. ft. Then, $3{,}680 \div 170 = 21.6$ cu. ft., the volume of limestone removed by 2,000 gal. of 15 per cent acid. This volume of limestone removed from the edges of the pores of a formation will substantially increase the permeability of the limestone and, consequently, free a greater volume of oil from the pore space in the reservoir rock.

Use is made also of hydrochloric acid in drilling. Tools often become stuck in a hole while drilling in limestone. This is due to rock particles falling down upon the tools and causing them to become wedged in the hole. By dissolving the limestone particles that cause the trouble, the tools are easily removed.

Water Softening.—Water treatment has come into importance in recent years in the oil industry because of the desirability of using water free from calcium and magnesium carbonates and sulfates in water-flooding programs and in boiler feed waters.

Rain waters fall to the earth as chemically pure water, neglecting the small amount of carbon dioxide, CO_2, traces of ammonia and dust, dissolved or suspended in it during its fall through the air. Rain water collects upon the ground, dissolving organic acids and other chemical impurities. Some portions of the water

[1] From the original and above equation, $\frac{73}{100} = \frac{2{,}686}{X}$; $X = 3{,}680$.

percolate through limestone, $CaCO_3$, or rocks containing magnesium carbonates, $MgCO_3$, iron oxides, Fe_2O_3, sodium and potassium salts and these salts being slightly water soluble are added to the dissolved chemicals in the water. Water containing dissolved calcium and magnesium salts is known as hard water. These salts react with soap to form a slime or curdy precipitate. No suds are possible until enough soap has been added to remove all the hardness (precipitate all the calcium and magnesium salts). Hard water caused by the presence of calcium bicarbonate, $Ca(HCO_3)_2$, the soluble form of calcium carbonate, becomes soft when heated by depositing calcium carbonate, $CaCO_3$, on the surface of the container. Such water is said to have "temporary hardness." The stony lining found in the tea kettle or on boiler pipes is attributed to this cause. The reaction is as follows:

$$\underset{\text{Heated}}{Ca(HCO_3)_2} \rightarrow \underset{\text{Insoluble}}{CaCO_2} + H_2O + \underset{\text{Gas}}{CO_2}$$

The dissolved calcium bicarbonate decomposes when heated, forming the insoluble calcium carbonate, water, and carbon dioxide.

The calcium and magnesium salts may be in the form of soluble chlorides or sulfates. Boiler and pipe corrosion is often caused by the presence of these salts. Heating does not cause precipitation of these injurious chemicals. Thus, the water is said to have permanent hardness.

Several methods are employed to soften water. One of these is through the use of a zeolite mineral, known under the trade name as Permutite. The approximate composition of the zeolite is $Na_2Al_2Si_2O_3$. For practical purposes the formula is usually written Na_2Z, the Z standing for the zeolite radical. Water containing calcium and magnesium chloride is caused to percolate through a filter bed of zeolite. The magnesium chloride reacts with the sodium zeolite to form the very soluble sodium chloride, NaCl, which passes off dissolved in the softened water and the insoluble calcium zeolite, which remains in the filter bed. In other words, the sodium zeolite is transformed into calcium zeolite. The reaction is as follows:

$$\underset{\substack{\text{Sodium zeolite}\\\text{(the filter)}}}{Na_2Z} + \underset{\substack{\text{Calcium chloride}\\\text{(in hard water)}}}{CaCl_2} \rightleftarrows \underset{\substack{\text{Calcium zeolite}\\\text{(remains in filter)}}}{CaZ} + \underset{\substack{\text{Sodium chloride}\\\text{(in softened water)}}}{NaCl}$$

After a time the filter bed becomes saturated with calcium so that it is necessary to treat it with a brine of common salt, NaCl, to regenerate the filter. The brine is forced slowly upward through the filter bed, reversing the above chemical reaction and removing the calcium from the filter in the sludge water.

A few pounds of lime water, $Ca(OH)_2$, and soda ash, Na_2CO_3, are added to every million gallons of industrial water in water-softening plants, to remove the objectionable calcium and magnesium salts. The reactions are as follows:

$$\underset{\text{Magnesium chloride}}{MgCl_2} + \underset{\text{Calcium hydroxide (lime water)}}{Ca(OH)_2} \rightarrow \underset{\text{Calcium chloride}}{CaCl_2} + \underset{\text{Magnesium hydroxide}}{Mg(OH)_2}$$

$$\underset{\text{Calcium chloride}}{CaCl_2} + \underset{\text{Sodium carbonate (soda ash)}}{Na_2CO_3} \rightarrow \underset{\text{Sodium chloride}}{2NaCl} + \underset{\text{Calcium carbonate}}{CaCO_3}$$

If hard water of either a permanent or temporary type is introduced into an oil sand, it is likely to tighten or cement the sand with precipitates of calcium, magnesium, and other chemicals. Hard water also increases the cost of repairs on pumps, pipe, and other metallic parts in contact with the water so that in many cases it has been found cheaper to soften water than to use it without softening and be forced to correct the damage that its use has caused.

CHAPTER IV

GENERAL PHYSICS

Physics is the science of the properties of matter and energy. It is primarily interested in what we can find out about bodies in the universe around us by the use of our physical senses, and what we can find out about the energy relations of bodies. This general definition of the field of physics does not sharply distinguish it from chemistry and, in fact, no definite dividing line can be drawn between the two sciences. In a general way, it may be stated that chemistry deals chiefly with questions regarding the composition and decomposition of substances. Even this division is not sharp and within the last twenty years a branch of both physics and chemistry, known as physical chemistry, has grown up dealing with problems of both general sciences which lie near the dividing line between them. It will be found that some of the material included in Chap. IV is included in many textbooks on physics and some of the subject matter is included in elementary chemistry texts.

The science of physics may be subdivided, for convenience only, into several parts: mechanics, wave motion, heat, electricity and magnetism, sound and light. We are directly concerned in this chapter with only a portion of mechanics, heat, and electricity. The student is referred to standard texts on physics if information is desired on other branches of the subject and he is urged to consult such texts in order to supplement the material given here.

THE PROPERTIES OF SOLIDS

We are now ready to discuss the general properties of solid bodies. By a solid body, we mean a body of matter which is sufficiently rigid to possess a shape of its own and which resists an attempt to change that shape. Some of the properties included here are also properties of liquids and gases. This situation will be indicated whenever it occurs.

Homogeneity.—A *homogeneous* body is one that has the same properties at all points, so that small spheres of equal radii, cut out of different parts of the body, would be identical in properties. Some crystals are nearly perfectly homogeneous, while many other solid substances are approximately homogeneous. Gases and liquids are also approximately homogeneous under ordinary conditions. It is obvious that the same substance may be homogeneous under one given set of conditions and not homogeneous (heterogeneous) under a different set of conditions.

Isotropy.—An *isotropic* body is one that has, at any point, the same properties in all directions. This means that if, at any point, a sphere were cut from the substance, there would be nothing in the properties of the sphere to indicate the original direction of any diameter. All liquids and gases as well as some solids are isotropic under ordinary conditions, although some crystals, wood, and cold-drawn metals are not isotropic.

Density.—The *density* of a body is its *mass per unit volume.* In metric units, the density is expressed in grams per cubic centimeter, while in English units, the density is expressed in pounds per cubic foot. Since the weight of 1 cc. of water at 4°C. is equal to 1 g., the density of water in metric units is unity. In the English system of measurement, 1 cu. ft. of water weighs 62.4 lb. Thus the density of water is 62.4 lb. per cu. ft. In order to remove this difficulty in units, the *specific gravity* is often used. The specific gravity of a body is the *ratio* of its density to that of some standard substance and is, therefore, independent of the units in which the density is expressed in calculating the specific gravity. The standard usually employed is water at 4°C. so that the density, when expressed in metric units, is numerically equal to the specific gravity. For example, 1 cc. of iron weighs 7.83 g.; its density is, therefore, 7.83 g. per cc. The specific gravity of iron is also 7.83 (an abstract number) because the density of water is also 1 g. per cc. and $7.83 \div 1 = 7.83$. The density of iron, in English units is, however, $7.83 \times 62.4 = 489.6$ lb. per cu. ft.

The specific gravity of a gas is referred to pure air as a standard base, instead of pure water. Air measured at 60°F. under 14.7 lb. pressure (atmospheric) divided into an equal volume of a gas, measured under the same standard conditions of temperature and pressure, equals the specific gravity of the gas.

The above definitions hold for both liquids and gases although, in general, solids have greater values of density than liquids and liquids greater than gases. If the body is homogeneous, the density is uniform. In case the body is not homogeneous, the *mean* or *average* density is obtained by dividing the total weight of the body by its total volume. This is known as the apparent density of the body.

Elasticity.—When the shape or volume of a solid is changed by the application of some force, there is, in most cases, a tendency to return to the original shape or volume when the force is removed. This tendency to recover from distortion is called *elasticity* and is a very important property since the usefulness of many bodies, such as springs and musical instruments, depends upon it.

The Strength of Solid Materials.—When a load or a force is applied to a piece of material, it naturally tends to lengthen or shorten or in some way to change its shape. This causes a reaction to be set up within the material to withstand the external force. These forces acting within a body and resisting external forces are called *stresses*. When the stresses within a body become great enough, the material may not be able to withstand them and it will either break or begin to deform. Such a change of shape due to stresses is called a *strain*, *rupture*, or *deformation*.

There are three kinds of simple stresses: *tension*, *compression*, and *shear*.

Tension stresses are those which oppose the pull out or stretch of the section. The cables on a crane are subjected to a tensile stress when a load is being lifted.

Compression stresses are those which oppose the push together or shortening of the section. The base of a heavy machine is in compression because the entire weight of the machine is bearing down and tending to crush the base.

Shear stresses are those which tend to oppose the sliding of one part of a section over another part. Punching holes in boiler plate or cutting any sheet metal is an example of shear. A particular type of shear stress, known as *torsion*, occurs when a rod is twisted. In this case, the stress is not uniform over the cross section of the bar, being zero at the axis and a maximum at the edge.

The most important *compound stress*—a stress made up of a combination of two or more simple stresses—is the combination of tension and compression known as *flexure.* A familiar example of flexure is a beam supported at both ends and loaded at the center, thus causing the beam to bend downward at its center. The upper surface of the beam is compressed and the bottom surface is stretched because the beam is no longer straight but forms an arc. The compressive stress is a maximum at the top of the beam and decreases to zero, at which point the stress changes to tension and increases to a maximum at the bottom surface of the beam.

The external forces that set up the stresses in a body are called *loads.* The load on a bridge, therefore, will be the weight of its own members plus the weight of anything passing over it. The most common forms of loads that act upon a material are the *steady* or *dead loads* and the *variable* or *live loads.* A dead load is one that always remains the same and creates the same strain in the piece it is acting upon. The weight of a building is the dead load in compression on the foundations. Wires stretched between poles have a dead load in tension. The rivets in a tank will have a dead load in shear if the pressure in the tank always remains the same. A variable load is one that is frequently changing or one that is alternately applied and removed. The load on a crane is a variable owing to the different weights being lifted. No material is as strong under variable loading as under a dead load.

Most materials of construction may be considered as perfectly elastic for small stresses. That is, when small stresses are set up in these bodies and small deformations occur, they will disappear when the stress is removed. In *elastic* bodies such as iron or steel the *deformation* resulting from small stresses will be in *direct proportion* to the stress that causes the deformation. This is known as *Hooke's law* and means that if a body is subjected to small stress and then this stress is doubled, any deformation that resulted from the first stress will be doubled under the doubled stress. If the stress is again doubled, then the deformation will again be doubled. If these stresses are continually made higher, a point will be reached where the material will break or the deformation will be greater than required by Hooke's law. And at this point it will also be

observed that, when the stress is removed, the body will *not* entirely go back to its original position. In other words, a part of the deformation has become permanent.

The point at which the stress ceases to be proportional to the deformation is called the *proportional limit.* The greatest stress that a material is capable of withstanding without permanent deformation upon complete release of the stress is known as the *elastic limit.* Owing to difficulties in differentiating between these points only one figure is commonly reported and is termed the *proportional elastic limit.*

An example will illustrate this point. A bar of metal 1 sq. in. in cross-sectional area, when subjected to a tensile stress, acted as follows: When the tension was 2,500 lb., the deformation, in this case the elongation or stretch, was found to be 0.01 per cent of its original length. When the tension was doubled to 5,000 lb., the elongation was found to be doubled to 0.02 per cent of the original length. For each additional tension of 2,500 lb. the elongation increased another 0.01 per cent, and this continued until the load in tension was 25,000 lb.

Up to this point, the elongation was obviously in proportion to the stress. When the next 2,500 lb. was added, however, making the total 27,500 lb. tension, it was found that the increase in elongation was not an additional 0.01 per cent, but rather almost 0.02 per cent. Hence, for this bar, the elastic limit was 25,000 lb. in tension. Values under this amount caused an elongation in proportion to the tension, while this relation did not hold for tensions over 25,000 lb. Also, if the bar is loaded with 25,000 lb. in tension or any value below that and the load then released, the bar will return to its original length. If loaded beyond 25,000 lb., however, the bar remains somewhat lengthened after release of the load.

If larger loads are continually applied after the elastic limit has been reached, the bar will stretch very rapidly. After the load on the above bar has reached a value of from 40,000 to 50,000 lb., it is found that the load will start to decrease, the specimen will continue to elongate and will ultimately break at a slightly smaller load. The *maximum* load is called the *ultimate tensile strength* of the material. The load where breaking occurs is called the *breaking strength* of the material.

Ceramic and other brittle materials exhibit no yield point but break suddenly when the elastic limit is exceeded.

In designing a part for a machine or for a structure, the directions and magnitudes of the forces acting on the piece are first determined. The piece is then made large enough so that it will withstand this total load without being subjected to a stress that will bring about a permanent deformation. Hence, the *allowable* stress will always be much less than the ultimate strength of the piece, and will be less than the elastic limit. If the stress on the piece is only one-half the ultimate strength, then it may be said that the piece is doubly safe, or if the stress is only one-third of the ultimate strength then the piece is three times safe. This relation of the actual stress in the piece to its ultimate strength is called the *factor of safety*. Hence, if a chain has an ultimate strength of 50,000 lb. and it is required to carry a maximum load of 10,000 lb., the unit is five times safe or its *factor of safety is 5*.

Since the factor of safety is based on the ultimate strength of the material, it follows that the ultimate strength and the factor of safety for all materials under all conditions must be known. These have been found by experiment and tested by long experience. Table 1-IV shows the ultimate strength of various

TABLE 1-IV.—ULTIMATE STRENGTH IN POUNDS PER SQUARE INCH

Material	Tension	Compression	Shear
Cast iron	18,000	85,000	9,000
Wrought iron	56,000	56,000	35,000
Steel castings	65,000	65,000	56,000
Soft steel	56,000	56,000	48,000
Machine steel	64,000	64,000	50,000
Structural steel	64,000	64,000	50,000
Wood	10,000	8,000	3,000
Brick	.....	3,000	
Stone	.....	6,000	

materials. When a value is omitted from the table, it means that the material is not used for that kind of stress. For example, brick and stone are used in compression only as in foundations, so that no values are given for tension and shear.

Table 2-IV shows the factors of safety that may be used for different classes of work. It will be noticed that materials that are comparatively uniform in structure, such as iron and steel, have a smaller factor of safety than uncertain materials.

The values in Table 2-IV are average ones and can be made larger or smaller depending upon the conditions. For example, if the load on a member is only slightly variable, then the factor of safety between the values for dead load and variable load may be chosen.

Stresses should always be given in pounds per square inch. Such stresses are called *unit stresses* and may be found by dividing the total stress by the square inches in the cross-sectional area. Hence, if the total stress on a bar is 30,000 lb. and it has a cross-sectional area of 2 sq. in., then the unit stress will be 30,000 divided by 2 or 15,000 p.s.i. Since the values in Table 1-IV were all expressed in pounds per square inch, they must always be multiplied by the area of the piece to find the ultimate strength of that piece. The following two examples will illustrate these points:

TABLE 2-IV.—FACTORS OF SAFETY

Material	Dead load	Variable load	Members subject to sudden shock
Cast iron	5	8	15
Wrought iron	4	6	10
Steel	2½	6	10
Timber	8	12	18
Brick and stone	15	30	

Problem: Find the ultimate strength and the allowable stress for a bar of structural steel 2½ by 1½ in., if it is to be used in tension and for a variable load.

Solution: The cross-sectional area of this bar will be $2\frac{1}{2} \times 1\frac{1}{2} = 3\frac{3}{4}$ sq. in. Table 1-IV shows that structural steel has an ultimate strength in tension of 64,000 p.s.i. Hence the ultimate strength of this bar will be

$$3\frac{3}{4} \times 64{,}000 = 240{,}000 \text{ lb.}$$

From Table 2-IV we find that the factor of safety for steel with a variable load is 6. Hence the allowable stress will be

$$240{,}000 \div 6 = 40{,}000 \text{ lb.} \qquad \textit{Ans.}$$

Problem: A wrought iron bar ½ in. in diameter is withstanding a load of 3,000 lb. in compression. Calculate the unit stress.

Solution: The cross-sectional area of a ½-in. bar will be

$$\frac{\pi(\frac{1}{2})^2}{4} = 0.196 \text{ sq. in.}$$

Hence,

$$3{,}000 \div 0.196 = 15{,}300 \text{ p.s.i.} \qquad \textit{Ans.}$$

The Crystalline State.—Solid substances are usually classified as being either crystalline or amorphous. In a crystalline solid, the atoms or molecules composing the substance are arranged in a definite manner. This definite arrangement gives the particles of the substance a certain regular shape, known as the crystalline form. The individual particles are known as crystals, if they occur in regular geometric shapes bounded by plane surfaces. A crystal may have only four faces or it may have a large number of faces, depending upon the chemical composition and the temperature and pressure under which crystallization of the element or compound took place. Many crystals are so perfectly formed that they appear to have been polished by a gem cutter while others are so distorted because of stresses placed upon them during formation that they can hardly be recognized as a crystal. In a solid mass the individual crystals cannot take their complete geometrical shape but must fill any available space within the "freezing" or crystallizing material. These are not crystals, strictly speaking, but are portions of crystals or crystal grains. Crystalline material is composed of many small intergrown crystal grains many of which are submicroscopic (smaller than can be seen with a microscope) in size.

Rock salt is a common example of a crystalline material, the crystals in many cases having the form of perfect cubes. Quartz crystals are in the form of hexagonal prisms with a six-sided pyramid on each end. Almost all solids are crystalline but in most cases the individual crystals are so small that they are not readily seen with the naked eye. Rocks, metals, snow, etc., are good examples of finely crystalline materials. The sizes of the crystals of a substance may vary widely, those of feldspar ranging from microscopic size up to several feet in length.

A discussion of the process of the formation and growth of crystals is beyond the scope of this chapter. However, it is

sufficient to say that in a crystal the atoms or molecules are held rigidly in place in their respective positions in the arrangement. This is the distinguishing feature of the solid state. In fluids (liquids and gases) the particles are free to move throughout the body of the substance. The fact that the particles are held firmly in place is the reason for the rigidity of solid bodies as compared with the fluidity of liquids and gases.

An amorphous substance is one that possesses no regular arrangement of its constituent atoms or molecules. In this respect an amorphous substance is like a liquid but those amorphous substances which are rigid are usually considered as solids. Glass is the most common amorphous material. Certain other extremely fine powders such as lampblack are considered amorphous because no crystals can be identified. Many ceramic bodies are solids that contain both crystalline and amorphous substances.

THE PROPERTIES OF FLUIDS

Liquids and gases are often classed together as *fluids* because they have several important properties in common. A fluid is distinguished from a solid by the absence of permanent resistance to forces tending to produce a change of shape of the body of the fluid. All fluids also have weight and inertia. By *inertia* is meant the property a body has of *tending* to persist in its state of motion or of rest, *i.e.*, a body in motion tends to stay in motion at constant velocity and, if at rest, to stay at rest unless acted upon by external influences. It is a further property of all fluids that, at any one point in the fluid, the pressure is the same in all directions. Also, the pressure of one part of a body of fluid cannot be increased without increasing the pressure in all parts of the fluid, *i.e.*, the pressure is equally transmitted in all directions (Pascal's principle). This principle is the basis of the hydraulic press.

Fluids also have the property of *viscosity* in common. Viscosity is defined as a transient or temporary resistance to deformation or change in shape. Although fluids offer no permanent resistance to change of shape and yield steadily to the smallest deforming force, the rate of yielding is different for different fluids. This rate of yielding is a measure of the viscosity of the fluid. For example, tar flows through an inclined tube much

more slowly than does water or alcohol, and the reason for this difference is that tar has a much greater viscosity. Gases have very low viscosities, so low, in fact, that quite sensitive measurements are necessary in determining this property. Viscosity is due to the internal friction of the molecules moving past one another when the fluid is in motion and, for any one fluid, is usually less the higher the temperature.

Viscosity is one of the most important physical characteristics of two classes of liquids: the molten silicates and the petroleum lubricants. The fact that each has a certain peculiar viscosity relationship makes them indispensable to our modern industrial civilization.

The manufacturing technique in all branches of the ceramic industry, with the exception of Portland cement, is based on the fact that molten silica is a very viscous liquid even above its melting point. In addition, silica confers this characteristic high viscosity on the liquids rich in silica and low in alkali content. At a sufficiently high temperature, these liquids are fluid enough to flow readily but, as the temperature is lowered, the viscosity increases very rapidly. When the freezing point of the liquid is reached, the viscosity is so great that crystallization is prevented and the liquid continues to cool without changing to the crystalline state. A liquid thus cooled below its freezing point is known as an *undercooled liquid.* As the temperature of this liquid is lowered, the viscosity continues to increase until the body of the liquid becomes rigid. The rigid liquid is then known technically as a *glass.* All glasses are the result of undercooling a viscous liquid. The silicate glasses are the basis of not only the commercial glass industry but also the clay products industries.

Metallurgical slags are another type of silicate liquid in which viscosity plays an important part. However, in the metallurgical operations a very fluid liquid is required rather than a viscous one. By adding such oxides as CaO, MgO, and FeO to SiO_2, a very fluid slag may be obtained, especially when the SiO_2 content is below 50 per cent. The general purpose of a slag is to protect the molten metal from oxidation and to purify it by dissolving the nonmetallic impurities carried into the metal from the ore. The rate of solution of these impurities depends upon the viscosity of the slag. The more viscous the slag the slower the rate of solution. In the open-hearth steel process it is

necessary to maintain accurate control of the slag viscosity. This is accomplished by close control of its chemical composition.

The moving parts of all machines are subject to friction. This friction lowers the efficiency of a machine and consumes a large amount of valuable power. Friction may be partly overcome by the use of a lubricant. The lubricant found to be most useful for machines is a viscous liquid that can get between the moving parts and form a liquid film. To be effective, this film must be tough enough to keep the metal parts separated at all times. The oils derived from petroleum have more nearly the correct viscosity range, for lubricants, than any other easily obtainable liquids. The lubrication of an internal-combustion engine is one of the most difficult problems. Here the oil must be able to stand high temperatures and still maintain its viscosity under very severe working conditions.

Liquids.—Liquids in general possess the property of *compressibility* to only a slight extent. Great pressures are necessary to decrease the volume of a liquid to even a small degree. For example, the fraction by which the volume of water is decreased by increasing the pressure 1 atm. (14.7 p.s.i.) is only 0.0000489.

We have already seen that the closeness with which the molecules of a liquid are packed together causes the forces of attraction between them to be quite great when compared to a gas at normal pressures where the molecules are so far apart that the forces of attraction are practically zero. In liquids, this attraction gives rise to a peculiar condition at the surface known as *surface tension.* If we consider a molecule of liquid water in the body of the liquid, it can be easily seen that it is attracted equally in all directions by molecules around it. If, on the other hand, we consider a molecule at the surface of the liquid, we can see that it will be drawn inward toward the body of the liquid because it is attracted by molecules below and at either side of it but is not attracted upward because of the lack of molecules above it. This unbalanced attraction at the surface leads to a compression of the surface layer of molecules, producing a film which exerts considerable resistance to attempts to break it. This is the explanation of why a needle or a razor blade, when carefully placed on the surface of water, will not sink although, if placed under the surface, will rapidly fall to the bottom. The compressed film at the surface has sufficient strength to

support its weight. A drop of water or liquid lead, in falling through air, assumes a spherical shape because of surface tension effects.

Gases.—The properties of gases were considered in Chap. I and will not be discussed further.

HEAT

Nature of Heat.—Early investigators in the field of physics thought that heat was a material substance composed of minute particles known as caloric. Ordinary matter had the power of absorbing these particles and, if the material were bent or subjected to frictional rubbing, the capacity to hold caloric was reduced and some of the particles were emitted. This was the explanation offered for the heat developed by friction and for the heat radiated from a hot body.

There are two very logical inconsistencies in the above explanation of heat: (1) if two pieces of material are rubbed together, the friction of rubbing will produce heat as long as the rubbing is continued and the supposed supply of caloric is never exhausted; (2) no change in weight takes place either during heating or cooling although it is obvious that there is a large change in the amount of heat in the body. If heat were a material substance as supposed neither of these observations would be possible.

After years of experimentation on the causes and the effects of heat, it was finally decided that *heat is a form of energy*. This energy, *kinetic energy*, is due to the motion of the particles (atoms or molecules) of a body. In a gas the particles are relatively far apart and move through space very rapidly. This is the basis of the kinetic-molecular hypothesis discussed in Chap. I. In the liquid state the particles are not so free to move as in the gaseous state and consequently the liquid is in a lower energy state than the gaseous. The crystalline state is a still lower energy state because the particles are not free to move about, their kinetic motion being confined to vibrations about a fixed point.

It is very important not to confuse *quantity of heat* and *temperature*. Temperature is the intensity or degree of heat while the quantity of heat is the actual amount of kinetic energy that a certain body contains. For example, if we have two blocks of the same substance, one exactly twice as large as the other but

both at the same temperature, the larger block will contain exactly twice as much energy as the smaller block because it contains twice as many molecules. Each molecule has the same vibration and therefore the same kinetic energy, at any one temperature. This consideration leads to a property of substances known as *specific heat.* It is defined as the amount of heat necessary to raise the temperature of one gram of the substance one degree centigrade. Specific heat is expressed in calories per gram per degree centigrade, one calorie being the amount of heat necessary to raise 1 g. of water from 14.5 to 15.5°C. Specific heat may also be expressed in English units as British thermal units per pound per degree Fahrenheit. The *British thermal unit,* usually called the B.t.u., is defined as the amount of heat necessary to raise one pound of water one degree Fahrenheit. In certain kinds of heat calculations it is convenient to change from the calorie to the B.t.u. (1 B.t.u. = 252 cal.). In plant practice, heat capacities of materials are usually expressed as B.t.u. while in scientific work the calorie is used. The specific heats or heat capacities of materials are of great importance in calculations involving the heating of furnaces and kilns, the drying of materials, the distillation of petroleum, and the firing and melting operations.

We have seen, in Chap. I, that every pure substance, when undergoing a change in state, either evolves or absorbs heat. This heat effect is caused by the change in the energy state of the atoms or molecules of the substance. For example, when ice melts, the water molecules which have been held fast in the ice crystals are able to move about in the fluid. This additional degree of freedom the molecules now possess is a result of their greater energy content. Thus, we see that it takes approximately 80 cal. of heat to change 1 g. of ice to 1 g. of liquid water. This amount of heat, known as the *heat of fusion,* is different for every substance.

When a substance is vaporized, a similar change takes place. In a liquid the molecules, although they can move around, are confined to the volume of the liquid. In the vapor state the molecules are separated by large distances and may move anywhere in free space. A gas has no boundary surface as do liquids and solids. In order to separate all the molecules to the condition of the gaseous state from that of a liquid, a relatively large

amount of energy in the form of heat is required. In the case of water, the heat of vaporization is 540 cal. per g.

Thermal Expansion.—Heat energy has a very important effect on the density of substances. At any one temperature the molecules of a substance have thermal vibrations, of a certain size, due to their energy content. When the heat energy of a body is increased, the thermal vibrations also increase. This increase in the vibrations of a molecule causes it to occupy a greater space while its weight remains the same. The temperature of a body is simply a measure of the amplitude of these thermal vibrations, *i.e.*, the greater the vibrations the higher the temperature and vice versa. Therefore, when the temperature of a body is increased, its density is decreased.

The force exerted by a body when it undergoes thermal expansion is very great. For example, if a piece of rock or glass is thrown into a fire, it will fly apart into many pieces even though it be a strong material. This breaking is due to the stresses set up when the hot parts of the body expand while the cooler portions remain the same size. Substances having a low thermal expansion are less liable to break on heating because the stresses set up are not so great as in materials having high expansion.

The expansion of a material with temperature is usually expressed as its *coefficient of expansion.* The coefficient of expansion is defined as the amount that a body expands per unit of length and per degree of temperature. The amount is actually very small and so the coefficient of expansion is a very small number, the coefficient for ordinary glass being about 0.000009 cm. per cm. of length, per °C. Although this expansion is small, the effects that it may produce are of great importance, especially in ceramic materials.

Transfer of Heat.—We are especially interested in the transfer of heat from one body to another because it is very important in connection with the firing operations used in industrial operations. The cost of fuel is a large item in the total manufacturing cost and inefficiency in the application of heat to the material increases its final cost. There are three methods of transferring heat: by convection, conduction, and radiation.

Convection is defined as the transfer of heat by moving matter. It occurs in liquids and gases and is due to the change in density produced by rise in temperature. A volume of liquid or gas that

varies in density in different parts is only in stable equilibrium when the densest portions are at the bottom and there is a regular decrease in density toward the top. Since (with the exception of water below 4°C.) liquids and gases expand on heating, thus diminishing in density, the heated portion will rise and there will be an upward convection current of hot fluid and a downward convection current of cold substance to take its place.

Heat is distributed through a body of water heated from the bottom in a teakettle almost entirely by convection currents in the liquid. The hot-water system of heating houses works on the same principle, as does the hot-air system of heating. The winds are largely convection effects, as are most of the ocean currents.

Conduction is defined as the flow of heat through and by means of matter unaccompanied by any motion of the matter. When a teakettle is put over a flame, heat reaches the water inside by conduction through the metal container. Heat always flows from a point at higher temperature to one at a lower temperature and never in the reverse direction. The greater the difference in temperature between two points, other conditions being equal, the more heat will flow per second. But with a given temperature difference, more heat can be transferred over a short distance than a long one. For instance, a kettle of water boils more quickly over a hot fire than a low one and it also boils quicker, the thinner the bottom of the kettle. If we designate the temperature difference between two points A and B as $t_A - t_B$ and the distance between the points as L, the average fall in temperature between A and B, called the *temperature gradient,* can be expressed as

$$\frac{t_A - t_B}{L}$$

From the above, we can arrive at the conclusion that the amount of heat conducted per second between two points is directly proportional to the temperature gradient. Other conditions being equal, a further factor is that the amount of heat conducted per second is directly proportional to the area through which it can flow.

Finally, the rate of flow of heat, other conditions being the same, depends greatly upon the material through which it must

flow. Substances can be roughly divided into "good conductors," which permit a large flow of heat under given conditions, such as metals, and "poor conductors," which permit only a small flow of heat under the same conditions, such as wood, glass, or asbestos. In general, metallic substances are good conductors and nonmetallic substances are poor conductors. The rate of heat flow through a body depends not only upon the substance composing it but upon its condition of subdivision and density. Thus, sawdust is a poorer conductor than wood and moist porous substances are better conductors than the same substances when dry because the water that fills the pores is a better conductor than air.

The characteristic of bodies that determines the rate of flow of heat through them is called their *thermal conductivity*. The quantity of heat flowing through a given body may be determined by the following equation:

$$Q = \frac{kA(t_2 - t_1)T}{L}$$

where Q = quantity of heat flowing through the section.
A = area of cross section.
L = thickness.
T = time during which heat flows.
t_2 = temperature of hot face of the section.
t_1 = temperature of the cold face of the section.
k = constant called the coefficient of thermal conductivity.

The coefficient of thermal conductivity is dependent upon the material under consideration and its temperature. The physical meaning of the coefficient may be seen by considering a special case in which it is assumed that $A = 1$, $T = 1$, $t_2 - t_1 = 1°$, $L = 1$, then $Q = k$. Hence k may be defined as the quantity of heat that will flow per unit of time per unit of area with uniform temperature gradient of one degree.

Since k varies with the temperature of the substance, the above equation is not true for any great temperature difference $(t_2 - t_1)$ unless k stands for the *mean* value of the coefficient between these limits and the temperature gradient is *uniform*. If heat must pass through several different materials in contact with each other, the equation becomes

$$H = \frac{T(t_2 - t_1)}{\frac{L_1}{k_1 A} + \frac{L_2}{k_2 A} + \frac{L_3}{k_3 A}}$$

where $t_2 - t_1$ is the total temperature drop over the three substances whose thicknesses are L_1, L_2, and L_3, of area A, and whose coefficients are k_1, k_2, and k_3. Table 3-IV gives the values of k in the English system, as in most practical engineering work involving heat flow this system is used. Attention should be called to the fact that because of variations in materials and methods for such determinations, there is considerable discrepancy between the coefficients given by different authorities. This table will give an idea of the great diversity in the values of conductivity for different substances, and among solids the great difference between the metals and nonmetals. The coefficient of thermal conductivity is expressed as B.t.u. per hour per square foot of cross-sectional area of path per degree Fahrenheit temperature difference per foot of length of path. This is usually abbreviated to B.t.u. per hr. per sq. ft. per °F. per ft. In metric

TABLE 3-IV.*—COEFFICIENT OF THERMAL CONDUCTIVITY
k = B.t.u. per ft. thickness per hr. per sq. ft. per °F.

Material	70°F.	212°F.	500°F.	1800°F.
Brass (70-30)	63	72.5		
Copper	227	220.0		
Iron (wrought)	35	35.0		
Iron (cast)	22–36			
Steel (0.1 per cent carbon)	26.1	25.8	25.0	
Alloy steel, austenitic chrome-nickel	.....	.....	10.4	
Calcium carbonate (scale)	0.5–1.5			
Porcelain	0.6			
Magnesia (85 per cent)	.....	0.04		
Asbestos (felt)	.....	0.12		
Cork	.....	0.03		
Portland cement	0.5			
Brick or mortar wall	0.4			
Concrete wall	.....	.....	0.505	0.70
Red brick	0.39	0.43	0.52	0.95
Firebrick and clay-bound silica	0.48	0.5	0.56	0.82
Sil-o-cel brick	0.125	.....	.....	0.125
Carborundum brick	.....	.....	5.6	6.4
Magnesite brick	.....	.....	3.5	2.3
Silica brick	.....	.....	0.7	1.15
Asbestos cement board (transite)	.....	0.23	.....	0.23

* NELSON, W. L., "Petroleum Refinery Engineering," 1936.

units, the coefficient is expressed as calories per second per square centimeter of cross-sectional area of path per degree centigrade temperature difference per centimeter of length of path; or cal. per sec. per sq. cm. per °C. per cm.

The thermal conductivity of liquids is generally about that of solids of low conductivity except for mercury, water, and some aqueous salt solutions, which are intermediate between the metallic and nonmetallic solid conductors. Gases have low thermal conductivities while those of small molecular weights have the highest conductivities. Convection and radiation in liquids and gases should not be confused with conduction. The conductivity of an alloy of two metals is not, in general, simply proportional to the relative amounts of the pure metals present but is often much below this calculated value. In nonisotropic solids, the conductivity is dependent upon the direction in which the heat flows, being different in different directions.

Example: Heat loss through a furnace wall. A furnace wall consists of 10 in. of firebrick, 5 in. of Sil-o-cel brick, 4 in. of red brick, and ¼ in. of transite board, respectively. The inside wall of the furnace is at 2000°F. and the outside wall at 200°F. Assume that the average temperature of the firebrick is 1800°F., the Sil-o-cel brick 1200°F., the red brick 250°F., and the transite 200°F. The conductivity coefficients[1] for these materials at approximately the average temperatures are given in Table 3-IV. The coefficients may be figured to the closest temperature given.

How much heat is lost through each square feet of surface in unit time?

$$Q = \frac{t_2 - t_1}{\frac{L_1}{k_1 A} + \frac{L_2}{k_2 A} + \frac{L_3}{k_3 A}}$$

$$= \frac{2{,}000 - 200}{\frac{10}{12 \times 0.82 \times 1} + \frac{5}{12 \times 0.125 \times 1} + \frac{4}{12 \times 0.43 \times 1} + \frac{0.25}{12 \times 0.23 \times 1}}$$

$$= \frac{1{,}800}{1.016 + 3.333 + 0.775 + 0.0906} = \frac{1{,}800}{5.215}$$

$$= 345 \text{ B.t.u. per sq. ft. per hr.}$$

[1] The coefficients are multiplied by 12 so that the coefficient, which is based on a foot of thickness, may be reduced to the terms of the problem's inches.

Radiation is the transfer of heat through space without the necessary presence of matter. While being transmitted in this way, energy is called *radiant* energy and not heat because heat has a definite relation to matter while radiant energy does not. The most striking difference between radiation and convection and conduction is the speed of transfer. The energy that reaches the earth from the sun is radiant energy and requires only about 8 min. to reach us, although the sun is 93,000,000 miles away. Radiant energy travels with the speed of light (186,000 miles per sec.). For our purpose here, we can consider radiant energy as a wave motion in space, analogous to water waves, which conveys the energy from point to point through space. The important factor in the determination of the energy in a beam of radiant energy is its *wave length* (the distance from crest to crest of the wave). The longer the wave length the greater the energy in the wave. Of the energy that reaches us from the sun, the major portion of the energy that can be converted into heat is in the form of waves of longer wave length than we can see, commonly known as infrared rays.

A hot body emits radiant energy in the form of waves. This process is known as *emission*. When these waves pass through matter and some are *absorbed*, the energy absorbed by the matter is converted into heat. If a hot body and a cooler one are placed in a vacuum at different temperatures, each body will radiate to the other, but the hotter will radiate more energy to the cooler one than it receives, thus lowering the temperature of the hotter body and raising the temperature of the cooler one. When equality of temperature is finally reached, the amount of energy radiated by each is equal, and they are in a state of equilibrium.

Some surfaces emit radiation better than others and the *emissivity* of a surface is the total radiant energy which the surface sends out per square centimeter per second, the radiation being caused by the heat of the surface. The emissivity of a surface increases with increase in temperature, *i.e.*, the hotter the body the more it radiates. The *absorbing power* of a surface is the ratio of the energy absorbed to the total energy striking it. The energy that is not absorbed is *reflected* from the surface in exactly the same manner that light is reflected by a mirror. The absorbing power of a body depends upon the substance itself, its surface condition, and the wave length of the radiation. A

highly polished surface is a much better reflector than a rough surface of the same substance. In general, it may be said that good absorbers of radiant energy are good radiators or *emitters.*

With regard to the application of heat transfer to industrial furnaces, it may be said that the heating of these furnaces is dependent mainly upon radiation of heat from the hot gases that are the products of combustion of the fuel, although convection currents in these gases play an important part. A large amount of the heat wasted in heating these furnaces is due to the conduction of heat through the furnace walls and roof.

Questions and Problems

1. What are the characteristics of a homogeneous body? Would you say that a steel ingot is homogeneous?

2. What is the characteristic of an isotropic body?

3. If the specific gravity of aluminum is 2.70, what is its density in both metric and English units?

4. What is the property of elasticity? Name one elastic and one inelastic substance.

5. Define stress and strain. What is the connection between them?

6. Describe and give illustrations of the simple stresses. What is flexure?

7. State Hooke's law. Define the elastic limit. How may the elastic limit of a material be measured?

8. What is the ultimate tensile strength of a material?

9. What is the relation of the allowable stress to the ultimate strength of a material? What determines the factor of safety of a material?

10. A structural steel member is to be designed so that it will support a dead load of 50,000 lb. in tension. What would be the cross-sectional dimensions of (*a*) a round and (*b*) a square piece suitable for this service? How much larger would these members have to be in order to support the same load, assuming it to be variable?

11. How do we classify solid substances? Give examples of each class. Is the atomic arrangement a specific property of a substance? Why?

12. What is viscosity? Give one example of its importance in ferrous metallurgy?

13. What is surface tension? Explain its cause.

14. What is the specific heat of a substance? How is it expressed in English and metric units?

15. If the specific heat of steel at ordinary temperatures is 0.107, how much heat (in calories) is required to raise 30 g. of the metal from 10 to 40°C.?

16. If the specific heat of a certain glass is 0.3 cal. per g. per °C., how many B.t.u. will be necessary to raise 110.3 tons of the glass from 72 to 2772°F.?

17. Define conduction, convection, and radiation. Give an example of each.

18. Find the amount of heat (in calories) conducted per hour along a bar of steel under the following conditions: temperature difference 30°C.; l = 10 cm.; diameter of bar = 2.5 cm.

19. An annealing furnace has the following dimensions and construction: The furnace wall is composed of 13.5 in. of firebrick, 4.5 in. of Sil-o-cel brick, and 4 in. of red brick. The temperature of the inside wall is at 1800°F. and the outside wall at 350°F. Assume an average temperature of the firebrick of 1600°F., of the Sil-o-cel brick 1000°F., and of the red brick 500°F.

What is the heat loss per day per square foot?

What is the cost per square foot per day using clean producer gas of 150 B.t.u. per cu. ft. at 5 cents per 1,000 cu. ft.?

20. Explain the relationship existing among emission, reflection, and absorption of radiant energy.

CHAPTER V

ELECTRICITY

The very large subject of electricity cannot be covered adequately in the space allowable in this volume. The following subject matter is given, in somewhat of an outline form, particularly for those who may be interested in this field of work. It should be supplemented by additional study in any good elementary physics text.

The Electrical Circuit.—The exact nature of an electric current is not known but the current is believed to be carried along the wire by the passage of electrons through the material. The flow of electricity in a circuit is similar in many respects to the flow of water in a hydraulic circuit. This likeness will become evident in the following discussion.

Rate of Flow—The Ampere.—The quantity of water that flows past a given point in a hydraulic system or the amount of water discharged through a pipe is expressed in gallons per second or cubic feet per minute. In an electric circuit the unit of quantity corresponding to the gallon or cubic foot is the *coulomb*, and that rate of flow which will cause one coulomb of electricity to be carried past a given point in an electric circuit in a second is called an *ampere*. Thus, a current of 10 amp. means a rate of flow of 10 coulombs per sec. Hence, the term ampere involves the time element and is, therefore, a unit of the same order as gallons per second or cubic feet per minute.

Pressure—The Volt.—In order to cause water to flow through a system of pipes, there must be a difference of head or level, or a pressure must be applied at some point in the system. There would be no flow whatever in a perfectly level system, unless pressure were applied somewhere. The pressure may be expressed in pounds per square foot or per square inch and may be supplied by a pump connected in the system or by a reservoir at a higher level.

In an electric circuit, in order to have current flow there must always be a difference in pressure or *potential* and the flow is

always from a higher to a lower potential just as water flows from a higher to a lower level. A battery or a generator is, therefore, the electrical equivalent of a pump and, when connected in an electric circuit, maintains a difference in potential between the different parts of the circuit. The unit of electrical pressure is the *volt*, a unit of the same order as the pound per square inch.

Resistance—The Ohm.—The amount of water that will flow through a system of pipes depends upon the size of the pipe and the resistance that the surface of the pipe offers to the flow. The quantity of electricity that a conductor will carry depends upon the size of the conductor and the material of which it is made. That property of a conductor which opposes the flow of current in the conductor is called the *resistance* of the conductor. The unit of electrical resistance is the *ohm* and its value is so chosen that a current of one ampere will flow through a circuit whose resistance is one ohm when a potential of one volt is applied to the terminals of the circuit. Resistance, therefore, tends to limit the flow of current in a circuit.

The Watt.—The watt is the unit of power. It is the rate of doing work, either useful or wasteful; it is useful in converting electricity into mechanical motion, in the heating to incandescence of the filament in the glow lamp, or in maintaining the arc of light (burning carbon) in the arc lamp. Work is wasteful in heating the conveying wires, the generator, or the motor.

Watts = volts × amperes; amperes × amperes × ohms; or volts × volts ÷ ohms.

$$\frac{\text{Volts} \times \text{amperes}}{746} = \frac{\text{amperes} \times \text{amperes} \times \text{ohms}}{746} = \frac{\text{volts} \times \text{volts}}{746 \times \text{ohms}} = \text{horsepower}$$

So, we find that the watt is $\frac{1}{746}$ of one electrical horsepower or 44.2359 ft.-lb. per min.

The units of electrical power, etc., are symbolized as follows:

Electromotive force or volt	E
Ampere or current	I
Resistance or ohm	R
Quantity or coulomb	Q
Energy	W
Power or watt	P

Electrical Symbols.—The language of electricity must of necessity be illustrated by symbols to shorten explanations. Figure 1-V illustrates symbols that will be used hereafter.

Measuring Instruments.—In order to find the value of current or voltage in an electrical circuit we must resort to instruments devised for that purpose.

Electrical currents are measured by an instrument known as the *ammeter* (originally ampere-meter, then ampmeter). These instruments measure the loss in voltage across a conductor of

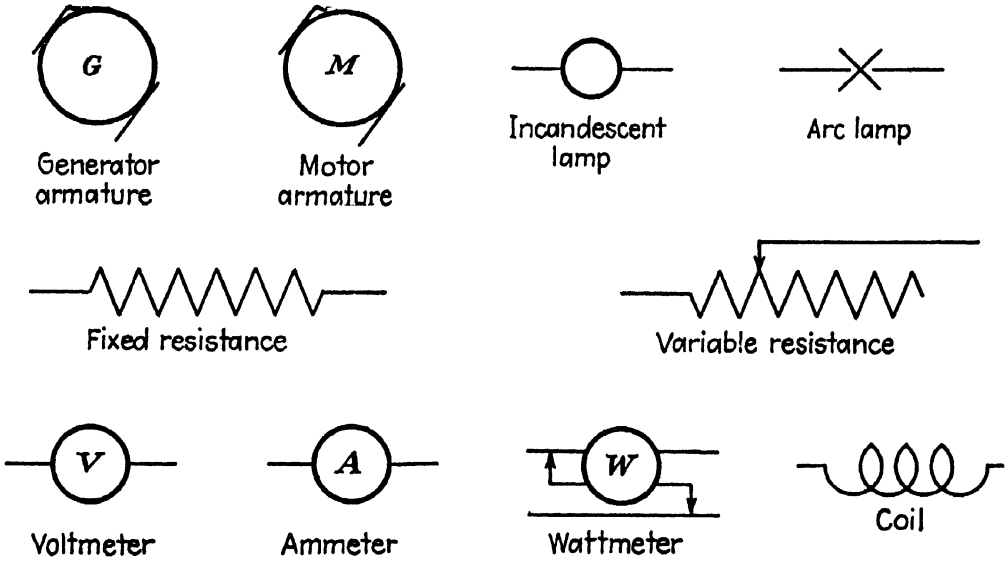


FIG. 1-V.

large capacity, called a *shunt*, which is inserted in the circuit in place of a length of conductor. Small ammeters have the shunt built in with the instrument so that connection to meter terminals is all that is necessary. Ammeters for high currents have the shunt separate from the meter which is connected by leads to the ends of the shunt.

The ammeter registers the current flowing in the circuit in which it is placed. In Fig. 2-V ammeter A_1 registers the current of the entire circuit (all the current flowing through the generator must pass through the ammeter) while ammeter A_2 registers only that current which flows through the arc lamp (the current splits and flows through the arc lamp and incandescent lamp circuits separately).

A current of higher amperage than that for which the ammeter is designed will destroy it. If there is reason to believe that a

circuit is carrying too high an amperage, a short-circuit switch should be inserted, as in Fig. 3-V, and kept closed. If the ammeter indicates a current flow when the switch is closed, there is too much current for the meter and a larger one should be used. If the ammeter shows no indication of current, it will be

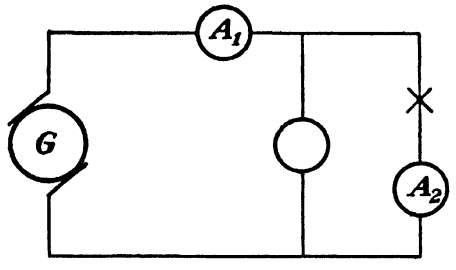


FIG. 2-V.

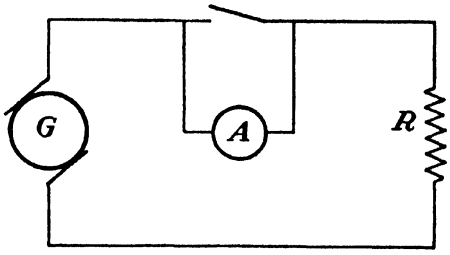


FIG. 3-V.

safe to open the switch and allow the current to flow through the meter.

Voltmeters are used to indicate the potential existing between any two points of an electrical circuit. The + terminal should be connected to the higher voltage conductor and the − terminal to the lower voltage conductor. Voltage is read by connecting *across* the circuit, not by placing the voltmeter in the circuit. Figure 4-V shows two ways of measuring voltage; V_1 registers the voltage across the terminals of the generator (also called the full circuit voltage) while V_2 measures the potential across the resistance R.

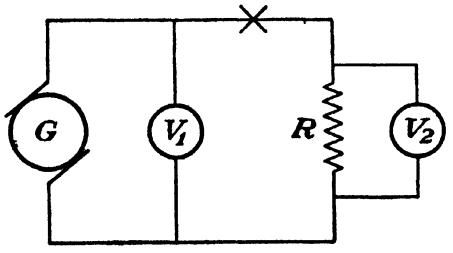


FIG. 4-V.

Ohm's Law.—The relation among voltage, current, and resistance is expressed by Ohm's law as follows:

The current in an electrical circuit is equal to the voltage across the circuit divided by the resistance of the circuit.

If we use I for current, E (electromotive force) for voltage, and R for resistance, Ohm's law is expressed symbolically as

$$I = \frac{E}{R}$$

This relation can be written in three different ways which the student should understand and remember for future use:

$$I = \frac{E}{R} \quad (1)$$

$$E = IR \quad (2)$$

$$R = \frac{E}{I} \quad (3)$$

Application of Ohm's Law.—In Fig. 4-V, if the pressure across the electric circuit as registered by V_1 is 60 volts and the resistance of the conductors, fixed resistance, and arc lamp totals 15 ohms, the current would be found as follows:

$$I = \frac{E}{R} = \frac{60}{15} = 4 \text{ amp.}$$

In the same figure, if the voltage drop across the fixed resistance is 52 volts as registered by V_2, what will be the value of this resistance?

If the loads that consume electricity, such as a resistance, arc lamp, or motor, form a part of a single circuit, as in this illustration, the current in the circuit must flow through each unit of load. Since this is the case, the current in R will be that found in the previous problem or will be 4 amp.

$$R = \frac{E}{I} = \frac{52}{4} = 13 \text{ ohms}$$

If a circuit has a resistance of 12 ohms and the current flowing equals 8 amp., what is the voltage or pressure of the circuit?

$$E = R \times I = 12 \times 8 = 96 \text{ volts}$$

The foregoing principles are stated as follows:

1. When Ohm's law is applied to the entire circuit, the current passing through the circuit is equal to the voltage across the entire circuit divided by the resistance of the entire circuit.

2. When Ohm's law is applied to any part of a circuit, the current in that part is equal to the voltage across that part (also known as voltage drop) divided by the resistance of that part only.

ELECTRICAL CIRCUITS

Types of Circuits.—A *series* circuit is one in which two or more pieces of apparatus are connected end to end or in tandem. In

Fig. 5-V the resistance and incandescent lamp are connected in series.

A *parallel* circuit is one in which two or more pieces of apparatus are so connected that there are as many paths for the current as there are pieces of apparatus using the current. Figure 6-V shows a resistance and an incandescent lamp connected in parallel

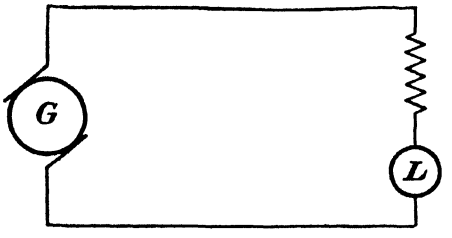


Fig. 5-V.

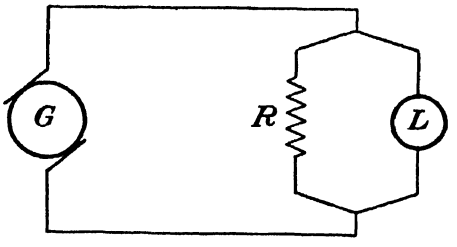


Fig. 6-V.

across an electrical circuit, thus making two paths for the current.

Although these two are the standard types of circuits there are many combinations in daily service. Figure 7-V shows a resistance R_1 and an incandescent lamp L in series with a parallel circuit consisting of R_2 for one path and R_3 for the other.

Series Circuit Relations.—The resistance of a series circuit equals the sum of the resistance of the separate parts composing

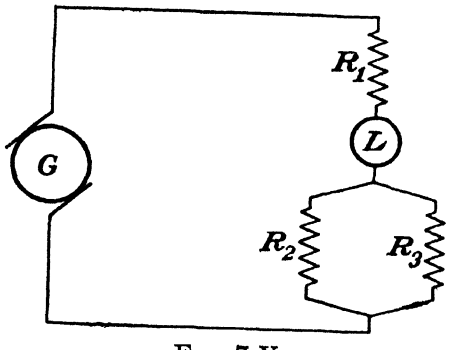


Fig. 7-V.

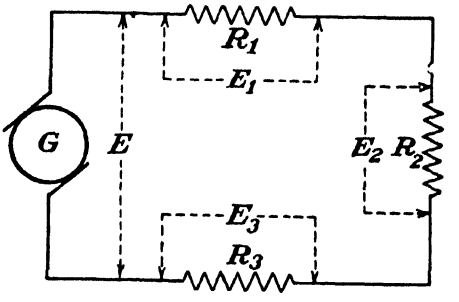


Fig. 8-V.

the circuit. In Fig. 8-V there are three resistances in series. The resistance of the circuit, not including that of the generator and the conductors, equals

$$R = R_1 + R_2 + R_3$$

The current flowing in the circuit must pass through each resistance since there is only one path. The current flowing, if

we know the voltage of the circuit, will be

$$I = \frac{E}{R} = \frac{E}{R_1 + R_2 + R_3}$$

The total voltage will be the sum of the voltage drops across the several resistances or will be

$$E = E_1 + E_2 + E_3$$

These relations hold for any number of resistances in series.

Problem: Four resistances of 2, 8, 5, and 9 ohms value, respectively, are connected in series across 120 volts. Find the total resistance, the value of the current in the circuit, and the voltage drop across each resistance.

Total resistance,

$$\begin{aligned} R &= R_1 + R_2 + R_3 + R_4 \\ &= 2 + 8 + 5 + 9 = 24 \text{ ohms} \end{aligned}$$

Circuit current,

$$I = \frac{E}{R} = \frac{120}{24} = 5 \text{ amp.}$$

Voltage drops:

$$\begin{aligned} E_1 &= R_1 \times I = 2 \times 5 = 10 \text{ volts} \\ E_2 &= R_2 \times I = 8 \times 5 = 40 \text{ volts} \\ E_3 &= R_3 \times I = 5 \times 5 = 25 \text{ volts} \\ E_4 &= R_4 \times I = 9 \times 5 = 45 \text{ volts} \\ E &= 10 + 40 + 25 + 45 = 120 \text{ volts} \end{aligned}$$

Problem: Two resistances, 50 and 15 ohms, respectively, are connected across a circuit. If the pressure drop across the 50-ohm resistance is 200 volts, find the current in the circuit, the drop across the 15-ohm resistance, and the voltage of the circuit.

$$I \text{ (for } R_1) = \frac{200}{50} = 4 \text{ amp. (also the current for the circuit)}$$

$$E \text{ (for } R_2) = R_2 \times I = 4 \times 15 = 60 \text{ volts}$$

$$E \text{ (for entire circuit)} = E_1 + E_2 = 200 + 60 = 260 \text{ volts}$$

There is always a voltage loss in generators and it should be added to circuit voltage to give the pressure of the entire circuit. This loss, however, cannot be measured by a voltmeter but is calculated from the difference in power input to the generator and power output to the electrical circuit. The voltage across the terminals of the generator is usually taken as the circuit voltage; it may also be given as terminal voltage. Line voltage would be that between the two lines or conductors and will vary depending on the point where the voltage is metered.

So far we have not considered the resistance of the conductors that carry the electric current. This resistance will be taken as so many ohms per foot of conductor and will be treated in the same manner as any other load or resistance. This is illustrated in the following case:

Problem: The resistance of a conductor is 0.1 ohm per 1,000 ft. A resistance of 100 ohms is placed across the line at a point 3,000 ft. from the generator which is carrying a terminal voltage of 230 volts. Find the loss in each conductor (called line drop) and the voltage (voltage across terminals) at the load.

Resistance of conductor (each leg) $= 3 \times 0.1 = 0.3$ ohms.

Total resistance of circuit $= 2(0.3) + 100 = 100.6$ ohms.

$$\text{Current of circuit} = \frac{230}{100.6} = 2.286 \text{ amp.}$$

Voltage loss in each conductor $= R \times I = 0.3 \times 2.286 = 0.6858$ volts.

Voltage drop across resistance $= R \times I = 100 \times 2.286 = 228.6$ volts.

Adding voltage losses: $2(0.6858) + 228.6 = 229.7756$ volts.

The difference between 230 and 229.7756 volts is lost in the calculation of voltages.

Parallel Circuit Relations.—When resistances are connected in parallel, the number of paths for current to flow is the same as the number of resistances. In such a case the voltage across the terminals of each resistance will be the same as the voltage across the combination. In Fig. 6-V the voltage across R is the same as across L, and in Fig. 7-V the voltage across R_2 is the same as across R_3.

E (across terminals of parallel circuit) $= E_1 = E_2 = E_3$, etc., in which E_1, E_2, and E_3 are the terminal voltages of R_1, R_2, and R_3, respectively.

The current in each branch of a parallel circuit is calculated by applying Ohm's law. The voltage across the terminals divided by the resistance of each leg will give the current for that leg. If we have three resistances, R_1, R_2, and R_3 in a parallel circuit, and the voltage across the terminals is E, the current in each leg will be

$$I_1 = \frac{E}{R_1} \qquad I_2 = \frac{E}{R_2} \qquad I_3 = \frac{E}{R_3}$$

The total current flowing in the circuit is the sum of the separate currents.

$$I = I_1 + I_2 + I_3$$

If we wish to find the resistance of a parallel circuit, we can best obtain this result by using the formula for total current and substituting values for E and R in it. For example,

$$I = \frac{E}{R}$$

or

$$\frac{E}{R} = \frac{E}{R_1} + \frac{E}{R_2} + \frac{E}{R_3} \text{ etc.}$$

Dividing by E,

$$\frac{1}{R} = \frac{1}{R_1} + \frac{1}{R_2} + \frac{1}{R_3} \text{ etc.}$$

Solving for R,

$$R = \frac{1}{\frac{1}{R_1} + \frac{1}{R_2} + \frac{1}{R_3}}$$

This formula is used for any number of resistances in parallel.

Problem: Three resistances of 8, 10, and 12 ohms, respectively, are connected in parallel across 120 volts. Find the current in each, the total current in the circuit, and the resistance of the combination.

$$I_1 = \frac{E}{R_1} = \frac{120}{8} = 15 \text{ amp.}$$

$$I_2 = \frac{E}{R_2} = \frac{120}{10} = 12 \text{ amp.}$$

$$I_3 = \frac{E}{R_3} = \frac{120}{12} = 10 \text{ amp.}$$

Total current,

$$I = 15 + 12 + 10 = 37 \text{ amp.}$$

Instead of solving for R, the resistance of the parallel circuit, by using the formula

$$R = \frac{1}{\frac{1}{R_1} + \frac{1}{R_2} + \frac{1}{R_3}}$$

we can solve by using the total voltage drop and the total current flowing, as follows:

$$R = \frac{E}{I} = \frac{120}{37} = 3.24+ \text{ ohms}$$

In order to show that we can get the same results by using the longer formula, let us substitute values as follows:

$$R = \frac{1}{\frac{1}{8} + \frac{1}{10} + \frac{1}{12}} = \frac{1}{\frac{37}{120}} = \frac{120}{37} = 3.24 \text{ amp.}$$

Problem: In Fig. 9-V, we have both series and parallel circuits and resistance of conductors in a problem. The resistance of each section of conductor is given as 0.1 ohm, a motor takes 20 amp., and a parallel circuit of three lamps takes 2 amp. in each leg. The problem is to find the voltage at the lamps and motor if the terminal voltage of the generator is 120 volts.

The conductors between the generator and points *A* and *B* will carry the entire current consumed by both the motor and the lamp bank. The total

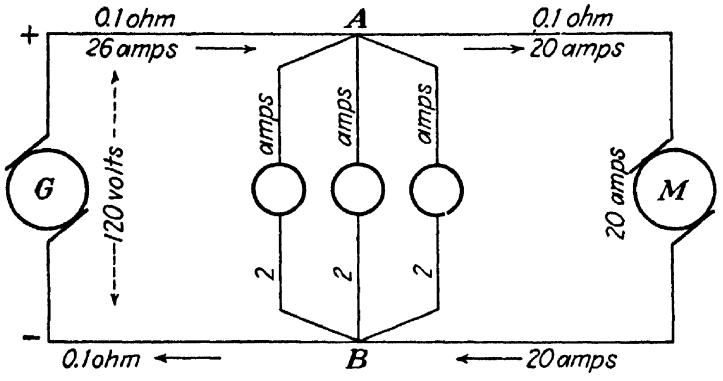


FIG. 9-V.

current of the lamp circuit will be

$$I \text{ (lamp bank)} = 2 + 2 + 2 = 6 \text{ amp.}$$

The motor and lamp bank are likewise in parallel so the current flowing between the generator and points *A* and *B* will be

$$I \text{ (circuit)} = 6 + 20 = 26 \text{ amp.}$$

Line loss between the generator and point *A* (and also between the generator and point *B*) will be

$$E = R \times I = 0.1 \times 26 = 2.6 \text{ volts}$$

Line voltage across *AB* will be

$$E \text{ (lamp bank)} = 120 - 2\ (2.6) = 114.8 \text{ volts}$$

Line loss between point *A* and the motor (also between point *B* and the motor) will be

$$E = R \times I = 0.1 \times 20 = 2.0 \text{ volts}$$

Line voltage at the motor terminals will be

$$E \text{ (motor)} = 114.8 - 2\ (2.0) = 110.8 \text{ volts}$$

If we reckoned line drop from the generator to the motor it would be

$$E = 2(2.6) + (2.0) = 9.2 \text{ volts}$$
$$E \text{ (motor)} = 120 - 9.2 = 110.8 \text{ volts}$$

Direct Current.—In the direct-current (d.c.) system the electric current always flows in the same direction. On this account it alone can be used for electrolytic processes, for storage batteries, etc. Owing to the present superiority of the d.c. motor for adjustable speed service, it is largely used in machine shops and similar installations.

Low voltages offer more safety with high cost for copper, while the high voltages are more dangerous with lower costs for copper. There are two great principles in the transmission of current. (1) The cost of copper wire varies inversely as the square of the voltage. Thus, supposing 2,000 lb. of copper are required to transmit a given quantity of power a certain distance with a given percentage of loss in the conductors at 50 volts, only 125 lb. will be necessary if the voltage is increased to 200 volts. $2{,}000 \times (\frac{1}{4})^2 = 125$ lb. (2) The heating effect of the current on the wires and the consequent loss of energy in transmission are determined by the amperes that are carried. Thus, if current is generated at 250 volts, and a load of 1,000 amp. is transmitted over a given line, the total energy will be expressed as 250 kilowatts (abbreviated form, kw.). If this same current of 1,000 amp. is generated at 500 volts, the energy will be 500 kw. The transmission wire for carrying 250 kw. at 250 volts could be used equally well for transmitting 500 kw. at 500 volts. Similarly, if the voltage were raised to eight times the amount, or 2,000 volts, then 2,000 kw. could be transmitted over the same wire, since the amperage is the same.

The limit of transmission of direct current at 250 volts may be taken at one mile, since beyond this point there is a large drop in voltage.

Alternating Current.—Alternating current is a current consisting of equal half waves in successively opposite directions; it flows back and forth in a circuit with as great a regularity as a piston moves to and fro in a cylinder of a steam engine, but with a much greater rapidity.

Alternating currents are represented by curved lines, as in Fig. 10-V, that indicate successive positive values of the current by loops, or half waves *A*-*B* above the horizontal line, and the negative values by loop *B*-*C* below the horizontal line. Distances along the horizontal line represent time, the points *A*, *B*, *C* represent instants when the current is zero; from *A* the current

increases in a positive direction to a maximum value, falls to zero at B, increases to a maximum negative value, and again decreases to zero at C, thus completing a cycle. These cycles are continually repeated, usually twenty-five to sixty or more times per second. The number of cycles per second is the *frequency* of the current and the time required for the current to complete a cycle is the *period*. An *alternation* is a half cycle and is represented by the curves between A and B, or between B and C.

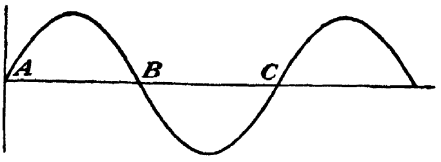


FIG. 10-V.

The alternating system is generally used where power is to be transmitted over considerable distances or in large amounts. The simplicity of the induction motor and its adaptability to most power requirements have also been responsible for the more extended use of the alternating system.

ELECTRICAL POWER CALCULATIONS

Work.—Work is done whenever resistance is overcome. Lifting a weight, pulling a car along a track, or turning a wheel against a roller bearing requires a certain amount of work in each case to overcome friction. The work accomplished in each case would be measured in *foot-pounds*. In lifting a weight of 50 lb. to a height of 5 ft. there is 5×50 or 250 ft.-lb. of work done. It matters not how long it takes to do a certain piece of work since time does not enter into the measurement of work.

Work done electrically is measured in *volt-coulombs*. That is, work is done when a quantity (coulomb) of electricity is sent through a circuit under a pressure of one or more volts.

Power.—If a weight of 50 lb. is lifted 5 ft. in 1 sec. by a certain person, and a second person requires 5 sec. to lift the same weight the same height, we say that the first person is more powerful or is capable of exerting greater power. In comparison, the first person is five times as powerful as the second since he required only one-fifth as much time to do the work.

Power is a comparison of ability to do work. Mechanical power is compared with a unit called a *horsepower* (hp.); this is the power that can do 33,000 ft.-lb. of work per minute or 550 ft.-lb. per sec. A machine rated at 5-hp. capacity is simply five times as powerful as a single horsepower machine.

In electrical measurements the unit of power is the *volt-coulomb per second.* Since the coulomb per second equals one ampere, the unit of power becomes the *volt-ampere* and one volt times one ampere equals one *watt.* Hence, in electrical terms:

$$\text{Power in watts} = \text{volts} \times \text{amperes}$$
$$P = E \times I$$

There is a definite relation between mechanical and electrical power. One horsepower (mechanical) equals 746 watts (electrical). This means that 550 ft.-lb. per sec. is equal to 746 watts (746 volt-coulombs per second).

As the watt is too small a unit to deal with in ordinary electrical calculations, a larger unit called the *kilowatt* which is equal to 1,000 watts is used. The horsepower is equal to 746/1,000 watts, or 0.746 kw.

Problem: A d.c. generator is supplying a power line with 250-volt power. A motor is taking 42 amp. of current. What power is the generator supplying?

$$P = E \times I = 250 \times 42 = 10{,}500 \text{ watts} = 10.5 \text{ kw.} = 14+ \text{ hp.}$$

Problem: A pump motor is taking 25 amp. and is located 500 ft. in from the trolley wire. The leads to the pump have a resistance of 1 ohm per 1,000 ft. If the voltage at the trolley wire is 220, find (*a*) the voltage at the motor, (*b*) the power consumed by the motor, and (*c*) the power lost in the pump leads.

(*a*) Resistance in two pump leads = 1.0 ohms.
Voltage drop between trolley wire and pump = $25 \times 1 = 25$ volts.
Voltage at pump motor = $220 - 25 = 195$ volts.

(*b*) Power consumed by motor = $E \times I = 195 \times 25 = 4{,}875$ watts = 4.875 kw.

(*c*) Power consumption at the trolley wire = $220 \times 25 = 5{,}500$ watts = 5.5 kw.
Power lost in pump leads = $5{,}500 - 4{,}875 = 625$ watts = 0.625 kw.

The power equation $P = E \times I$ can be written several ways. We know that $E = I \times R$ and substituting this value for E in the power equation we get

$$P = (I \times R) \times I = I^2R$$

We also have the form $I = E/R$. Substituting this value for I in the power equation we get

$$P = E \times \frac{E}{R} = \frac{E^2}{R}$$

Problem: A soldering iron has a resistance of 10 ohms and draws 4 amp. How much power does it use?

$$P = I^2R = (4)^2 \times 10 = 160 \text{ watts}$$

Problem: How much power will a 15-ohm resistance use when connected across 110 volts?

$$P = \frac{E^2}{R} = \frac{(110)^2}{15} = 806.67 \text{ watts}$$

Energy Kilowatt-hour.—If a customer is using a machine which consumes 5 kw. of power and which runs 8 hr. a day and 24 days of the month, and he pays $38.40 for the service, he is paying 4 cents per hour per kilowatt of energy

$$(5 \times 8 \times 24 = 960 \text{ kw.};\ 3{,}840 \div 960 = 4)$$

Energy is sold on the basis of kilowatt-hours (kw.-hr.) and one kilowatt-hour is equal to the energy supplied in one hour to a machine consuming power at the rate of one kilowatt. It will be readily seen that

$$\text{Kw.-hr.} = \text{kw.} \times \text{hours} = \frac{\text{volts} \times \text{amperes} \times \text{hours}}{1{,}000}$$

Problem: An electric flatiron takes 4 amp. at 110 volts for 5 hr. Find the kilowatt-hour used.

$$\text{Kw.-hr.} = \frac{110 \times 4 \times 5}{1{,}000} = 2.2$$

Problem: If electrical energy costs 5 cents per kilowatt-hour, what will it cost to operate the flatiron in the previous problem for one month of 24 days if it is used 8 hr. each day?

$$\text{Kw.-hr.} = \frac{110 \times 4 \times 8 \times 24}{1{,}000} = 76.8$$

$$\text{Cost of operation} = 5 \times 76.8 = \$3.84$$

TABLE 1-V.—EQUIVALENTS OF ELECTRICAL UNITS

1 kilowatt	= 1,000 watts
1 kilowatt	= 1.34 horsepower
1 kilowatt	= 44,236 ft.-lb. per min.
1 kilowatt	= 56.87 B.t.u. per min.
1 horsepower	= 746 watts
1 horsepower	= 33,000 ft.-lb. per min.
1 horsepower	= 42.41 B.t.u. per min.
1 B.t.u.	= 778 ft.-lb.
1 B.t.u.	= 0.2930 watt-hr.

Convenient Rules for Calculation.—To find the watts consumed in a given electrical circuit, such as a lamp, multiply the volts by the amperes.

To find the volts, divide the watts by the amperes.

To find the amperes, divide the watts by the volts.

To find the electrical horsepower required by a lamp, divide the watts of the lamp by 746.

To find the number of lamps that can be supplied by one electrical horsepower of energy, divide 746 by the watts of the lamp.

To find the electrical horsepower necessary, multiply the watts per lamp by the number of lamps and divide by 746.

To find the mechanical horsepower necessary to generate the required electrical horsepower, divide the latter by the efficiency of the generators.

To find the amperes of a given circuit of which the volts and the ohms resistance are known, divide the volts by the ohms.

To find the volts, when the amperes and the ohms are known, multiply the amperes by the ohms.

To find the resistance in ohms, when the volts and the amperes are known, divide the volts by the amperes.

Questions and Problems

1. Define the terms coulomb and ampere. How is electricity conducted along a wire?

2. Define the term volt. How may it be likened to the pressure in a hydraulic circuit?

3. State Ohm's law. Give an example of its operation.

4. Show by examples how a parallel and a series circuit are hooked up.

5. The filament of a 25-watt tungsten lamp has a resistance when cold of 40 ohms and a resistance of 400 ohms when burning on a 110-volt circuit. What will be the change in current from the closing of the switch until the lamp is at full brightness?

6. An ammeter of 100-amp. capacity was found to have a resistance of 0.0005 ohm. What current would flow if this instrument were by mistake connected across 120 volts?

7. If a motor armature has a resistance of 0.1 ohm, how much extra resistance will have to be connected in series with the armature to keep the current down to 100 amp. if it is connected to a 120-volt circuit?

8. The average resistance of a 25-watt 110-volt tungsten filament lamp when burning is 480 ohms. What is the total resistance of the lamps in a building where 12 of these lamps are used in parallel?

9. A voltmeter having a resistance of 10,000 ohms is connected so as to measure the drop across a 100-ohm resistance. An ammeter connected in the circuit reads 2 amp. What is the true current in the resistance?

10. Three resistances of 100, 120, and 150 ohms, respectively, are connected across a 100-volt circuit so that the current flows through the 120-ohm resistance, then divides and flows through the other resistances in parallel. What is the resistance of the combination and the current in each resistance?

CHAPTER VI

PYROMETRY

Pyrometry is defined as the science of temperature measurement. The temperature of a body may be qualitatively defined as that property of a body which determines the sensation of warmth or coldness received from it. More exactly, temperature is a measure of the kinetic energy of the molecules of a substance. It is important not to confuse temperature with heat. Heat is the total amount of energy available in a body because of the motion of its molecules. The sense organs of a person are entirely inadequate in measuring temperatures with accuracy. Until quite recent years the operators of heat-treating furnaces estimated temperatures entirely by eye, using a color-temperature relationship much as is given in Table 1-VI. Inspection of this

TABLE 1-VI.—COLOR SCALE FOR TEMPERATURES

	°C.	°F.
Lowest visible red	475	875
Lowest visible red to dark red	475–650	875–1200
Dark red to cherry red	650–750	1200–1375
Cherry red to bright cherry red	750–825	1375–1500
Bright cherry red to orange	825–900	1500–1650
Orange to yellow	900–1090	1650–2000
Yellow to light yellow	1090–1320	2000–2400
Light yellow to white	1320–1540	2400–2800
Dazzling white	1540 and over	2800 and over

table will show the rough degree of approximation attainable, the accuracy under a given set of conditions depending upon the knowledge and experience of the observer under those conditions and none others. Furthermore, it has been shown that accurate pyrometric equipment is always more economical in the long run than dependence upon the eye and judgment of the operator, and the increased demands of uniformity for all products have about

done away with personal judgment of temperatures. There are still a few places, however, where even present-day pyrometric equipment has been found inadequate for one reason or another.

Many properties of substances that are more or less accurately measurable are used in pyrometric instruments for determining temperatures. The important properties, together with examples of each, are given below:

1. Increase in dimensions. Mercury in glass thermometers.
2. Increase in pressure, if confined. The gas thermometer.
3. Change in electromotive force developed when in contact with some other substance. Thermocouples.
4. Change in electrical resistance. Resistance thermometers.
5. Increase in the amount of radiation from the surface of the body. Optical and total radiation pyrometers.
6. Change in color of the body. Temper colors observed in some heat-treating operations.
7. Change in state. Melting points of pure elements and compounds, and pyrometric cones.

From the scientific standpoint, thermoelectric, optical, and total radiation pyrometers are the most important types and will be dealt with in this chapter. The less important types will be considered in the following paragraphs. For details on all types of pyrometers and their use, the student is referred to the reading list at the end of this chapter as the subject is much too large to give more than a brief survey in a single chapter.

Mercury thermometers are widely used for measuring temperatures up to about 300°C. (572°F.) as the volumetric expansion of mercury is a very satisfactory means of measuring temperatures within this range. Being a liquid, the change in volume of a large volume of mercury in the bulb, induced by a slight temperature change, may be confined to the capillary stem and made readily apparent. The volume coefficient of expansion of mercury is large and fairly uniform while its low freezing point (−40°C.) and high boiling point (356°C.) make a fairly large working range. It is not compressible, its surface tension is such that it does not adhere to glass, and it is readily observable in the containing tube because of its high reflecting power for light.

There are several precautions to be observed in using mercury thermometers. The glass of which it is made must be aged

before construction because the glass shrinks slowly and, if not aged, the calibration is spoiled. In measuring temperature with it, the thermometer must be inserted as far as the mercury rises in the stem. Otherwise, the mercury in the stem will be at a lower temperature than that immersed in the substance and a low reading will result. The upper limit of the useful range of mercury thermometers can be increased to 650°C. (1202°F.) by using nitrogen under pressure above the mercury column to raise its boiling point and by making the bulb and stem of fused silica instead of glass. To lower the range below −40°C., toluol, alcohol, or pentane may be used instead of mercury. With pentane, the range may be lowered to −200°C. (−328°F.).

The constant-volume gas thermometer utilizes the change of pressure of hydrogen with change of temperature to measure temperatures. This gas, in the range in which it is used, obeys the ideal gas laws very closely and the small deviations can be corrected for. A column of mercury is used to record the change in pressure. This instrument has been selected as the fundamental and standard temperature-measuring device. It is rather cumbersome to operate, however, and the corrections are many and laborious to calculate if accurate results are to be obtained. It is mainly used as a laboratory tool for these reasons.

Electrical resistance thermometers are based upon the principle that the electrical resistance of pure metals increases fairly uniformly with temperature. The mathematical relationship between temperature and resistance is slightly complicated and will not be gone into here because of space limitations. The resistance coil is made of a sufficient length of fine platinum wire to give a resistance of 10 to 20 ohms at 0°C. It is wound on a mica grid and enclosed in and insulated from a metal tube. Lead wires connect the coil, which is immersed in the substance or furnace, the temperature of which it is desired to measure, to the electrical instrument that measures its resistance. The resistance thermometer is a valuable measuring instrument at temperatures up to 1000°C. and also down to very low temperatures. It has the disadvantages of requiring time to come to equilibrium at a given temperature. It is fairly fragile and extreme care must be taken to prevent the platinum from becoming contaminated with impurities. Nickel can be used instead of platinum at lower temperatures.

One type of fluid thermometer deserves mention because it is used to measure temperatures of fluids in pipe lines and other places equally suited to its uses. A bulb containing an incompressible liquid is placed in the pipe line and connected by a flexible tube to the instrument which is placed in a convenient spot. The instrument contains a flattened tube in the shape of a helical spring. The bulb, flexible tube, and coil are filled with the liquid and an increase in temperature at the bulb causes the coil to open out slightly. This, in turn, causes a pointer on a long rod to move through a large arc. The pointer can be equipped with a pen and be made to record the temperature on a circular chart revolved by clockwork. Another type of pyrometer is composed of strips of two metals fastened together which have widely different coefficients of expansion. When this composite strip is heated, the strip tends to straighten out if it is in the form of a spiral or to bend if it is in a straight section. This movement may be used to cause an indicating arm to move through an arc. Neither of these types can be used above 1000°F.

THERMOELECTRIC PYROMETERS

A simple thermoelectric pyrometer consists of a thermocouple, an indicator of some type, and suitable lead wires connecting the two. A thermocouple is made by welding two dissimilar metal wires together at one end. If this junction is heated and the opposite ends of the wires are connected to an instrument that measures e.m.f. or potential, the value of the e.m.f. generated in the wires can be determined. If the cold ends of the thermocouple are kept at a constant and known temperature, there will be a uniform increase in e.m.f. as the temperature of the hot end of the couple is increased. It is then possible to calibrate this system and make a temperature-measuring device.

Thermocouples.—Figure 1-VI shows a simplified thermocouple installation in which the directions of the currents flowing are indicated at a time when the hot junction is being heated. The total e.m.f. generated in the system is the resultant of two thermoelectric effects: the Peltier and Thomson effects. Peltier discovered in 1834 that when two different metals are in contact, a difference in electrical potential exists between them and that this potential difference varies with the temperature of this

junction. This is a direct and continuous variation in some cases, while in others the e.m.f. may rise to a maximum and then decrease with further increase in temperature. Thomson discovered in 1854 that when a single length of metallic wire is heated at one end a difference of potential exists between the ends. In some cases, the hot end may be at a higher potential than the cold end, while in other cases the reverse may be true.

For thermocouples to be capable of producing over-all potential differences large enough to measure with accuracy, the various e.m.fs. indicated above must not be opposed to each other. In other words, the currents that may flow as a result of these e.m.fs. must all flow in the same direction. In order to accomplish this it is necessary to choose two wires whose Thomson

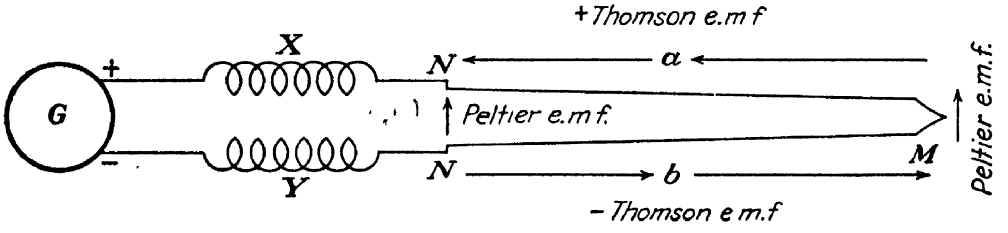


FIG. 1-VI.—Simplified sketch of a thermoelectric pyrometer. (*From Wood and Cork, "Pyrometry."*)

effects are in opposite directions and vary directly and uniformly with temperature. Furthermore, the Peltier e.m.f. at the hot junction of the couple must be such that the wire showing the negative Thomson e.m.f. must be the positive element as far as the Peltier e.m.f. is concerned, while this effect must also vary directly and as uniformly as possible with temperature. With these conditions fulfilled, as shown in Fig. 1-VI, all the e.m.fs. are additive, and their sum will vary directly and continuously with temperatures, provided the cold junctions of the wires are held at a constant temperature. *M* is the hot junction of the couple, *N* the cold junction, *a* and *b* the positive and negative wires, respectively, *G* the galvanometer or indicating instrument, and *X* and *Y* the lead wires.

It should always be kept in mind that the e.m.f. generated by a thermocouple is a function of the difference in temperature between the hot and cold junctions of the couple—between *M* and *N* of Fig. 1-VI. For the values indicated by the galvanometer to mean anything, the two wires at *N* must be at the same

temperature, and this temperature must be a known and constant value. The reason for this is that the lead wires are usually of copper and at the points N they are connected to the thermocouple wires, the connection being made through the galvanometer. This situation results in a small Peltier effect in the reverse direction at N. If these points are allowed to fluctuate in temperature, this Peltier e.m.f. will vary and will cause errors in the total e.m.f. produced as a result of the temperature of the hot junction. Also, any variation in cold-junction temperature will cause a variation in the Thomson e.m.fs. generated in the two thermocouple wires, further affecting the total e.m.f. generated. On the other hand, the temperatures of the thermocouple and lead wires may vary widely along their lengths without affecting the over-all e.m.f. generated if the hot- and cold-junction temperatures remain constant. The reason for this is that any counter e.m.fs. produced by this change in temperature balance each other and are inactive. The only exception to this is when the lengths of wires are not homogeneous in themselves. For example, if the hot junction of a couple is at 1800°F. and the cold junction is at 32°F., heating one or both thermocouple wires at a spot between these junctions to 2000°F. will not affect the value of e.m.f. developed by the thermocouple if no current is flowing through it.

The e.m.f. developed by thermocouples is always very small, being measured in thousandths of volts (millivolts, mv.) rather than in volts. There is a considerable variation in different types of couples in regard to the e.m.f. produced, the maximum range being from zero to about 75 mv. Figure 2-VI shows the temperature-e.m.f. relation of metals and alloys commonly used in making thermocouples with platinum as the other wire in each case (cold junction at 0°C.). In this method of representation, platinum is at the base line (zero millivolts), those positive to platinum are above the base line, and those negative to platinum are below the base line. The e.m.f. of a combination of any two of these materials can be found at a given temperature by measuring the vertical distance between the curves.

Besides the consideration of e.m.f. of thermocouples and the necessity for its direct and continuous variation with temperature, there are several other properties required of thermocouples in order to make them useful. Of these, resistance to corrosion

and oxidation is of obvious importance. Thermocouples that deteriorate rapidly under service conditions have too short a life and too high a replacement cost for industrial use. A thermocouple that develops a relatively large e.m.f. in the temperature range in which it is desired to use it is more desirable than one that develops a very small e.m.f., because instruments that will accurately measure small values of e.m.f. are necessarily delicate and not suited to many industrial purposes. Thermocouples in industrial installations should develop the same value of e.m.f.

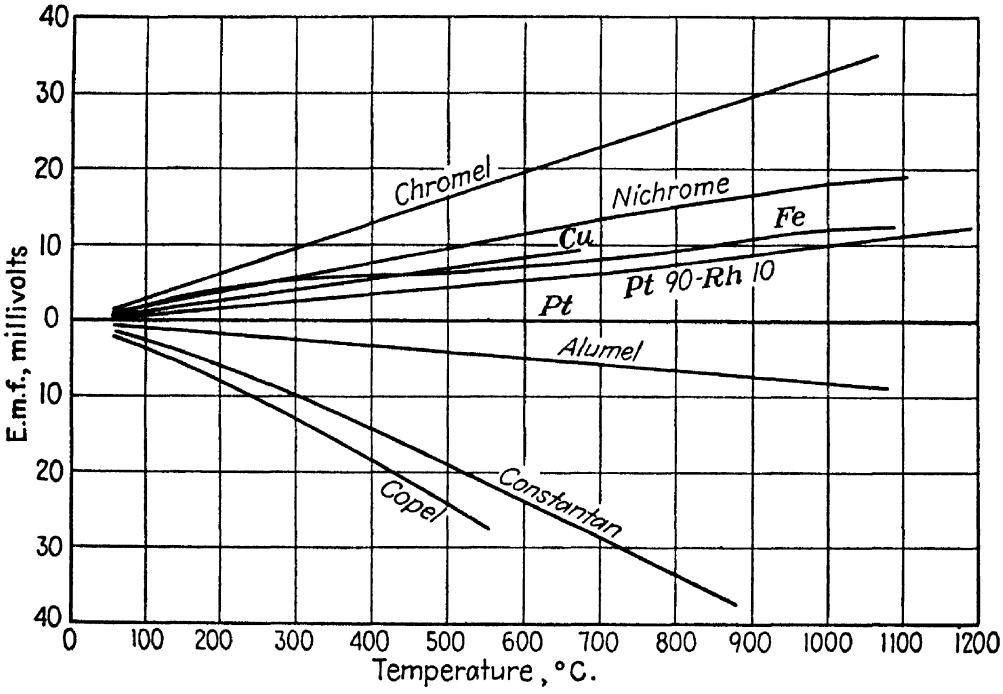


FIG. 2-VI.—Thermoelectric power of thermocouple elements (against Pt). (*From Wood and Cork, "Pyrometry."*)

at a given temperature over relatively long periods of time. This means that the metals making up the wires must be stable at operating temperatures and must either be kept free from contamination with substances that might change their composition by suitable protection or be relatively impervious to such attack. Any inhomogeneity of composition caused by contamination will change the e.m.f.-temperature relation of the thermocouple. Finally, the question of reproducibility of thermocouples is of great importance in industrial installations where large numbers are in use and several are connected to one instrument which is graduated to read directly in degrees. Under such conditions, couples made from the same coil of wire should possess the same

e.m.f.-temperature characteristics. Otherwise, a correction is required for each thermocouple, a situation that is not practicable when a great many are being used. The different types of thermocouples in commercial use will now be taken up.

The so-called "noble-metal couple" is composed of a positive wire of a 90 per cent platinum and 10 per cent rhodium alloy and a negative wire of pure platinum. The wires can be welded together at one end by means of an electric arc or a small oxygen-illuminating gas flame. No flux should be used. An acetylene flame should not be used because carbon combines with platinum, forming platinum carbide which embrittles the metal wires. The couple should then be annealed for about an hour at a temperature of about 1500°C. in order to remove any inhomogeneity in the wires. This can most easily be done by connecting the thermocouple in a 110-volt electrical circuit and passing a current of from 10 to 14 amp. through it, depending on the size of the wire. In preparing it for use, the wires are insulated from each other by two-hole porcelain insulators and then placed in a closed-end gastight porcelain tube. The open end of the tube is closed with a cemented cap carrying two binding posts by which the leads and thermocouple wires may be mutually connected.

The *Pt-PtRh thermocouple* possesses the advantages of being resistant to oxidation and of being able to be used continuously at temperatures up to 2600°F. It may be used at higher temperatures for short periods without serious detriment. It is probably the most accurate of the thermocouples when properly handled and a calibration by the Bureau of Standards is certified to within ±3°C. over the range from 300 to 1200°C. Its disadvantages are that it is very expensive and fragile and requires three points for a primary calibration, as will be explained later. These couples are used in furnaces where high temperatures are attained, or where the conditions are too severe for other types of couples.

Owing to the high cost of the noble-metal thermocouple, several cheaper substitutes have been devised which are satisfactory in many cases over a more limited temperature range. The essential data on the more important varieties are given in Table 2-VI. A thermocouple composed of chromel-*X* (64 per cent Ni-25 per cent Fe-11 per cent Cr) as the positive element and Copel (45 per cent Ni-55 per cent Cu) as the negative element is used to a small extent at temperatures below 1000°F. The

couples given in Table 2-VI can be used at higher temperatures than those listed but such use generally results in permanent injury to the couple. Base-metal couples have the general advantages of being cheap and, therefore, easily replaceable, sturdy, of developing high e.m.fs., and of requiring only two points for a primary calibration since their e.m.f.-temperature relationship is a straight line in the useful range, *i.e.*, their e.m.f.-

TABLE 2-VI.—COMMON BASE METAL THERMOCOUPLES

Metal or alloy	Composition	Element	Useful range, °F., continuous operation	E.m.f. developed at upper limit useful range,* mv.
Chromel	90 % Ni—10 % Cr	Positive		
Alumel	94 % Ni—2 % Al—3 % Mn—1 % Si	Negative	To 2000°F.	44.80
Iron	100 % Fe	Positive		
Constantan	60 % Cu—40 % Ni	Negative	To 1650°F.	51.76
Copper	100 % Cu	Positive		
Constantan	60 % Cu—40 % Ni	Negative	To 600°F.	15.32

* Cold junction at 32°F.

temperature relationship may be expressed by the equation:

$$E = a + bt$$

This fact also simplifies cold-junction corrections. They have the disadvantages of more limited temperature range than noble-metal couples and shorter life due to greater danger of contamination. They also are less accurate. These couples can be made up by welding either in an electric arc or a gas-air torch, using borax as a flux.

The *chromel-alumel thermocouple* is the most widely used base-metal couple because of its large useful temperature range and because it will give good service for several months of continuous operation without much attention. The alumel wire should be protected from strongly reducing atmospheres because it becomes brittle. For this reason, small sizes of alumel wire should not be wrapped with asbestos cord or they will fail within a short time; the larger sizes will last longer under these con-

ditions but will ultimately fail owing to embrittlement. The *iron-constantan thermocouple* gives excellent service if properly protected from oxidation and contamination. It is usually covered with one and sometimes two protection tubes, the outer one often being packed with some substance of a reducing nature. The couple develops a very high e.m.f. but is not used where service conditions are strongly oxidizing because it deteriorates too rapidly. The *copper-constantan couple* is widely used for moderate temperatures because it develops a high e.m.f. and the e.m.f.-temperature relationship is a straight line even down below the boiling point of water. It has been used for very low temperature work, as low as −253°C. in fact.

Calibration.—The values of millivoltage developed by the various types of thermocouples at different temperatures have been worked out and are obtainable from nearly all manufacturers of pyrometric equipment. If a great degree of accuracy is not required, the thermocouples can be used without initial calibration by assuming that they conform to the results given in the standard charts. Even under such conditions, however, it is best to select two or three thermocouples from a group made from the two coils of wire and check them to ensure that the couples are accurate and that the coils of wire are homogeneous throughout their length. If considerable accuracy is required, each thermocouple should be calibrated against a standard of some sort. Since thermocouples deteriorate with age, owing to oxidation or contamination by vapors, all couples in service should be checked periodically. The higher the temperature of service, the more frequently they should be checked. For instance, a chromel-alumel couple used at 2000°F. should be checked at least once a week. Two types of calibration are in use: primary and secondary calibrations.

The primary calibration of a thermocouple is made by taking advantage of the fact that when a pure substance changes from the liquid to the solid state, the conversion takes place at constant temperature and is indicated by an evolution of heat. It is obvious that the millivoltage indicated when a pure substance undergoes this change of state can be used in calibration if the freezing point of the substance is accurately known. Since more than one such point is required for calibration, the two or three substances used as check points must have melting points

spread over the range of temperature in which the couple is to be used in service. A list of pure substances commonly used for this work is given in Table 3-VI. The highest possible degree of

TABLE 3-VI.—FREEZING POINTS OF SUBSTANCES USED IN CALIBRATION

Substance	°C.	°F.
Tin	232	449
Lead	327	621
Zinc	419	787
Aluminum	660	1220
Sodium chloride (common salt)	801	1474
Copper	1083	1981

purity is required in these substances in order for the calibration to be accurate because impurities lower the freezing point and cause the transformation to take place over a range of temperature rather than at a constant temperature.

The Pt-PtRh thermocouple requires three points for a primary calibration because the e.m.f.-temperature relationship is not a straight line but is a curve represented, between the temperatures of about 300 and 1200°C. (572 and 2192°F.), by the equation

$$E = a + bt + ct^2$$

where E = e.m.f., t = temperature in °C. or °F., and a, b, and c are constants that differ for each couple. The values of e.m.f. are observed at three different freezing points, substituted in the foregoing equation to produce three equations which can be solved simultaneously for the constants a, b, and c. These values can then be substituted back into the general equation, the result being an equation in E and t, from which a calibration curve of e.m.f. versus temperature can be drawn up.

Example: If a noble-metal couple develops 2.55 mv. at 621°F., 5.84 mv. at 1220°F., and 10.53 mv. at 1981°F. on calibration, the cold junction being at 32°F. in each case, by substituting in the general equation, three simultaneous equations can be obtained from the data, as follows:

$$2.55 = a + 621b + 386{,}000c \quad (1)$$
$$5.84 = a + 1220b + 1{,}488{,}000c \quad (2)$$
$$10.53 = a + 1981b + 3{,}925{,}000c \quad (3)$$

Solving (1) for a,

$$a = 2.55 - 621b - 386{,}000c$$

Substituting this value in (2) and (3) we get two equations in two unknowns:

$$3.29 = 599b + 1{,}102{,}000c \quad (4)$$
$$7.98 = 1360b + 3{,}539{,}000c \quad (5)$$

We can eliminate b by multiplying (4) by 1,360 and (5) by 599 and subtracting (5) from (4), thus,

$$\begin{array}{rrrr} 4480 = & 815{,}000b & + & 1{,}500{,}000{,}000c \\ 4785 = & 815{,}000b & + & 2{,}120{,}000{,}000c \\ \hline -305 = & 0 & - & 620{,}000{,}000c \end{array}$$

and $c = 0.000000492$

Substituting this value of c in (4), we obtain

$$3.29 = 599b + 0.543$$
$$b = 0.00459$$

Finally, by substituting these values of b and c in (1), we find

$$a = 2.55 - 2.855 - 0.19 = -0.495$$

The final equation derived from the results of calibration is

$$E = -0.495 + 0.00459t + 0.000000492t^2$$

This equation does not apply below 300°C. (572°F.), while above 1200°C. (2192°F.) a small correction, given in Table 4-VI, must be added. Care must be taken to keep the cold junction at a constant and known value for all freezing-point determina-

TABLE 4-VI

Temperature computed from equation		Correction to add	
°C.	°F.	°C.	°F.
1200	2192	0	0
1300	2372	2	4
1400	2552	6	11
1500	2732	14	25
1600	2912	25	45
1700	3092	39	72

tions and the substances must be cooled to their freezing points slowly enough to ensure practical equilibrium.

The e.m.f.-temperature relationship for base-metal couples is a straight line. That is, this relation can be expressed by the equation

$$E = a + bt$$

only two points being needed for a primary calibration. Few base-metal couples are calibrated by the primary method, however, but are usually calibrated by comparison with a standard thermocouple, which is usually a noble-metal couple carefully calibrated by the primary method. This is the so-called secondary method of calibration. Owing to the straight-line relationship existing between temperature and e.m.f., the percentage error in the readings of a thermocouple from the values on the chart supplied by the manufacturer is constant and one point only need be checked by comparison with a standard thermocouple. If the thermocouple to be checked can be conveniently removed from its permanent setting, the most convenient method of checking it is to immerse it, together with the standard, in a bath of fused metal or salt, kept at a constant temperature, the temperature being in the range in which the couple is used in service. Both couples, fastened together with their hot junctions in close proximity, are immersed to the same depth, allowed to come to equilibrium, and the millivoltage developed by each read. The correction to apply to the couple being checked can then be easily calculated. In case the bath will contaminate the couple, both of them may be placed in the same protection tube.

On the other hand, it is desirable in many cases to check the couple in its permanent installation under its exact service conditions. This method is highly desirable from many standpoints, but it is a difficult one to carry out accurately. It is best to have a second hole in the furnace wall closely adjacent to the permanent installation, through which the standard couple can be immersed in the furnace to the same depth as the permanent one. The hot junctions should be in very close proximity, if not touching. This method is adequate if extreme accuracy of temperature measurement is not desired. It should be remembered that if there is a difference in temperature of

20°F. between the two couples in close proximity, the furnace temperature varies so widely that the calibration need not be more accurate than 20°F.

The Cold Junction.—We have already seen that the cold junction of a thermocouple must be at a constant and known temperature for the e.m.f. readings to be of any value but, since errors in the operation of thermoelectric pyrometers are so often due to the cold junction, the subject is worthy of further mention. In order to obtain the true temperature of the hot junction of a couple that has been calibrated with a cold-junction temperature of t but is used with a cold-junction temperature of t_1, the following value must be added to the observed temperature:

$$(t_1 - t)K$$

where t = calibrated cold-junction temperature, °C. or °F.
t_1 = actual cold-junction temperature, °C. or °F.
K = factor dependent upon the type of couple employed and upon the temperature of the hot and cold junction.

The factor K varies from a value of 1.5 to 0.3[1] but for practical purposes it may be assumed to be 1.0 for base-metal couples and 0.5 for rare-metal couples.

As an example of the application of this correction in the case of the base-metal couples, let us suppose that in Fig. 1-VI the hot junction M of a chromel-alumel thermocouple is such that the couple develops 40.60 mv., the temperature in the neighborhood of the galvanometer is 60°F., but the points N are at 80°F., due to being close to the furnace setting. The cold junction is at N in this case and not at the indicating instrument, yet the latter temperature is often incorrectly taken as the true cold-junction temperature, resulting in an error. If the thermocouple is calibrated for a cold-junction of 32°F., and if the 40.60 mv. developed corresponds on the calibration curve to 1800°F., the true temperature is then found as follows:

$$\text{True temperature} = 1800 + (80 - 32)1 = 1848°\text{F.}$$

In the case of a rare-metal couple such as a Pt-PrRh, the correction is made in the same manner. Let us assume that the

[1] FOOTE, FAIRCHILD, and HARRISON, Pyrometric Practice, *U.S. Bur. Standards Tech. Paper* 170, 1921, Government Printing Office, Washington, D.C.

couple has been calibrated with a cold-junction temperature of 32°F. and that in operation the cold-junction temperature has risen to 70°F. If the hot junction of the couple is such that it develops 9.36 mv., which from the calibration curve corresponds to 1800°F., the true temperature may be found as follows:

$$\text{True temperature} = 1800 + (70 - 32)0.5 = 1819°\text{F.}$$

Many methods are used in securing a constant and known value of the cold-junction temperature and several devices are in use for automatically compensating for a change in cold-junction temperature. *Extension leads*, usually made of stranded wire of the same composition as the thermocouple wires, are used to carry the cold junction of the couple back to the measuring instrument or to a place where the temperature may be conveniently regulated. The fact that the temperature of the earth is practically constant at a depth of 10 ft. or more is often utilized by sinking an iron pipe to this depth and locating the cold junction at the bottom. Indicating and recording instruments often have either manual or automatic cold-junction compensation but extension leads are necessary to carry the cold junction back to them.

If a large number of couples are connected through a selective switch to one indicating or recording instrument, the cost of extension leads for all of them becomes prohibitive. The *junction box* is often used in such cases, being merely a box in which the cold junctions of the couples are located and can all be kept at the same temperature. The welded junction of another thermocouple is buried deeply in the ground or otherwise kept at a constant temperature while the cold junction (actually the hot junction in this case because it is at a higher temperature) is located in the junction box. This auxiliary couple is connected into the circuit in such a way that when each couple is connected to the measuring instrument by means of the selective switch, the e.m.f. generated by this auxiliary couple is also fed into the circuit, the result being that the e.m.f. recorded at the measuring instrument is the sum of the e.m.fs. developed by the two couples. Thus, if the temperature of the junction box rises, the e.m.f. of the thermocouples decreases, but this rise in temperature increases the e.m.f. of the auxiliary couple enough exactly to compensate for this decrease. In this way, only one buried

junction is necessary. The measuring instrument may be located at any distance from the couples as only one set of copper leads is required.

Measuring Instruments.—Instruments for measuring the e.m.f. generated by thermocouples fall into two general classes: the galvanometer or millivoltmeter type and the potentiometer type. Instruments combining the principles of both are in use to some extent. Both of the general types are in wide use at the present time and it cannot be said that either is the better under all conditions. Both have their uses and the advantages and disadvantages of each type will be covered in the following paragraphs.

A *millivoltmeter* consists of a permanent magnet, a moving coil of fine copper wire mounted to turn between the poles of the magnet, a long and lightweight pointer attached to the coil, and a scale divided into millivolts or degrees, or both, to read the deflections of the pointer and coil. The principle of operation of the meter is much like that of an electric motor except that the moving coil operates against a spring which keeps it from turning too far. An electric current forced around the electrical circuit—composed of the couple, leads, and instrument—by the e.m.f. of the thermocouple causes the coil to turn and the amount of deflection of the coil and pointer is directly proportional to the current passing through the coil. The amount of current depends, in turn, upon the e.m.f. developed by the thermocouple and the resistance of the circuit. That is, the deflection of the pointer is proportional to the e.m.f. of the thermocouple *if*, and only if, the resistance of the circuit is constant.

Two types of millivoltmeters are built: low resistance and high resistance. One objection to millivoltmeters in general lies in the fact that the e.m.f. indicated is always less than the actual amount developed by the couple, since the indicator requires that current be delivered by the couple which results in some fall of potential in the couple. This can be cared for by arbitrarily calibrating the scale to read correctly with a fixed line and couple resistance. It is obvious that if the external resistance varies, an error is introduced in the reading and the magnitude of this error depends upon the ratio of the change in resistance to the total resistance of the circuit. If the internal resistance of the millivoltmeter is high, a variation in line resist-

ance of 1 ohm introduces only a very slight error, while if the millivoltmeter resistance is low, a variation of 1 ohm in line resistance makes a large error in the reading. Another way of stating the same thing is to say that a millivoltmeter measures the potential drop across its own resistance and the larger the ratio of its own to the total resistance the smaller the percentage error introduced by a given change in total resistance. Table 5-VI shows the effect of variation in line resistance on the readings of two millivoltmeters, one being of 10 ohms internal resistance and the other of 600 ohms internal resistance. Both were calibrated for a line (external) resistance of 2 ohms.

From the foregoing it is clear that from the standpoint of line resistance variations, a high resistance millivoltmeter is to be greatly preferred over one of low resistance. On the other hand,

TABLE 5-VI.—EFFECT OF RESISTANCE ON MILLIVOLTMETER READINGS*

Line resistance, ohms	Error in indicated reading, per cent		Error in °C. at 1000°C. (1832°F.)	
	600 ohms	10 ohms	600 ohms	10 ohms
1	+0.16	+ 9.1	+1.6	+ 91.0
2	0.0	0 0	0.0	0 0
3	−0 17	− 7 7	−1 7	− 77 0
4	−0 34	−14 3	−3 4	−143 0

* WOOD and CORK, "Pyrometry," 2d ed., McGraw-Hill Book Company, Inc., New York, 1941.

an instrument of low internal resistance can be made much sturdier because, since the deflection of the pointer is proportional to the current, a larger current results from a fixed e.m.f., the smaller the total resistance. In other words, high resistance millivoltmeters must be made delicate in order to measure the small currents accurately and can be moved around from point to point in the plant only with extreme care. Variable line resistance may be due to oxidation of the wire, poor contacts, variable depth of immersion of the thermocouple, temperature variations in the line, and partial fracturing of the lead wires. Several methods of checking and correcting for variable line resistance are incorporated in most modern millivoltmeters. Most of

them depend upon having the instrument itself indicate the amount of change in line resistance from the calibrated value and then correcting by adjusting a variable resistance in the meter itself.

Millivoltmeters may be made to record the temperature on a chart by placing a pen on the end of the pointer and placing a mechanism above the pointer that will depress the pointer to make contact with the chart at definite intervals. By causing the chart to move uniformly, a continuous record of the temperature can be obtained. The instrument may be further modified and made to maintain the temperature automatically at a desired value. A contact point is placed on either side of the pointer so that the pointer may vary a few degrees on either side of the desired value of temperature without touching either contact. If this arrangement is used to control an electric furnace, the current through the furnace is on until the temperature rises slightly above the desired value. When the pointer comes in contact with the upper contact point, it closes an auxiliary circuit and operates a relay which, in turn, either shuts off the furnace current or reduces it greatly. The temperature then falls until the pointer makes contact with the lower contact point, when the relay is operated to return the current to the furnace. The same arrangement can be used in gas- or oil-fired furnaces by having the relay operate an electric motor which opens and closes the fuel valves. In this way, the temperature varies through a narrow interval, the average value of which is the desired temperature.

The advantages of millivoltmeters as indicating instruments are that they are the least expensive of the measuring instruments and that readings may be taken by observing the position of the pointer so that manual adjustment by inexperienced hands is unnecessary. The line resistance can be checked by an expert from time to time. The disadvantages are that current is drawn by the instrument, thus lowering the e.m.f. of the couple below its true value, and that a change in line resistance will cause an error, depending upon the internal resistance of the millivoltmeter and the total resistance of the circuit. An instrument with an internal resistance of 10 ohms is about the satisfactory lower limit while a resistance of above 200 ohms is desirable and should always be used if the meter can be permanently installed

somewhere. Low resistance instruments should never be used unless facilities are at hand for accurately measuring the resistance of the circuit. The manufacturer always marks on the instrument the value of resistance for which the instrument is calibrated. This exact value should always be used in practice.

A *potentiometer* is a device for measuring potential differences by balancing an unknown e.m.f. against one whose value is known by comparison with a known e.m.f. such as a standard cell. A simplified potentiometer hookup is shown in Fig. 3-VI. AB is a single wire of fairly high but uniform resistance along which the contact C is free to move. AB is in the circuit with

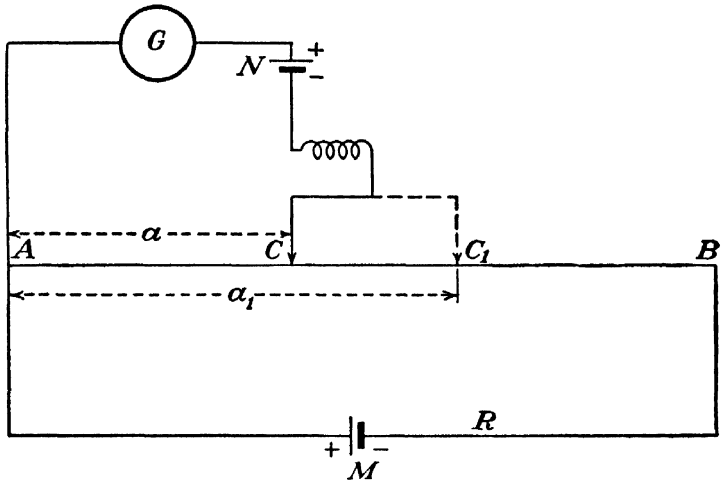


FIG. 3-VI.—Simplified potentiometer hookup.

the dry cells or cells M, thus causing a potential drop from A to B. The unknown e.m.f. is placed at N and connected in such a way that its e.m.f. is opposed to that of the battery M. Then, if the potential drop from A to B is greater than the e.m.f. of the unknown (N), there will be some point C where the unknown e.m.f. is exactly balanced by the potential drop in the wire AB, at which point the galvanometer G will register zero because no current is flowing through the circuit containing the galvanometer. If we let E represent the unknown e.m.f. placed at N in Fig. 3-VI, p the resistance per unit length of the wire AB, a the distance AC, and i the current in AB, the value of the unknown e.m.f. is given by the following equation when a balance is obtained (zero galvanometer reading):

$$E = api \tag{1}$$

because $a \times p$ = the total resistance from A to C, i is the current, and from Ohm's law we know that $E = IR$.

If we next substitute a standard cell E_s in place of the unknown e.m.f. at N, a balance will be obtained at some other point C_1, at a distance a_1 from A. The following equation may then be written:

$$E_s = a_1 pi \tag{2}$$

Dividing equation (1) by (2) and solving for E, we obtain

$$E = E_s \frac{a}{a_1}$$

and the exact value of E may be calculated because the e.m.f. value of the standard cell is known and a and a_1 have been measured.

If the potential drop from A to B is maintained at a constant value and the wire AB is divided into equal divisions of length, unknown values of e.m.f. can be measured directly, since the distance from A to C along AB is then exactly proportional to the potential drop between these two points. A constant potential drop can be maintained from A to B by placing a variable resistance at R. The potentiometer can then be made direct reading by carrying out the following procedure: Insert a standard cell at N and set the sliding contact at a value equal to the certified e.m.f. of the standard cell. Now adjust the rheostat R until the galvanometer is brought back to zero. When this is done, the e.m.f. drop over the wire AB coincides with the graduated e.m.f. scale of the wire AB and unknown e.m.fs. may be substituted at N and their values determined directly. Unfortunately, the current through AB does not remain constant for long periods and it is necessary to make periodical readjustments of R against the standard cell.

Potentiometers used for measuring the e.m.f. developed by thermocouples operate on the same principle as that discussed above but are more convenient to operate. The portable potentiometer, shown in Fig. 4-VI, is an accurate and rugged instrument. The galvanometer is shown at the upper left, the slide-wire dial at the right center, the scale directly above it and the binding posts for the thermocouple connections at the upper right corner of the panel. Of the two switches at the lower

left of the panel, one connects the thermocouple and the other the standard cell contained in the instrument while the rheostat (R of Fig. 3-VI) is manipulated by inserting the handle, kept

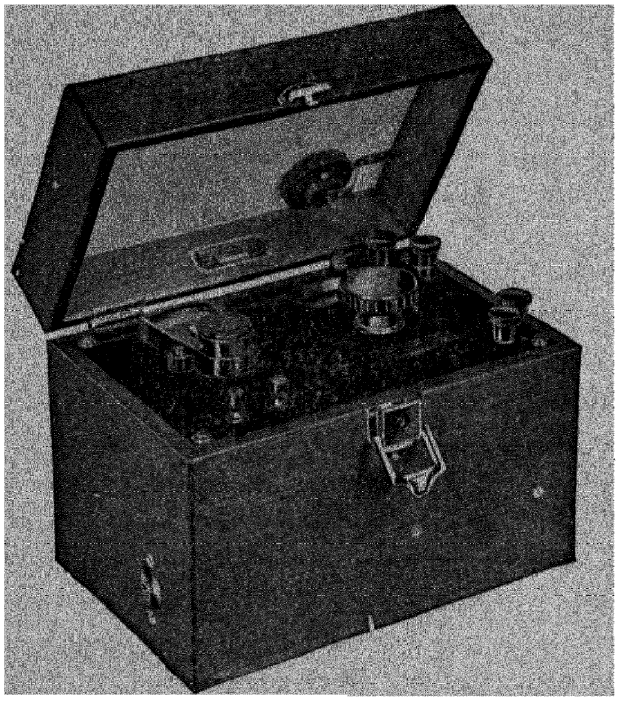


FIG. 4-VI.—A portable potentiometer. (*Courtesy of Leeds and Northrup Company.*)

inside the cover, in the circular plate at the lower left side of the case. If cold-junction compensation is included in the instrument, a dial at the left of the panel can be adjusted for correction of cold-junction temperature. Potentiometers can be modified in design to make them recorders by having a motor-operated set of cams which will automatically balance the thermocouple e.m.f. against the primary e.m.f. circuit. An extra rheostat and relay, properly connected, transform the recorder into a controller. One type of potentiometer recorder is shown in Fig. 5-VI.

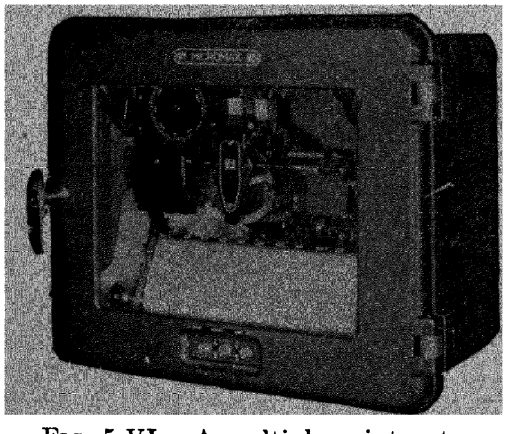


FIG. 5-VI.—A multiple-point potentiometer recorder. (*Courtesy of Leeds and Northrup Company.*)

Potentiometers possess the advantages of being accurate and not being dependent upon variations in resistance since no current flows when a balance is obtained. The portable instrument is rugged and requires little attention. Care should be taken to see that the galvanometer needle is locked when the instrument is being moved or permanent injury to the delicate suspension will occur. Their disadvantages are high first cost and operation so complicated as to require a trained operator.

Thermocouple Installation.—It is obvious that no matter how accurate the measuring devices used and what care is taken in providing cold-junction compensation, etc., accurate results will not be obtained unless the thermocouple is correctly and intelligently installed. If a millivoltmeter is being used, the line resistance should be kept at the lowest possible value to reduce the chance of error because the e.m.f. and current generated by a thermocouple are very small under the best of conditions. Furthermore, a couple placed in one corner of a large furnace may indicate a value of temperature far different from the average temperature of the furnace. No general rules for procedure can be given because each installation is a special case in itself, but it is well to have the hot junction of the couple as close to the work as possible and near a point where average temperature conditions exist. In large furnaces it is a good plan to have a couple in each corner and one in the center and, in electric furnaces, to have each couple control a heating element adjacent to it. Thus accurate and uniform temperature can be maintained.

The "depth of immersion" or the length of couple that lies in the heated zone is of great importance. If the heated portion is not of sufficient length, conduction of heat from the hot junction along the wires will occur, resulting in a low reading of the thermocouple. It is a good rule to immerse the couple as far as possible in order to avoid this effect. It is also well to remember that thermocouples should always be adequately protected from oxidation and contamination with undesirable substances as failure in this regard will drastically shorten the life of the installation. If it is desired to measure the temperature of a molten metal bath, the wires should not be welded together at their ends but should be immersed in the bath in such a position that they will not touch. The wires should be removed from the bath as soon as they reach temperature equilibrium

and the value is read because they dissolve rapidly in some molten metals.

RADIATION PYROMETERS

Radiation pyrometers may be defined as those which measure temperature by means of the light emitted from bodies at high temperatures. Two main classes are in use: the optical pyrometer and the total radiation pyrometer. Several types of each class of radiation pyrometer are on the market but as they vary only in detail, one prevalent type of each class will be selected to illustrate the principles involved.

Black Body Conditions.—We know that bodies radiate energy in the form of waves. The radiation emitted consists of waves of many wave lengths. At low temperatures, the major portion of the energy is carried by waves of long wave lengths but as the temperature of the body rises progressively, the larger portion of the energy is carried by progressively shorter wave lengths until, at very high temperatures, the energy radiated by a body is mainly in the form of waves of short wave length. In order for a wave of radiant energy to be visible to the eye it must have a value of wave length lying between about 0.00008 and 0.00003 cm., the former value being the longest wave length visible and the latter the shortest visible by the human eye. There is also a direct relationship existing between the length of the wave and the color sensation produced when we observe it. The longest observable wave length produces a sensation to the eye corresponding to a red color while the shortest visible wave length has a violet color. Wave lengths in between these limits cause the various shades of color between red and violet. The above facts account for the change in color of bodies as they are heated, as well as why the eye is able to estimate temperature by color (see Table 1-VI). The reason one can feel the radiation coming from a hot body but cannot see it is that the body is at too low a temperature to emit an appreciable quantity of waves of shorter wave length than 0.00008 cm.

Whereas the quantity of radiation emitted by a body per unit of time increases with increase in temperature and the major portion of the energy carried by the waves shifts to lower values of wave length, radiation from all bodies is not the same at a given temperature. For example, if carbon and polished platinum

are both heated to a temperature where the carbon becomes incandescent, it can be easily seen that the platinum emits much less light than the carbon, even though they are at the same temperature. In fact, all substances possess different emitting power, or *emissivity*, at the same temperature. The state (solid, liquid, or gaseous) of any one substance often makes a considerable difference in its emissivity. These facts would seem to make it impossible to measure the temperature of different substances by observation of the radiation emitted from them. The conception of the black body, however, has removed the major portion of the difficulty.

Since all bodies have different emissivities, it is possible to conceive of a body that has a maximum emissivity. Such a hypothetical body is called a *black body*, and its emissivity is assigned as unity (1). The emissivities of all other bodies are, therefore, fractions of the emissivity of a black body. A black body may be defined as one that absorbs all radiation falling upon it and reflects or transmits none, so that the radiation from a black body would be due to temperature alone. All known substances absorb part of the radiation falling upon them and reflect or transmit the remainder. The radiation coming from such bodies is not due to temperature alone. For example, a brick wall in direct sunlight has a large amount of radiation coming from it but nearly all of it is reflected light and hardly any is due to the temperature of the wall.

Both optical and total radiation pyrometers are calibrated in terms of black body conditions and this conception is used as a basis for all radiation work. The emissivity of a substance is the ratio of the intensity of radiation from the body to the radiation from a black body at the same temperature. The emissivity of a body also depends upon the wave length of the radiation and a wave length of 0.000063 cm. is used for comparison in most cases of selective emission. Table 6-VI gives the selective emissivities of several substances at the above value of wave length.

The temperature indicated by a radiation pyrometer is always less than the true temperature of the body because the instrument is always calibrated for black body conditions. It would seem that large corrections would be necessary in order to use radiation pyrometers, but a great many commercial

operations requiring high temperatures are carried out under conditions that approach very closely those of a black body. An almost perfect black body is produced by uniformly heating the walls of a hollow opaque enclosure and observing the radiation through a small aperture. The radiation thus observed is due to

TABLE 6-VI.—EMISSIVITIES OF METALS AND OXIDES

Substance	Emissivity	
	Solid	Liquid
Copper	0 10	0 15
Nickel	0.36	0 37
Iron	0.37	0 37
Manganese	0 59	0 59
Carbon	0.9	
Nichrome (1200°C.)	0 80	
Nickel oxide (NiO)	0.89	0 68
Iron oxide (Fe_3O_4)	0 63	0.53
Refractories	0.70	
Glazed brick	0 75	
Red brick	0 93	

temperature alone and is not affected by light from other sources. Almost any furnace, then, is a black body, and temperatures in them can be quite accurately measured with radiation pyrometers provided there is no incandescence from flames to affect the results. Also, since most metals oxidize and their oxides generally have quite high emissivities, the error in measurement is further reduced.

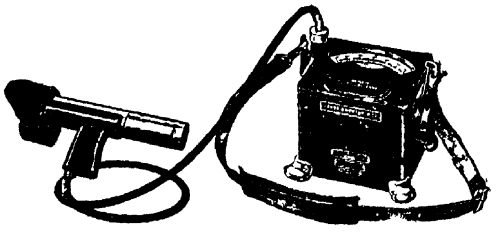


FIG. 6-VI.—A disappearing filament type of optical pyrometer. The adjusting rheostat is on the right side of the instrument case. (*Courtesy of Leeds and Northrup Company.*)

Optical Pyrometers.—Optical pyrometers operate on the principle of obtaining a color match, under carefully controlled conditions, between the hot body and an electric lamp filament placed in the instrument. The Morse disappearing-filament type of optical pyrometer has been selected for description because it is by far the most common type and the following remarks apply specifically to this instrument. Figure 7-VI is a drawing of the important details of the pyrometer. The essential parts

of the instrument are an eyepiece E; an objective lens L; a red glass R which absorbs all radiations except a narrow wave-length region in the red (0.000063 cm.); the filament of an electric lamp F placed in the common focal plane of both E and L; a milliammeter (shown at the bottom) to measure the current through the filament F; a battery; and a variable resistance.

In operation, the eyepiece is first focused upon the lamp filament. This is done by the manufacturer in most cases and is not subject to change. The telescope is then pointed at and focused upon the high-temperature source by changing the length of the tube, near the end of which the lens L is situated. The filament, whose temperature and hence brightness may be

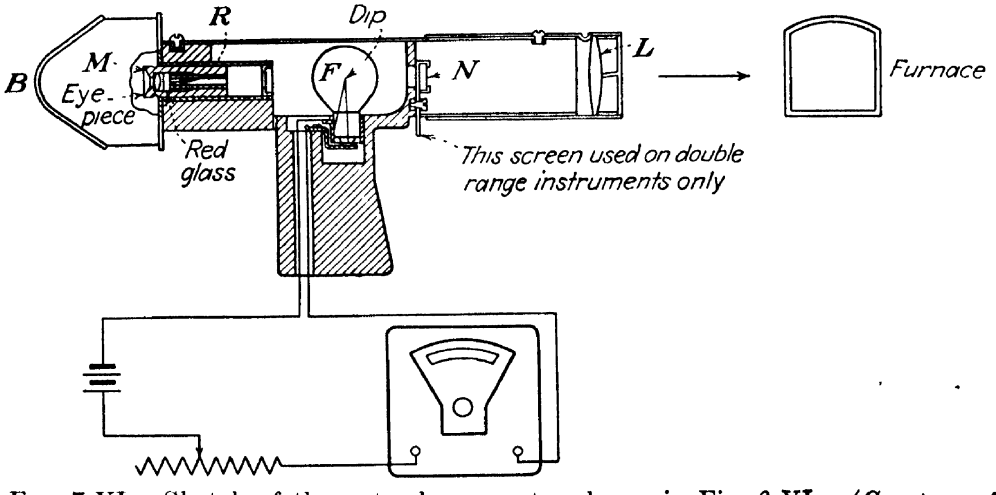


FIG. 7-VI.—Sketch of the optical pyrometer shown in Fig. 6-VI. (*Courtesy of Leeds and Northrup Company.*)

changed by varying the resistance in the electrical circuit, is superimposed upon the image of the high-temperature source by the objective lens L. The setting of the pyrometer then consists in adjusting the variable resistance until the tip of the filament, which is generally made with a downward loop, just merges in brightness with the bright background of the image of the high-temperature source. If the filament current is too low, the filament will appear black against the source; if too high, it will appear red. The best procedure to follow is to increase the filament current until the filament is red and then slowly reduce the current until the bottom of the loop just becomes invisible. The reading of the milliammeter for this condition of color match can then be used as an indication of the temperature of the source.

In order to calibrate an optical pyrometer accurately, milliammeter readings for a color match at three different values of temperature should be recorded, inserted in the equation

$$I = a + bt + ct^2$$

The equation is solved by the method given previously and a calibration curve drawn to represent the temperature-current relationship of the instrument. Temperatures up to the melting point of platinum may be obtained by placing a calibrated Pt-PtRh thermocouple (with protection tube) in a small muffle furnace which can be uniformly heated and whose temperature can be accurately controlled. The end of the production tube is heavily coated with carbon or other material which has an emissivity of nearly 1. The optical pyrometer is sighted through a small hole in the furnace wall and focused directly upon the end of the thermocouple protection tube. Under these conditions, nearly perfect black-body conditions may be obtained and the milliammeter readings may be recorded against the temperatures measured by the thermocouple. The muffle is necessary in order to guard against incandescence.

The measurement of the temperature of a heated body out in the open (not under black body conditions) by means of an optical pyrometer is attended by considerable difficulty owing to the emissivity of the body generally being well below unity. If the emissivity of the substance is known, the apparent temperature (lower than the true temperature) can be measured with the optical pyrometer and the true temperature calculated by means of the equation:

$$\frac{1}{T} - \frac{1}{T_a} = \frac{\log_{10} E}{9{,}880}$$

where T is the true and T_a the apparent temperature as measured by the instrument, both in degrees centigrade absolute (°K.), and E is the emissivity of the substance for a wave length of 0.000063 cm. If the body is reflecting light from other sources, the calculated true temperature will be in error by the amount of radiation reflected.

If a substance that can absorb the radiation from the high-temperature source is interposed between the source and the pyrometer, the instrument will read low in proportion to the

absorbing power of the medium. For high-temperature work, a red glass screen is placed in the instrument tube (*N* of Fig. 7-VI) so that excessive currents will not have to be passed through the filament in order to obtain a brightness match. The instrument is calibrated both with and without this screen in place. Smoke and dust in the air between the source and the pyrometer act as effective absorbing media and cause an error where measurements are made under such conditions. If the air is clear, however, the effect of distance of the source from the instrument is negligible, provided the pyrometer is correctly focused upon the source.

The constancy of calibration depends largely upon the filament of the lamp and care should be taken to see that excessively large currents are not used and that the lamp is turned on only when actual temperature measurements are being taken. The lenses and tube should be protected from dust at all times. The advantages of the optical pyrometer lie in the fact that it is able, under correct conditions, to measure temperatures accurately over a wide range of temperature—in fact, the upper end of the range is practically limitless; the instrument is easily portable and self-contained; and it need not be exposed to oxidizing or contaminating influences. Its disadvantages are that its accuracy is dependent upon the attainment of black body conditions; there is often an uncertainty due to absorbing media between the source and the instrument; and it is not readily adapted to use as a controller or a recorder.

Total Radiation Pyrometers.—We have already seen that optical pyrometers depend for measurement upon the relationship between the temperature of a body and the intensity of radiation of a certain wave length. In the case of total radiation pyrometers, on the other hand, the total radiation intensity is taken as a measure of the temperature as this value also increases continuously with increase in temperature. Several types of total radiation pyrometers are in use, of which one common example has been selected for description.

The Thwing total radiation pyrometer consists of a long tube, blackened inside, lined with nonreflecting diaphragms and so constructed that radiation from sources other than the high-temperature source being measured cannot enter if the instrument is correctly installed and used. At the back end of the

tube, a hollow conical mirror directs all the radiation entering the open end of the tube on to the bead of a very small thermocouple which is placed at the focal point of the mirror. The thermocouple is connected to a very sensitive millivoltmeter which accurately measures the rise in temperature of the hot junction of the thermocouple. The instrument is set up with the tube sighted on the high-temperature source. The radiation coming from it is a function of the rise in temperature of the hot junction of the couple. If the thermocouple has a straight-line relationship between temperature and e.m.f., the relation between the deflection (D) of the millivoltmeter pointer and the absolute temperature (T) of the high-temperature source is expressed by the following equation:

$$D = aT^4 + b$$

and the instrument may be calibrated by means of two known temperatures.

There are several important sources of error in connection with total radiation pyrometers which require mention. There is a certain minimum size of the high-temperature source necessary for accurate results which is dependent upon the distance of the tube from the source as well as the size of the tube. These values are given by the manufacturer and should be adhered to strictly. Also, the reflecting power of the mirror should remain unchanged in order for the calibration to be of any value. For this reason, the tube should be kept free from dust and should be cleaned occasionally. Furthermore, since the radiation is liable to absorption by dust or smoke in the atmosphere, the atmospheric conditions should be watched carefully. Certain gases, although transparent to visible radiation, absorb the longer wave lengths quite readily. For these reasons, the instrument should be calibrated under its service conditions in this regard and, in general, total radiation pyrometers should not be used where radiation from the source must pass through intervening media of appreciable density.

If the temperature of a body is not measured under black body conditions and its total emissivity, which is generally different from its selective emissivity at a specified wave length, is known, the apparent temperature of the body may be measured and its true temperature calculated from the expression:

$$E = \frac{T_a^4}{T^4}$$

where E is the total emissivity, T_a is the apparent and T the true temperature, both in degrees absolute. The error introduced by nonblack body conditions is often serious as shown in Table 7-VI which gives the apparent temperatures of certain sources under nonblack body conditions when the true temperatures are as indicated in the first column.

Total radiation pyrometers possess the advantages of not depending upon a color match for measurement of temperatures and of being adaptable to recorder and controller work. Most of the possible disadvantages are evident from the foregoing discussion of the possible sources of error. In addition, the millivoltmeter must be made very sensitive and hence can be moved from point to point only with care.

TABLE 7-VI*

True temperature, °C.	Apparent temperature, °C.		
	Iron oxide, coated	Nickel oxide, coated	Copper oxide, coated
600	572	495	
700	668	600	590
800	763	705	675
900	858	815	755
1000	953	925	850
1100	1048	1035	
1200	1142	1145	

* WOOD and CORK, "Pyrometry," 2d ed., McGraw-Hill Book Company, Inc., New York, 1941.

Suggested Questions and Problems for Study and Class Discussion

1. What is pyrometry? Why is it so important in present-day industrial operations?
2. List the properties of substances used as an aid in measuring temperatures. Give concrete examples of each.
3. What are the advantages and disadvantages of mercury thermometers? Of electrical resistance thermometers? Give an example in your own experience where each might be used to advantage and explain why.
4. Explain the Peltier and Thomson e.m.fs.
5. What are the requirements of a thermocouple?
6. Explain fully the necessity for keeping the cold junction of a thermocouple at a known and constant temperature.

7. The following data were gathered in calibrating a Pt-PtRh thermocouple:

At 1000°F. the e.m.f. was 4.69 mv.

At 1900°F. the e.m.f. was 10.10 mv.

At 2400°F. the e.m.f. was 13.41 mv.

The cold junction was at 32°F. during calibration. Derive the e.m.f.-temperature relationship for this couple. If this thermocouple read 12.00 mv. and the cold junction was at 60°F., what was the true temperature of the furnace:

8. What are the advantages and disadvantages of base-metal thermocouples?

9. A chromel-alumel thermocouple was calibrated and the following data obtained:

At 1000°F. the e.m.f. was 22.30 mv.

At 2000°F. the e.m.f. was 44.80 mv.

The cold junction was at 32°F. during calibration. Derive the calibration equation. If this couple read 1850°F. with a cold junction at 0°F., what would be the true furnace temperature?

10. What methods are in use for compensating for varying cold junctions? Describe one method in detail.

11. What are the advantages and disadvantages of millivoltmeters as indicating instruments? How may they be made into recorders?

12. What is the principle upon which the potentiometer operates? What are the advantages and disadvantages of potentiometers for measuring thermocouple e.m.fs.?

13. What is the effect of depth of immersion on the reading of a thermocouple?

14. Explain what is meant by a black body. What is its significance in radiation pyrometry? How may it be attained experimentally?

15. Explain in detail how the Morse-type optical pyrometer operates. What are its advantages and disadvantages?

16. A Morse-type optical pyrometer gave the following reading on calibration under black-body conditions:

At 1470°F.—349.3 Ma.

At 1832°F.—391.0 Ma.

At 2200°F.—456.2 Ma.

Derive the calibration equation. If this instrument were used to measure the temperature of molten metal as it flowed from a furnace in open air and a value of 523 Ma was recorded by the instrument, what was the true temperature of the stream of metal? Assume an emissivity of 0.43.

17. What are the essential differences in operation between an optical and a total radiation pyrometer? Compare their advantages and disadvantages.

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CHAPTER VII

METALLURGICAL FUELS AND THEIR COMBUSTION

INTRODUCTION AND CLASSIFICATION

In the production of heat and power three general types of fuels are used: solid, liquid, and gaseous. The more important, classified as to their being either natural or manufactured, are given in Table 1-VII.

Only two of the solid fuels have industrial uses. Of the primary solid fuels, bituminous coal is the only one that has industrial uses, it being used in coal-fired furnaces, in the production of coke, in the manufacture of gas, and in the production of electrical and steam power Anthracite coal is almost entirely a domestic (home) fuel, while lignite and peat are of too low a grade of fuel to be of industrial importance at present, although they will become more important as the reserves of bituminous coal diminish. Wood has ceased to be an industrial fuel because of its high price and large moisture content. The waste from sawmills is used to a slight extent in the calcination of limestone in some places. Coke, the most important solid fuel, has its principal use in the iron blast furnace.

Petroleum, the natural liquid fuel, is a mixture of hydrocarbons and has a heating value ranging from 18,000 to over 20,000 B.t.u. per lb., depending upon several factors. Most petroleum is subjected to partial distillation in order to separate and save the very volatile portion (gasoline, kerosene, etc.) and the heavy lubricating oils. The products obtained from this treatment and used for fuel oil are, therefore, the middle portions of the crude substance. Alcohol is not a commercial fuel at present but may become an important petroleum substitute as the reserves of this substance near exhaustion. Colloidal fuels are prepared by making a suspension of finely ground solid fuel (coal, peat, wood, etc.) in fuel oil. This fuel is not much used at present but has future possibilities. Tar is a by-product of coke manufacture and is sometimes burned in

high-temperature furnaces together with gas from the coke ovens. It is a black, very viscous liquid and is composed principally of hydrocarbons and compounds containing nitrogen and sulfur as well as some free carbon.

TABLE 1-VII.—CLASSIFICATION OF FUELS*

Type	Natural or primary	Manufactured or secondary
Solid	Anthracite coal Bituminous coal Lignite Peat Wood	Coke Charcoal Briquets
Liquid	Petroleum	Tar Petroleum distillates Petroleum residuums Alcohols Colloidal fuel
Gaseous	Natural gas	Coal gas Water gas Oil gas Producer gas Blast-furnace gas Acetylene

* HASLAM and RUSSELL: "Fuels and Their Combustion," McGraw-Hill Book Company, Inc., New York, 1926.

Natural gas, the primary gaseous fuel, is of very great importance in the heavy manufacturing industries. It is composed chiefly of the hydrocarbons, methane and ethane, although small amounts of hydrogen and nitrogen may be present. Its heating value ranges between 700 and 1500 B.t.u. per cu. ft. This is approximately twice the heating value of coke-oven gas and four to five times the value of producer gas. The raw gas is usually treated to remove the valuable liquid compounds that it contains. These are volatile and may be blended with gasoline. Natural gas is a clean, easily handled, and concentrated fuel. Where there is an abundant supply, it is relatively cheap. About 1925 the supply of natural gas seemed to be rapidly diminishing. However, since that time vast new gas fields have been discovered

and tapped. Today, approximately twice as much natural gas is used as was used fifteen years ago.

Gas formed by the destructive distillation of coal is known as coal gas, illuminating gas, or coke-oven gas, depending somewhat upon the method of manufacture. If coke is being made for blast-furnace use, the gas usually has a different composition than when the gas is the principal product desired, as in coal or illuminating gas manufacture. Such gas has a heating value of between 550 and 600 B.t.u. per cu. ft. and is composed mainly of methane, unsaturated hydrocarbons, and hydrogen. Water gas, sometimes called blue water gas, consists mainly of hydrogen and carbon monoxide and is made by the action of steam on incandescent carbon. It has a heating value of about 300 B.t.u. per cu. ft. unless enriched with gases from decomposed oil, when it may have a heating value of from 400 to 600 B.t.u. per cu. ft. It is then known as carbureted water gas. Oil gas is made by the thermal decomposition or "cracking" of hydrocarbon oils into hydrocarbon gases and ordinarily has a heating value of from 450 to 650 B.t.u. per cu. ft. Producer gas, made by the partial combustion of bituminous coal with a mixture of air and steam, consists principally of carbon monoxide, hydrogen, and nitrogen and has a heating value of between 140 and 185 B.t.u. per cu. ft. Blast-furnace gas, one product of the iron blast furnace, has a heating value of about 90 B.t.u. per cu. ft., while acetylene, C_2H_2, is a gas formed by the action of water on calcium carbide, CaC_2.

COAL

Formation.—Coal is still the most important fuel in industry and is very likely to remain in that position for a long time to come. Coal from different localities varies widely in character and heating value, and to understand this we must first consider its origin and then its classification.

Coal is generally considered to have been formed by the decay of vegetation under water and the subsequent compression of this decayed matter by the heavy pressure of material deposited on it and by the squeezing of mountain-forming movements. Hundreds of thousands of years ago much of the eastern part of this country was covered by shallow water in which vegetation grew in great profusion. As these plants died, they fell

into the shallow water and decay set in, aided by bacteria. If they had fallen on dry land, they would have been completely rotted away but the water prevented the necessary oxygen from reaching them and the decay was only partly complete. The black muck formed by this decomposition gradually increased in thickness until the entire space was filled, forming what is known as a *peat bog* (see Fig. 1-VII).

After the formation of the peat bogs, further decomposition of the vegetable matter was halted, either by changed conditions that caused the bogs to dry out, by the death of the organisms that were the principal cause of the decay, or by burial of the

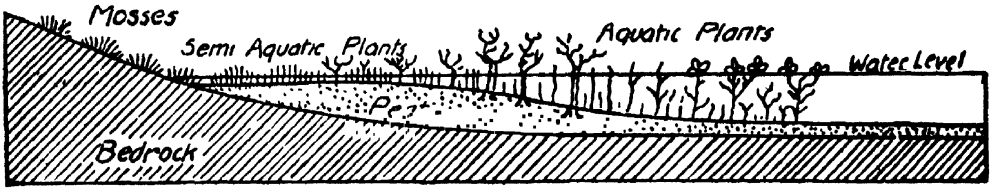


FIG. 1-VII.—Section of a typical peat bog in the process of formation. (*Modified from Pirsson and Schuchert, Introductory Geology.*)

peat by deposition of sediment. The original vegetable matter (plants, trees, etc.) is mainly composed of carbon, hydrogen, oxygen, and nitrogen. It also contains some mineral substances, while the plant framework is cellulose, $C_6H_{10}O_5$. The decay of this matter under water is caused by the growth and action of the bacteria. The absence of a free supply of oxygen prevents the complete oxidation to CO_2 and H_2O. This causes some of the hydrogen to be removed as H_2O, some of the carbon as CO_2, and some of both as methane CH_4. The material that is left, the peat, is much richer in carbon and poorer in hydrogen than the original vegetable matter.

The time necessary to form these peat bogs has been roughly estimated by geologists to be about 2 ft. in one hundred years. From this it can be seen that the process is a very slow one and, in addition, it takes many feet of peat to form a coal seam 1 ft. in thickness. Peat beds are in the process of formation in many parts of the world at the present time. Several examples in this country are the Dismal Swamp of North Carolina and Virginia and the Okefenokee Swamp in Georgia. It is estimated that there are 672,000,000 tons of peat available in Dismal Swamp.

All the various grades of coal are the result of the slow removal of water and volatile matter from peat. This devolatilization is caused by heat and pressure, the heat being due principally to the tremendous pressure applied. It is believed that our modern coal beds were formed by a change in natural conditions which caused the peat beds to be buried deeply under the immense weight of earth deposited upon it by erosion, thus stopping decay and compressing the peat. Furthermore, very great pressures are brought about by movements of the earth's crust, as in forming mountains. This may cause almost complete removal of the volatile matter in the coal as has occurred in the eastern part of Pennsylvania. This severe compression of the peat gradually changes it into coal and the greater the pressure and the longer it acts, the lower the volatile matter and the higher the carbon content of the coal. The coal is also made more dense and is cemented together, being gradually dehydrated, devolatilized, and compacted. The time consumed in such a process is enormous, many millions of years being required to form the coal from peat.

In general, the variations in coal may possibly be due to one or more of the following causes:

1. Difference in types of vegetation going to form the peat.
2. Differences in the extent of decay produced by bacteria.
3. Differences in the extent of devolatilization due to pressure, particularly the horizontal or *thrust* pressure often due to mountain-forming movements.

Evidence of the type of vegetation from which the coal was formed can often be observed in the coal itself. This is a minor factor, however, as coals from the same type of vegetation vary widely in properties. If the decay of the vegetation was not very great, the resulting coal may be woody in appearance—that is, show evidences of the fibers of the original vegetation. In other cases where the decay reduced the vegetation to a pulp, no fibrous portions can be seen. The difference is mainly one of appearance and has only a minor effect upon the qualities of the coal itself. The important factor has been found to be the amount of thrust pressure and its effect on devolatilization. In the eastern part of Pennsylvania where the thrust pressures were high, the coal is of high rank (anthracite), being high in carbon and low in volatile matter. In the western part of the

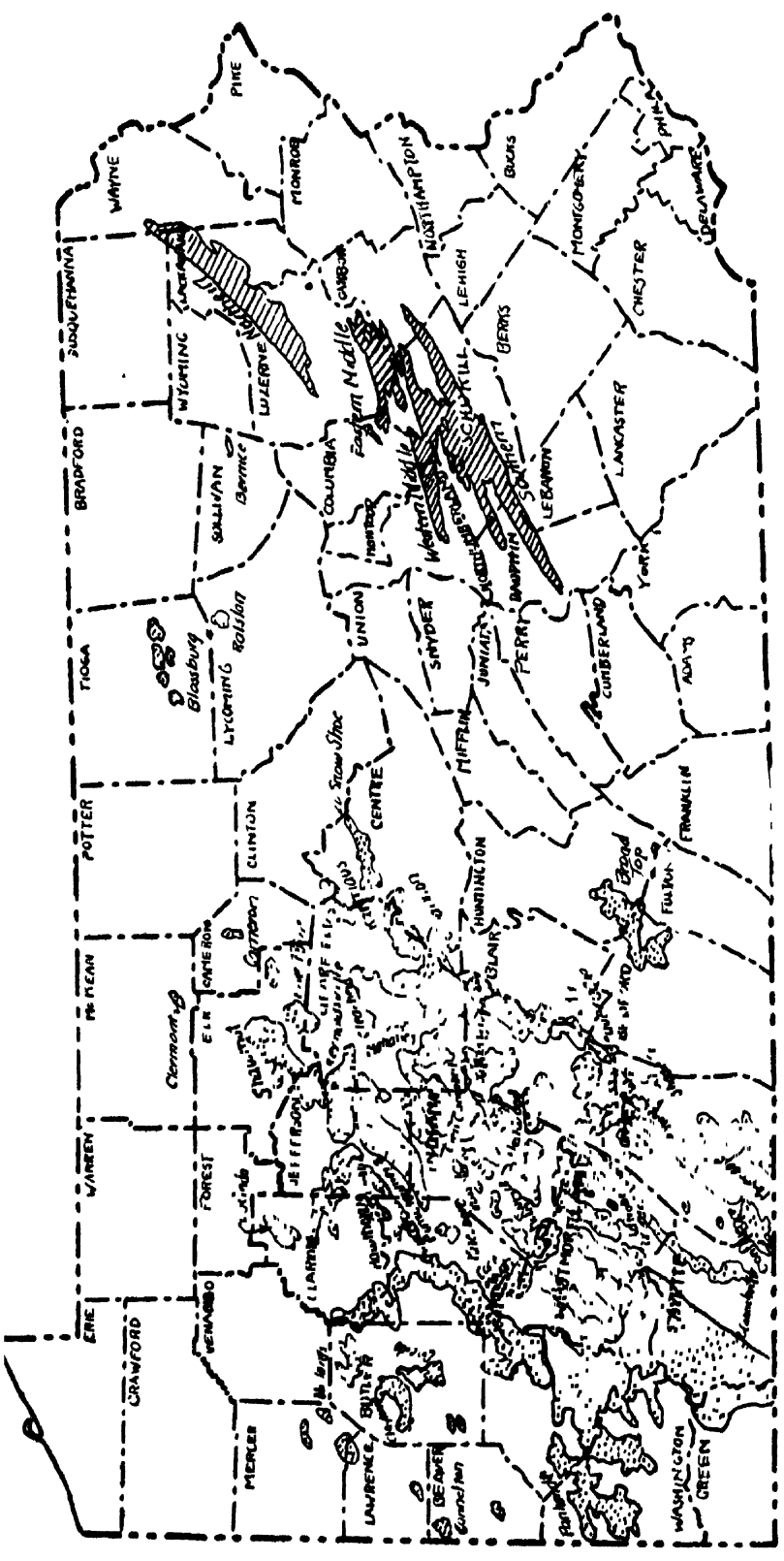


FIG. 2-VII.—Map of the producing coal fields of Pennsylvania. (*From R. E. Murphy, The Mineral Industries of Pennsylvania.*)

state where the thrust pressures were much lower, the coal is of lower rank (bituminous), being considerably lower in carbon and higher in volatile matter. Figure 2-VII, showing the coal-producing fields of the state, illustrates this effect very well, the anthracite fields being in the eastern and the bituminous fields in the western part of the state.

Composition.—All coal contains various combustible materials left from the alteration of the vegetable matter, moisture, and varying amounts of mineral matter which appear as ash after burning. The usual means of determining the composition of a coal are (1) by an *ultimate* analysis and (2) by a *proximate* analysis.

The ultimate analysis of coal consists in determining the percentages of the "ultimate" constituents: carbon, hydrogen, oxygen, sulfur, nitrogen, and ash in the dry coal. The amounts of carbon, hydrogen, and nitrogen are determined by the standard methods of quantitative analysis and need not be gone into here. Sulfur is often determined by analyzing the residue in the calorimeter after the determination of the heating value of the coal. The oxygen is determined by difference and is usually assumed to be equal to 100 minus the sum of carbon, hydrogen, nitrogen, ash, and five-eighths of the sulfur.

The proximate analysis of coal is much easier and quicker than the ultimate analysis and is the one more commonly made since it furnishes most of the data necessary to determine the commercially important properties of coal. It consists in determining the moisture, volatile combustible matter (V.C.M.), fixed carbon (F.C.), ash, and sulfur content of the coal. The amount of moisture is determined by the loss in weight of a small sample on heating for from 1 to 1½ hr. at from 220 to 230°F. The volatile matter is determined by heating a 1-g. sample of the coal in the "as received" condition in a closed crucible under specified conditions for 7 min. The percentage of volatile matter is the percentage loss as thus determined minus the percentage of moisture. Ash is determined on the dried sample from the moisture determination by completely burning off all combustible matter until the ignited material reaches a constant weight. The percentage of fixed carbon is equal to 100 minus the sum of moisture, volatile matter, and ash. Sulfur is usually included in a proximate analysis, being determined as indicated in connection with the ultimate analysis.

Coal ash is a mixture of oxides, silicates, and sulfates, the relative percentages of which vary widely in different coals. It is composed of *free* ash and *fixed* ash, the former being due to bits of clay, shale, iron sulfide, etc., mechanically held in the coal as well as fragments from the roof and floor of the mine. The latter is due to impurities present as an intimate mixture in the coal substance, derived from ash in the original vegetation or from sedimentation during the coal formation. The washing treatment to which coal is often subjected before marketing is primarily used to reduce the free ash content of the coal by elimination of the mechanically held particles.

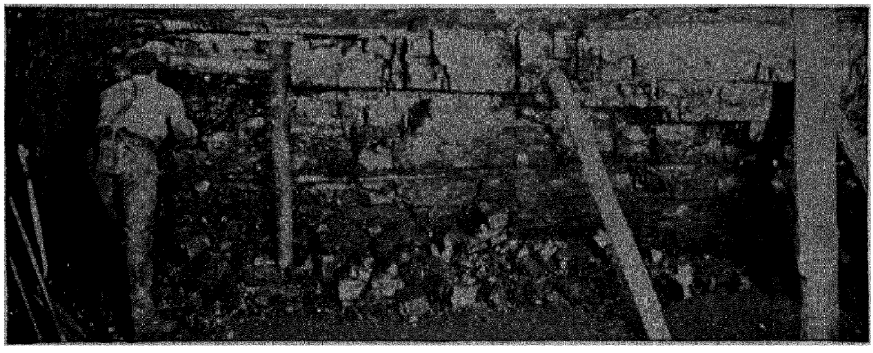


FIG. 3-VII.—The mining of coal. (*Courtesy of the Jones and Laughlin Steel Corporation.*)

Classification.—The different varieties of coal are classified into grades or classes in an arbitrary manner depending upon their proximate analyses and physical characteristics. The names of the grades of coal in order of increasing rank are *subbituminous*, *bituminous*, *semibituminous*, *semianthracite*, and *anthracite*. Typical analyses of these grades are given in Table 2-VII as well as of wood, peat, and lignite for purposes of comparison. These different grades cannot be differentiated sharply, since the properties of one class or grade gradually merge into the properties of another without rigid dividing lines. Two coals may differ considerably in composition and still be of the same class. The physical characteristics of these classes will now be briefly discussed.

Peat is the first stage of coal formation and, while not strictly a variety of coal, is included for purposes of comparison. It varies in appearance from a woody material to a black jellylike substance and is relatively high in oxygen and water content.

It must usually be dried and compressed before it can be used as a fuel. Peat has no commercial significance in this country at the present time because of the abundance of fuels of higher rank.

Lignite is a brown coal of distinctly woody or claylike appearance. It contains from 30 to 40 per cent of water as it comes from the mine. Upon losing this water during weathering, it splits up into slabs. There are fairly large deposits of lignite in Montana, but it is burned only close to the mine where it can compete with the more costly coals from the East.

Subbituminous is the name used for coals lying between bituminous coal and lignite. They are usually glossy black in color and can be distinguished from the lignites by their apparent lack of woody structure. They contain a large amount of water compared to bituminous coal and crack irregularly on losing their moisture by weathering. Such coals are found in Wyoming and are used in that locality as they are cheaper to use than the eastern bituminous coals because of the transportation charges on the latter.

Bituminous coal, "soft coal," is the main fuel for industrial purposes, being used under steam boilers, in the manufacture of coal gas, producer gas, and coke, and for direct heating of furnaces. The main distinguishing feature of bituminous coal is the higher content of volatile matter as compared with semibituminous coal. Bituminous coal is laminated in structure, burns with a long yellowish flame, and gives off a heavy yellow smoke of a characteristic odor. If bituminous coal cakes together in a solid mass on heating, it is known as a coking coal. If, on the other hand, it does not soften and cake on heating, it is called a noncoking coal.

Semibituminous is the class name used for those coals which are slightly higher in fixed carbon and lower in volatile matter contents than bituminous coal and are, therefore, of higher rank. Owing to its low V.C.M., semibituminous is practically a "smokeless" coal and is used as a domestic fuel in many sections of the country. The best coals of this variety have a higher heating value than any other class and are in great demand for steam power plant use.

Semianthracite, although a hard coal, is not so hard as anthracite, does not have so high a fixed carbon content, but has a

TABLE 2-VII.—CLASSIFICATION OF COALS BY RANK*[1]

F.C. = fixed carbon; V.M. = volatile matter; B.t.u. = British thermal units

Class	Group	Limits of fixed carbon or B.t.u. mineral-matter-free basis	Requisite physical properties
I. Anthracite.....	1. Meta-anthracite...	Dry F.C., 98% or more. (Dry V.M., 2% or less)	
	2. Anthracite.....	Dry F.C., 92% or more and less than 98%. (Dry V.M., 8% or less and more than 2%)	
	3. Semianthracite....	Dry F.C., 86% or more and less than 92%. (Dry V.M., 14% or less and more than 8%)	Nonagglomerating[2]
II. Bituminous[3].....	1. Low-volatile bituminous coal	Dry F.C., 78% or more and less than 86%. (Dry V.M., 22% or less and more than 14%)	
	2. Medium-volatile bituminous coal	Dry F.C., 69% or more and less than 78%. (Dry V.M., 31% or less and more than 22%)	
	3. High-volatile A bituminous coal	Dry F.C., less than 69%. (Dry V.M., more than 31%); and moist[4] B.t.u. 14,000[5] or more	
	4. High-volatile B bituminous coal	Moist[4] B.t.u., 13,000 or more and less than 14,000[5]	
	5. High-volatile C bituminous coal	Moist B.t.u., 11,000 or more and less than 13,000[5]	Either agglomerating or nonweathering[6]
III. Subbituminous..	1. Subbituminous A coal	Moist B.t.u., 11,000 or more and less than 13,000[5]	Both weathering and nonagglomerating
	2. Subbituminous B coal	Moist B.t.u., 9500 or more and less than 11,000[5]	
	3. Subbituminous C coal	Moist B.t.u. 8300 or more and less than 9500[5]	
IV Lignitic.....	1. Lignite.....	Moist B.t.u. less than 8300	Consolidated
	2. Brown coal.....	Moist B.t.u. less than 8300	Unconsolidated

* From A.S.T.M. Standards on Coal and Coke, prepared by Committee D-5 on Coal and Coke, October, 1938, Published by American Society for Testing Materials.

[1] This classification does not include a few coals which have unusual physical and chemical properties and which come within the limits of fixed carbon or B.t.u. of the high-volatile bituminous and subbituminous ranks. All these coals either contain less than 48 per cent dry, mineral-matter-free fixed carbon or have more than 15,500 moist, mineral-matter-free B.t.u.

[2] If agglomerating, classify in low-volatile group of the bituminous class.

[3] It is recognized that there may be noncaking varieties in each group of the bituminous class.

[4] Moist B.t.u. refers to coal containing its natural bed moisture but not including visible water on the surface of the coal.

[5] Coals having 69 per cent or more fixed carbon on the dry, mineral-matter-free basis shall be classified according to fixed carbon, regardless of B.t.u.

[6] There are three varieties of coal in the high-volatile C bituminous coal group: Variety 1, agglomerating and nonweathering; Variety 2, agglomerating and weathering; Variety 3, nonagglomerating and nonweathering.

higher percentage of V.C.M.—in fact, high enough to produce a slightly yellow flame when ignited. It is not found in large quantities and is usually sold as anthracite for domestic purposes.

Anthracite, "hard coal," burns with a short blue flame, gives off but little odor, and does not soften or cake. It is hard and black in appearance and is an exceptionally good domestic fuel. The sizes too small for domestic use are sometimes used for steam-raising purposes.

Table 2-VII shows that as the rank increases, the V.C.M. decreases and the F.C. increases progressively. With increase in rank, the heating value in B.t.u. per pound increases to a maximum in semibituminous coals and decreases with further increase in rank. Semibituminous coals have the best combination of V.C.M. and F.C. to produce a maximum heating value.

Production.—Geographically, North America has the greatest supply of coal, although Europe, Australia, and Eastern Asia have vast supplies. Africa and South America are comparatively poor in coal resources, but neither continent has been as fully surveyed geologically as the other continents and may have much larger resources than are suspected. South America contains, at present knowledge, less than 1 per cent as much coal as the northern continent.

The coals of North America are not equally distributed geographically. The United States had, previous to mining, more than three times the coal resources of Canada, although they are very nearly the same size. Newfoundland and the Central American countries have negligible quantities of coal. The United States alone has greater coal resources than any other country or continent, at least with our present knowledge of coal resources.

In the United States, Pennsylvania has played a prominent part in coal production. In amount of coal resources, Pennsylvania ranks third, both Illinois and West Virginia having greater quantities. In point of combined production of bituminous and anthracite, however, Pennsylvania has led from early times until recent years. Table 3-VII indicates the original estimated coal resources, including class of coal, and the production in 1930, 1939, and 1940 for the six leading coal producing states of this country. About 90 per cent of the coal produced in the country is

consumed by general manufacturing, railroads, domestic heating, and coke production, listed in order of decreasing consumption.

TABLE 3-VII.—ESTIMATED COAL RESOURCES AND COMPARATIVE PRODUCTION FOR THE SIX LEADING COAL-PRODUCING STATES IN THE UNITED STATES

State	Estimated original resources* (in million metric tons—2,204 lb.)				Production† (in million short tons —2,000 lb.)		
	Known coal area, square miles	Bituminous	Semi-bituminous	Semi-anthracite and anthracite	1930	1939	1940
Pennsylvania:							
Anthracite	480	.....	.....	19,056 3	69.4	51.5	51.5
Bituminous	14,200	93,080	9,074	. . ..	124 46	92.1	112.9
West Virginia	17,000	111,293 5	27,132	... .	121.47	107.8	126.2
Kentucky.	15,170	111,913	..	... ...	51.20	42 7	48.4
Illinois	35,600	182,758 4	..	.... ..	53 73	46 4	49 5
Indiana... ..	6,500	48,140 7	.... .	.... ..	16.49	16.7	18.6
Ohio..... .	12,660	85,270	.. .	.....	22.55	19.6	22.1

* MOORE, E. S., "Coal," John Wiley & Sons, Inc., New York, 1940.
† *Minerals Yearbook*, 1940.

PETROLEUM AND NATURAL GAS

Although its principal product, gasoline, is not a source of industrial heat, petroleum contributes a large amount of fuel for industrial purposes in the form of fuel oil, a by-product of gasoline and lubricating oil refining. Where fuel oil is available at low cost, it is a strong competitor of coal and natural gas. Because of their common origin, petroleum and natural gas will be considered together.

Origin of Petroleum and Natural Gas.—Petroleum is undoubtedly of organic origin, but whether of vegetable or animal origin is still a matter of some doubt—both very probably had a part in it. The source beds of the petroleum deposits were laid down millions of years ago at the bottoms of shallow, warm saline waters. In such shallow seas, especially those which were relatively stagnant, all kinds of life were very abundant. Sea plants and animals of all kinds were, therefore, very prolific

and lived on the bottom, swam in the water, or floated at or near the surface. When these plants and animals died, their remains sank to the bottom and were gradually buried by deposits of fine mud or sand. Decay, produced by bacteria, proceeded until deep burial by later sediments prevented further decomposition. These partly decayed organic remains became intimately intermingled with the sediments and, after collecting in this manner for thousands of years, were slowly buried under thousands of feet of sediment because of changed conditions.

Very little petroleum was formed during the period of deposition but it was formed as a result of slow distillation caused by

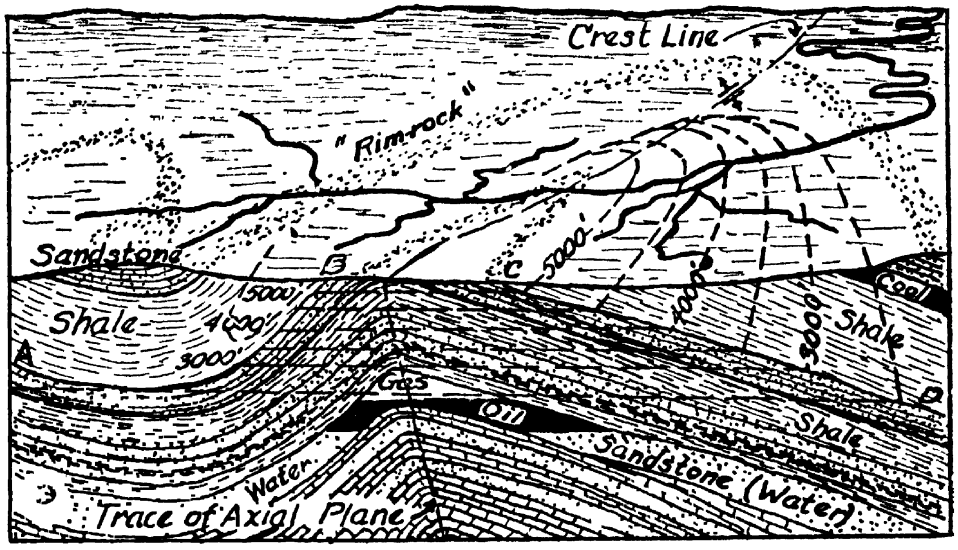


FIG. 4-VII.—A structural trap showing the manner of accumulation of commercial pools of oil and gas.

intense pressure. The weight of the thousands of feet of overlying material changed the sediments deposited with the organic remains into hard rocks—shales, sandstones, and limestones. This pressure, together with the increase in temperature caused by deep burial, started a slow distillation of the organic remains into oil and natural gas. It has been estimated that 84,000 years were required for 1 per cent of the organic matter in a bed 9,000 feet below the surface to be converted into petroleum. Internal forces in the earth's crust, such as mountain-forming movements, accelerated this action by increasing the pressure very greatly.

As this slow distillation proceeded, the more volatile products formed natural gas and the less volatile ones formed petroleum.

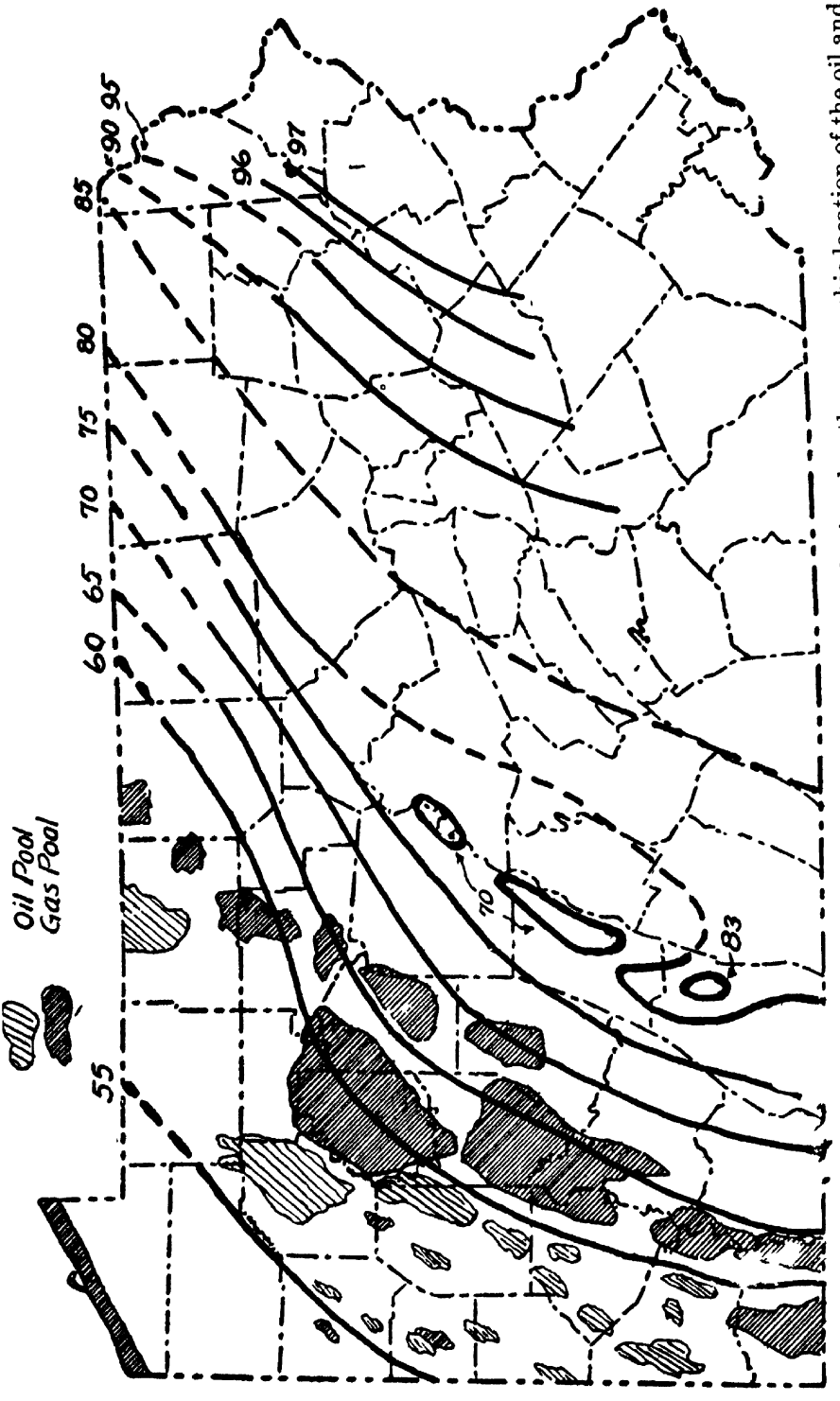


FIG. 5-VII.—Isocarb map of Pennsylvania, showing the relation of rank of coal to the geographic location of the oil and gas belts. (*After David White.*)

Both began to migrate through the porous sandstone or limestone formations toward the surface until stopped by a geological formation which prevented further rise. Gas and oil, trapped in a structural formation such as is shown in Fig. 4-VII, form a commercial pool from which some of the oil may be taken by drilling methods. Owing to difference in specific gravity, the gas is at the top of the trap, the oil beneath it, and water (usually salt water squeezed from the sedimentary rock by the pressure) below the oil.

The effect of thrust pressure (mountain-forming movements) on the distillation of organic remains is to convert more of this material into natural gas. Pools of natural gas are found in regions of high thrust pressure and oil pools in regions of lower thrust pressure. Gas is always found in conjunction with oil, however. This is well illustrated in Pennsylvania by the fact that the large natural-gas pools are located east of the oil fields because the thrust pressure was greater in the eastern portion of the state than in the western portion and decreased rather uniformly from east to west. Figure 5-VII shows the location of the oil and gas pools of the state with relation to the carbon ratio of the coal deposits. The carbon ratio is determined by calculating the fixed carbon content from coal samples from all known beds on an ash- and moisture-free basis and plotting the results on the map. Lines of equal carbon ratio are drawn through the plotted results and are known as *isocarb* lines. It can be seen that the gas pools are located in regions of higher carbon ratio than the oil pools and that these lines follow the direction of the mountains in the state, *i.e.*, the thrust pressure increased from west to east.

Composition.—Petroleum is a very complex mixture of hydrocarbons containing some nitrogen and sulfur, the base being either asphalt, paraffin, or a mixture of the two. The ultimate analyses of several representative crude oils are given in Table 4-VII.

Most crude petroleums are subjected to fractional distillation in order to separate the various products. This process consists essentially in heating the crude petroleum in a still and condensing the volatile constituents after they separate from the crude. Fuel oil has been defined as "any petroleum product used for the generation of heat," and commonly falls into one of four

classes: (1) crude petroleums, (2) distillate fuel oils, (3) residual fuel oils, and (4) blended fuels.

The crude petroleums that are used as fuel oils are of relatively low commercial value otherwise. Weathered crudes, those which have lost an appreciable quantity of the more volatile constituents by evaporation during storage, often find use as fuel oil. Undistilled crudes are somewhat more dangerous from the standpoint of fire hazard than other types because of their volatile constituents. Distillate fuel oils are obtained from rather complete refining operations. They consist of the frac-

TABLE 4-VII.—ULTIMATE ANALYSES OF REPRESENTATIVE CRUDE PETROLEUM*

Source	Per cent				Gravity, °Bé
	Carbon	Hydrogen	Oxygen + nitrogen	Sulfur	
Pennsylvania	84 9	13 7	1 4	.	28
West Virginia	83.5	13 3	3.2	. .	30
Ohio	84.2	13 1	2.7	. .	28
Calif., Bakersfield	81.5	10.0	6.9	0 55	15
Texas, Beaumont	84 6	10 9	2.9	1 63	22
Mexico	83 7	10 2		4.15	22
Russia, Baku	86 6	12 3	1 1	. .	17

* HASLAM and RUSSELL, "Fuels and Their Combustion," McGraw-Hill Book Company, Inc., New York, 1926.

tions with boiling points lying between those of kerosene and lubricating oils and are free from heavy residual tar. Residual fuel oils are those resulting from "topped" crudes. The crude is given an incomplete distillation to recover the valuable gasoline and kerosene as well as remove the objectionable water content. The remainder is used as fuel oil and is much safer to handle than crude petroleum. The blended fuels are mixtures of any or all of the above three classes.

The specifications for fuel oil are relatively simple. They must be low enough in viscosity at ordinary temperatures to be pumped to the burners, and they must be sufficiently free from volatile matter to permit safe handling. A flash point (the temperature at which the oil can be ignited) above 150°F.

is usually specified. Water and sediment are usually limited to not over 1 per cent for the less viscous oils and not over 2 per cent for the more viscous ones. The U.S. Government specifications cover four grades of fuel oil known as Navy Standard and Bunker A, B, and C. The requirements are shown in Table 5-VII. The heating value is usually about 18,500 B.t.u. per lb.

TABLE 5-VII.—UNITED STATES GOVERNMENT FUEL OIL SPECIFICATIONS*

Name and grade	Flash point, Pensky-Martens, minimum, °F.	Water, maximum, %	Sediment, maximum, %	Water and sediment, maximum, %	Furol viscosity at 77°F., maximum, seconds	Furol viscosity at 122°F., maximum, seconds	Sulfur, maximum, %
Navy Standard. . .	150	. .		1 0	100	. . .	1.5
Bunker A . .	150		.	1 0	100		
Bunker B .	150	.		1 0	. . .	100	
Bunker C	150	1 75	0 25			300	

* *U.S. Bur. Mines, Tech. Paper* 323B.

Composition of Natural Gas.—The chemical composition of natural gas varies from field to field but for the most part methane, CH_4, constitutes from 85 to 99 per cent. Ethane, C_2H_6, propane, C_3H_8, butane, C_4H_{10}, and heavier hydrocarbons are found in varying amounts. Hydrogen sulphide, H_2S, nitrogen, helium, and carbon dioxide also occur in some natural gases. Table 6-VII gives some typical analyses of gases produced in this country.

The source of the samples is as follows:

1. Alma gas field, Crawford County, Arkansas.
2. Torrance field, California.
3. Green County, Pennsylvania.
4. Follansbee district, Brooke County, West Virginia.
5. Rattlesnake anticline, New Mexico.

Propane, butane, and pentane are heavy gases with boiling points in the range of atmospheric temperatures. By the application of moderate pressures it is possible to liquefy these gases and separate them from ethane and methane. These easily condensed gases are becoming increasingly important as sources of gaseous fuel where pipe lines are not available. It is possible

to ship these gases in tank cars under pressure. While under pressure, the compounds are liquid; when the pressure is released, they either vaporize spontaneously or may be vaporized with a very small addition of heat. The heating values of the com-

TABLE 6-VII.—TYPES AND VARIETIES OF NATURAL GASES*

Constituent	Percentage				
	1	2	3	4	5
Methane, CH_4	99 2	87 04	73 14	..	9 83
Ethane, C_2H_6	.	4 13	23 81	21 8	27 58
Propane, C_3H_8		2 56	..	77 7	41 57
Butane, C_4H_{10}		2 00	..	....	19 7
Pentane and heavier, $C_NH_2N_2$		3 42			
Nitrogen, N_2	0 6		2 85	0.5	1.14
Carbon dioxide, CO_2	0 2	1 11			

* Taken from "Geology of Natural Gas," The American Association of Petroleum Geologist, Tulsa, Okla. "Natural Gas," by Henry A. Ley, Geologist, Fort Worth, Tex.

mon gaseous compounds found in industrial fuels are given in Table 7-VII.

TABLE 7-VII.—HEATING VALUES OF COMMON GASEOUS COMPOUNDS

Gas	B.t.u. per Cu. Ft.
Methane, CH_4	1000
Ethane, C_2H_6	1760
Propane, C_3H_8	2550
Butane, C_4H_{10}	3200
Pentane, C_5H_{12}	4090
Hexane, C_6H_{14}	4880
Hydrogen, H_2	325
Carbon monoxide, CO	323

COMBUSTION OF FUELS

Theoretical.—We have seen that the primary fuels, coal, petroleum, and natural gas, vary greatly in both physical and chemical characteristics. In addition, they are very complex mixtures of compounds that are very complicated in themselves. Although the number of compounds existing in coal or petroleum is uncertain, it is known that they number in the hundreds. From the standpoint of combustion, however, these various compounds can be divided into three classes and the individual

compounds have the characteristics of one of the classes. For example, although all hydrocarbons burn somewhat differently from one another, such a great similarity exists between them that they may be considered as belonging to a single class. In the same way, minor differences occur in solid carbonaceous fuels, but they are all sufficiently alike to be grouped together.

We may, therefore, consider the various complex fuels as being mixtures of three simple or elementary fuels: (1) solid carbon, (2) gaseous hydrocarbons, and (3) a mixture of carbon monoxide plus hydrogen. The complex fuel may be a simple mixture of elementary fuels or the elementary fuels may be formed by decomposition of the complex fuel but before actual combustion starts. Coal gas is an example of the former type, being a mixture of gaseous hydrocarbons and carbon monoxide plus hydrogen.

Coal, on the other hand, is decomposed before combustion although the process is a very rapid one. When coal is fed into a fire, it is first distilled by the heat, giving off gaseous hydrocarbons, carbon monoxide, and hydrogen, and leaving behind a residue of solid carbon (coke). The combustion of coal consists, therefore, in its decomposition into all three of the elementary fuels, followed by the combustion of these elementary fuels. Also, in the burning of fuel oil, the oil is first volatilized into gaseous hydrocarbons before actual combustion. When the fuel oil burns with a smoky flame, however, it means that the complex constituents of the oil are decomposed or "cracked," to a greater or less extent, into the elementary fuels, solid carbon and hydrogen. This action is practically instantaneous, and it may be said that the decomposition of the complex fuel may take place either before the final combustion of the elementary fuels (coal) or simultaneously with it (fuel oil).

The mechanism of the combustion of *solid carbon* is as follows: Hot carbon unites with air passing over it, forming carbon dioxide, some carbon monoxide, and an intermediate complex substance C_xO_y. This last compound breaks down to from CO_2 and CO, which are given off and more C_xO_y formed. At low temperatures, the products of combustion consist largely of CO and at high temperatures, as those encountered in the fuel bed of a furnace, the initial product of combustion is CO_2. This CO_2 may either, entirely or partly, be reduced to CO, the

extent of this secondary reaction being dependent upon the relative amounts of carbon and oxygen, the time of contact between the CO_2 and carbon, the ability of the carbon to react, and the temperature. In the presence of excess oxygen over that theoretically required to burn solid carbon completely, CO_2 is the end product. If insufficient oxygen is present, however, CO is the principal product.

The mechanism of the combustion of *gaseous hydrocarbons* is as follows: When hydrocarbons burn, there is first an addition of oxygen to the hydrocarbon molecule, producing unstable compounds which, at high temperatures, form compounds known as *aldehydes*. These aldehydes are, in turn, broken down or oxidized to produce the compound formaldehyde, CH_2O. The formaldehyde may break down to form CO and hydrogen, or it may burn to either CO and water or CO_2 and water, depending upon the amount of oxygen present. This mechanism is partly illustrated for the case of methane in the following equations:

$$2CH_4 + O_2 \rightarrow 2CH_3OH$$
$$2CH_3OH + O_2 \rightarrow 2CH_2O + 2H_2O \text{ (formaldehyde formation)}$$
$$CH_2O \rightarrow CO + H_2 \text{ (thermal decomposition)}$$
$$2CH_2O + O \rightarrow 2CO + 2H_2O \text{ (insufficient oxygen supply)}$$
$$CH_2O + O_2 \rightarrow CO_2 + H_2O \text{ (excess supply of oxygen)}$$

The mechanism is essentially the same for more complex gaseous hydrocarbons.

If sufficient oxygen is present so that all the hydrocarbons may be transformed into formaldehyde, no smoke or soot is produced. The more complex hydrocarbons, however, may also decompose into carbon (soot) and hydrogen. For example, the hydrocarbon decane, $C_{10}H_{22}$, may decompose into carbon and hydrogen according to the simplified equation

$$C_{10}H_{22} \rightarrow 10C + 11H_2$$

This is an example of the process known as *cracking*. Under ordinary combustion conditions, both cracking of the hydrocarbons and their oxidation to CH_2O take place, but one reaction gains the ascendency over the other depending upon the conditions. If the conditions are favorable to oxidation to formalde-

hyde, called *hydroxylation*—preheating of hydrocarbons and air as well as allowing time for entrance of oxygen into the hydrocarbon molecule—there will be no soot. If the conditions favor cracking—insufficiency of air and limited time—the hydrocarbon decomposes into soot and hydrogen and burns with a smoky flame.

Under the conditions of most importance in ordinary combustion work, mixtures of CO and hydrogen burn as if the reactions were

$$2H_2 + O_2 \rightarrow 2H_2O$$
$$2CO + O_2 \rightarrow 2CO_2$$

The conditions under which the above occur are

1. Quiet burning under approximately atmospheric pressure and at temperatures between 1300 and 2700°F.
2. Combustion occurring in a free space.
3. The two gases burning at the same time with an excess of oxygen.

Under these conditions, hydrogen burns nearly three times as fast as carbon monoxide. The actual mechanism of combustion of this mixture is oftentimes more complicated but the over-all result is the same as that given in the equations.

From the preceding discussion it can be seen that the combustion of all the fuels discussed depends ultimately on a comparatively few reactions, regardless of the complexity of the fuel. These reactions are given in Table 8-VII together with the heats of the reactions in B.t.u. under varying conditions. In column (1) are given the heats evolved or absorbed with the initial substances at 60°F. and the products cooled back to 60°F. after combustion. Column (2) gives the heats of reaction at 1832°F. (1000°C.), both the initial and final substances being at that temperature. These values are often of greater use than those in column (1) when the fuels are preheated. Column (3) shows the heat available above 1832°F., the initial substances being at 60°F. and the final substances being cooled to 1832°F. after combustion. The same conditions are true for the values in column (4) except that air is used instead of oxygen. The difference lies in the fact that the inert nitrogen must be heated to 1832°F. All values are for conditions of constant pressure and represent the heat evolved or absorbed when the weights

of the substances, expressed in *pounds*, react to the equations. For example, when 12 lb. of carbon and 32 lb. of oxygen react to form 44 lb. of CO_2, 174,600 B.t.u. are evolved under the conditions set up in column (1).

The direct oxidation of carbon to CO [reaction (1)] does not occur in most combustion work, although CO may be formed to a very limited extent in some cases. Reaction (1) is usually the result of reaction (2) followed by reaction (3). This can be shown to be true by adding reactions (2) and (3) algebraically, as follows:

$$\begin{array}{r} C + O_2 = CO_2 \\ CO_2 + C = 2CO \\ \hline CO_2 + C + C + O_2 = CO_2 + 2CO \end{array}$$

TABLE 8-VII.—HEATS OF REACTION OF MOST IMPORTANT COMBUSTION REACTIONS AT CONSTANT PRESSURE IN B.T.U. PER POUND MOL

Reaction	(1)	(2)	(3)	(4)
(1) $C + \frac{1}{2}O_2 = CO$	+52,200	+53,200	+39,400	+15,300
(2) $C + O_2 = CO_2$	+174,600	+175,000	+154,800	+106,600
(3) $C + CO_2 = 2CO$	−70,200	−68,600	−95,800	
(4) $C + H_2O = CO + H_2$	−70,900	−54,500	−96,500	
(5) $C + 2H_2O = CO_2 + 2H_2$	−71,600	−40,400	−117,000	
(6) $CH_4 = C + 2H_2$	−36,800	−49,600	−69,800	
(7) $CH_4 + 2O_2 = CO_2 + 2H_2O$	+384,000	+340,800	+295,000	+198,600
(8) $C_2H_4 = 2C + 2H_2$	+27,000	+13,300	−13,400	
(9) $C_2H_4 + 3O_2 = 2CO_2 + 2H_2O$	+622,400	+578,700	+513,600	+369,000
(10) $2CO + O_2 = 2CO_2$	+244,800	+243,600	+205,200	+157,000
(11) $2H_2 + O_2 = 2H_2O$	+246,200	+215,400	+177,000	+128,800
(12) $CO + H_2O = CO_2 + H_2$	−700	+14,100	+33,300	

* HASLAM and RUSSELL, "Fuels and Their Combustion," McGraw-Hill Book Company, Inc., New York, 1926.

This reduces to $2C + O_2 = 2CO$ which is just twice reaction (1). Reaction (2) may be considered to be nonreversible under the conditions present in the fuel bed of a furnace while it takes place practically instantaneously at 1800°F. and higher temperatures. The reduction of the product (CO_2) with carbon [reaction (3)] is of great importance in the gas producer. At the same time that this reaction is taking place, CO is dissociating relatively slowly, according to the equation $2CO \rightarrow C + CO_2$. This is the reverse of reaction (3) and is the reason why reaction (3) never goes to completion, some CO_2 always being left unreduced.

Reactions (4), (5), and (12) are of great importance in both producer and water-gas manufacture. When steam reacts with carbon, reactions (4), (5), and (3) go on almost simultaneously and are also accompanied by reaction (12). The velocities of these reactions are relatively slow below 1800°F. but increase rapidly with increase in temperature, becoming practically instantaneous at 2700°F. and higher. These four reactions will be considered again later in this chapter.

Reaction (6) represents the cracking of methane while reaction (7) indicates the over-all effect of the combustion of methane, the actual mechanism of which has been discussed. Reactions (8) and (9) are essentially the same as (6) and (7) except that they are for the simplest of the so-called "unsaturated" hydrocarbons. Reactions (10) and (11) represent the combustion of CO and H_2, respectively. Both (10) and (11) are reversible but the extent of dissociation of CO_2 [reaction (10)] at 2800°F. is only 0.4 per cent. This leads to the conclusion that there can be little, if any, free CO in combustion gases containing free oxygen under the conditions encountered in combustion practice. The dissociation of H_2O [reaction (11)] is also very slight, being only 0.37 per cent at about 3200°F.

Combustion of Coal.—By far the majority of the coal that is burned in furnaces is burned on grates. When the green coal is put into the furnace, the volatile matter distills off, leaving coke on the grate. The volatile matter consists essentially of the elementary fuels, gaseous hydrocarbons, and CO plus hydrogen. The final products of combustion of these elementary fuels are water and CO_2, while the coke left on the grate is partly burned to a mixture of CO_2 and CO, the CO being burned later to CO_2. On the fuel bed, therefore, distillation of the coal occurs, followed by partial combustion of the coke (to $CO + CO_2$). Over the fuel bed, combustion of the volatile matter (CH_4, H_2, CO, etc.) takes place as well as the combustion of the CO resulting from the partial combustion of the coke. The distillation of the volatile matter begins at about 660°F. and is quite rapid at 1300°F., the hydrocarbons appearing first followed by H_2 and CO at higher temperatures. The volatile constituents, tar, etc., which are distilled off carry about 30 per cent of the heat of the coal. In addition, the coke on the grate is incompletely burned and further raises the above figure so that from 40 to 60 per cent of

the heat in the coal is usually developed in the combustion space over the fuel bed. Part of the air required for combustion enters under the fuel bed, passes up through it, and burns the coke to a mixture of CO and CO_2. This portion of the total air required is called the *primary* air. The very important additional air which must be admitted over the fuel bed in order to burn the volatile matter and CO is called *secondary* air.

The fire bed may be divided into four zones, from bottom to top: the ash, oxidation, reduction, and distillation zones. In the *distillation zone* at the top, the coal is separated by distillation into coke and volatile matter. Part of the coke thus formed is burned to CO_2 in the *oxidation zone* by the primary air entering at the bottom of the fuel bed. The CO_2 thus produced travels up through the bed and is partly reduced to CO by hot coke in the *reduction zone*. The *ash zone* below the oxidation zone protects the grate bars from excessive heat. Under ordinary conditions the rate of burning of the fuel and hence the heating capacity of a given furnace is dependent upon the amount of primary air, other factors being equal. The amount of secondary air admitted into the combustion space above the fuel bed controls the *efficiency* of the furnace. If too much air is admitted, the efficiency is low because the air that is not used must be heated by the furnace. If too little air is admitted, the efficiency is again low because the volatile matter and CO are not completely burned and the full heating value of the fuel is not recovered. If less than about 20 per cent total excess air is admitted to the furnace, however, complete combustion is not generally possible and more than this amount is generally used in practice.

One of the drawbacks of hand-fired furnaces is that much smoke is often produced, creating a nuisance and lowering the efficiency of the furnace. Smoke is due to incomplete combustion and, in order to prevent it, the volatile gases rising from the top of the fuel bed should be mixed with air and then passed over the hot coals in order to promote combustion before the gases are chilled. This can be done by allowing the secondary air to enter through the fire door and sweep over the fuel bed. The coal should be fired in small amounts at frequent intervals in order to keep the amount of volatile matter released small and uniform in amount. Moistening the coal slightly may slow

down the rate of volatilization and make the evolution of volatile matter more uniform.

A further troublesome feature is clinker formation, caused by the softening and fusing together of the coal ash. It can best be avoided by keeping the ash as cool as possible. A thin fuel bed should be used to permit cooling of the ash by primary air rising through the grates. It is also important to refrain from disturbing the fuel bed as such a disturbance brings the ash up into the hot reducing zone where it will clinker readily. Burning coal must be kept out of the ash pit. The draft should be regulated by a stack damper and the ash-pit door kept open to admit air under the grates. The practice of admitting steam under the grates does aid in keeping the ash cool but it lowers the efficiency and should be used only when other methods fail.

In order to operate a hand-fired furnace with maximum efficiency, the following should be observed:

1. The fuel bed should be kept thin and uniform, *i.e.*, the same depth at all times.

2. The bed should be kept free of thin spots, particularly around the edges of the grate where air leakage may cause clinker formation.

3. The coal should be fired frequently in small amounts to obtain the maximum heat from the volatile matter.

4. The ash-pit door should be kept open (primary air entrance), the fire door opening fixed (secondary air entrance), and the draft regulated by the stack damper.

5. The excess of secondary air should be kept low and the leakage of air into the furnace through cracks kept at a minimum.

6. Draft gauges should be used, one just over the bed and the other in the breeching. The first shows the draft or pull through the fuel bed and the other the total draft of the furnace.

Mechanical stokers overcome the principal objections to hand firing by admitting the coal frequently in small amounts and by causing the volatile matter to be distilled in an oxidizing atmosphere. Furthermore, mechanical stokers possess the advantages of saving in labor, greater efficiency, and the ability of stoker-fired boilers to carry great overloads for short periods of time.

When coal is fired intermittently, there is a loss due to unburned volatile matter immediately after firing while during the remainder of the interval there is a large loss due to excess

air. With mechanical stokers, on the other hand, the coal is fired uniformly and continuously, the fuel is heated slowly, and the volatile matter is driven off continuously. This permits the use of a uniform draft and, therefore, a constant admission of the proper amount of air for efficient combustion. Furthermore, a thinner fuel bed can be carried with mechanical stokers, giving a higher capacity per cubic foot of free combustion space because the gases leaving the fuel bed are higher in CO_2. This means that the combustion is more complete in the fuel bed, *i.e.*, there is less chance for reduction of CO_2 to CO in the fuel bed and hence less free space is required for CO and hydrocarbon combustion above the fuel bed.

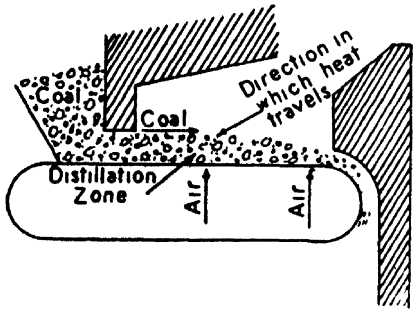


FIG. 6-VII.—Sketch of traveling-grate stoker.[1]

Three main types of mechanical stokers, shown in Fig. 6-VII, 7-VII, and 8-VII, are in use, known as the traveling grate type, the overfeed type, and the underfeed type. In the *overfeed* stoker, the grate is inclined downward into the furnace and pushers receive the coal from hoppers and push it down the inclined grates. The coal is coked and the volatile matter distilled in the upper part of the furncae by the heat

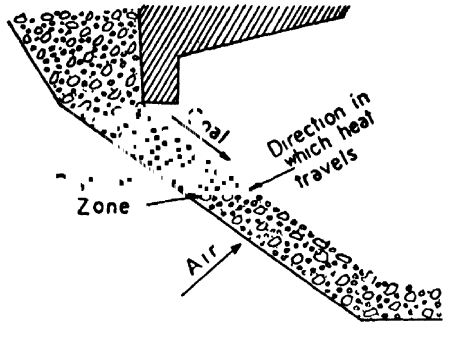


FIG. 7-VII.—Sketch of overfeed stoker.[1]

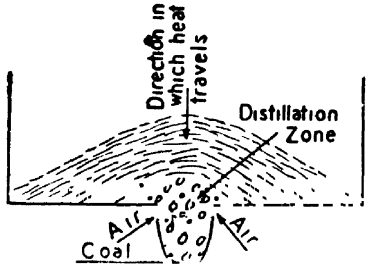


FIG. 8-VII.—Sketch of underfeed stoker.[1]

reflected from an arch, while the coke burns as it travels down the grates. The ash falls over the end of the grate into the ash pit.

The *chain* or *traveling-grate* stoker consists of parallel transverse grate bars fastened to two endless chains at both ends of the bars.

[1] HASLAM and RUSSELL, "Fuels and Their Combustion," McGraw-Hill Book Company, Inc., New York, 1926.

The endless chains pass over sprocket wheels at either end, thus forming a traveling grate, one sprocket being powered. The green coal is fed onto this moving horizontal grate from automatic hoppers, the coal is coked, and the volatile matter distilled by the heat reflected from an arch just inside the furnace. The resulting coke is burned during its travel through the furnace while the ash is dumped over the end sprocket into the ash pit.

In the *underfeed* type of mechanical stoker, the grate is inclined into the furnace, and the green coal is fed in by pushers situated in front of the furnace and is pushed in underneath the coal already on the grate. In this way, the distilled volatile matter passes up through the bed of incandescent coke.

In all types, the primary air enters through the bottom of the grate while the secondary air is admitted over the fuel bed. In overfeed and chain-grate stokers part of the primary air and, in underfeed stokers, practically all of the primary air passes through the green coal as it is being distilled. The distillation of volatile matter, therefore, takes place in an oxidizing atmosphere, thus causing the tendency for cracking and soot deposition to be minimized. The amount of coal fired and the amount of air supplied to the furnace may be regulated automatically with practically all types of stokers and it is, therefore, possible to feed into the furnace the coal and air properly proportioned and in amounts depending upon the load.

There is one further method of burning coal that deserves mention, and that is the firing of coal in powdered form. We have already seen that when coal is fired in lump form, the volatile matter is driven off first and the remaining coke combines with the primary air, the entire process taking place relatively slowly. With powdered coal, on the other hand, the fuel mixed with the proper amount of air for economical combustion is injected into the hot furnace in a finely divided condition. Under these conditions the distillation of the volatile matter takes place almost instantaneously and the small size of the resulting coke particles makes it relatively easy for them to combine with oxygen with great rapidity. This is due to the fact that the rate of reaction between oxygen and solid carbon depends upon the amount of exposed carbon surface. Since a cubical piece of coal 1 in. on a side has 6 sq. in. of surface while the same piece when ground to pass a 200-mesh screen has over

4,400 sq. in. of surface, it is easy to see why the combustion of powdered coal is so much more rapid.

The usual large powdered coal installation includes a crusher, drier, pulverizer, storage bins, apparatus for conveying the powdered coal to the furnaces, and burners for introducing the coal and air into the furnaces. The coal is first crushed to about a 1-in. size in roll crushers and then passed over a magnetic separator to remove any scrap iron that might be present. The free moisture is then removed in a drier heated by waste gases or steam. This step is necessary because free water in the coal reduces the capacity of and increases the difficulties with the pulverizing equipment. The coal is then finely pulverized in any of several types of fine grinders until of the desired size. Several types of grinders are equipped with air separators by means of which the particles of the correct size are removed from the machine to storage bins by the air flow and the coarser particles remain until they are ground finely enough to be carried out by the air current. The power cost for pulverizing is the largest single item in the cost of powdered coal firing and depends upon the degree of pulverization desired, the amount of moisture in the coal, and the physical character of the coal itself.

From the storage bins, the powdered coal is blown by compressed air to the furnace bins from which it is fed to the burners. The burners used are of two general types: (1) those having a mechanically operated screw conveyer which brings the coal into the path of the air for combustion and (2) those in which the fuel is fed by compressed air. The latter type is the simpler and the more common, the air pressure being low (2 to 8 oz. per sq. in.) unless long cutting flames are desired when high-pressure injectors (40 to 100 p.s.i.) are used. In one example of the second type, the burner is composed essentially of two concentric tubes. The powdered coal drops into the inner tube through an opening in the top and is picked up by the current of primary air and blown into the furnace. The secondary air is admitted to the annular space between the tubes and mixes with the coal and primary air just as combustion begins.

The advantages of powdered coal installations may be summarized about as follows:

1. *Flexibility.*—Powdered coal installations are able to change rapidly from almost no load to peak loads. Also, all of the

feeding equipment is outside the furnace and does not have to be cooled down in case of mechanical breakdowns to make repairs as do stoker-fired furnaces.

2. *Efficiency.*—Owing to nearly perfect combustion conditions, powdered coal can be almost completely burned with only small amounts of excess air. Close regulation of the desired rate of combustion can be easily maintained. The labor required is small, and the fuel distribution is easy.

3. *Range of Fuels.*—A wide range of fuels may be used successfully in powdered form. Coals of all types, from the low-grade fuels, such as lignite or high-ash graphitic anthracites, to the high-quality bituminous coals have been adapted for powdered coal firing.

4. *Control of Combustion.*—Practically smokeless combustion can be secured, even with high volatile fuels. Equally important is that the characteristics of the flame are under control, both as to length and as to its odixizing or reducing character.

The important disadvantages of powdered coal as a fuel are

1. *Cost of Equipment.*—The chief disadvantage of powdered coal is the cost of equipment necessary for its preparation. It is great enough to bar the use of powdered coal in small installations. Also, it is doubtful in many cases whether the savings possible will justify the replacement of up-to-date stokers with powdered coal equipment, owing to the high cost of the latter.

2. *Ash Fusion.*—The speed of combustion is so great that the small particles of ash present are often in the liquid state. This makes ash removal difficult. Where this ash strikes the furnace lining, rapid erosion of the brickwork often occurs. The ash is so finely divided that it is blown along with the stack gases and, in many cases, rapidly chokes up regenerators through which the gases may pass. In addition to its action on the furnace itself, the coal ash may also damage or contaminate the contents of the furnace.

The difficulty encountered in the elimination of the ash has operated against the use of powdered coal in many types of furnaces. However, in the past few years more attention has been given to this problem and in the future it may be possible to extend this economical and efficient method of firing.

Combustion of Fuel Oil.—The main problems in burning fuel oil consist in maintaining a uniform flow of heated oil to the

burners, in atomizing (producing very small droplets) the oil thoroughly, and in mixing it with the proper amount of air for combustion. The equipment necessary to handle the oil consists of storage tanks, strainers for removing dirt, pumps, oil heaters, piping, and burners.

The oil for the furnaces is usually stored underground in cities and towns to reduce the fire hazard. Steam-driven duplex reciprocating or electric pumps are most often used to bring the oil from the tanks to the burners. Strainers are inserted in the pipe line both before and after the pump to remove any foreign material that might plug either the pumps or the burners. Fuel oil is usually heated to lower its viscosity and to permit it to be atomized easily and efficiently. Where there is an appreciable fire risk, the oil is not heated above the flash point. The heaters are heated either by steam or waste gases from the furnaces.

There are four main types of oil burners in use: (1) The *spray* type, in which the oil is divided into a fine spray by being dropped into the path of compressed air or steam. The atomized oil is then mixed with air either inside or outside the burner proper. Burners using low-pressure air atomization are easier to regulate and are frequently used. (2) The *rotary* type, in which oil drops into the inner section of a revolving hollow cone or plate and is atomized by the action of centrifugal force. The air for combustion is supplied by a fan mounted directly behind the atomizing unit. (3) The *mechanical* type in which the oil under high pressure is atomized by forcing it through small slots. The accompanying reduction in pressure causes the hot oil to vaporize partly, thus aiding in atomization. The air is blown through an air pipe surrounding the burner. The oil pressures used are from 100 to 300 p.s.i. and the temperatures are from 140 to 280°F. (4) In the *vapor* type, the oil is vaporized, not atomized, in a stream of preheated air. These burners are used on furnaces where the air can be preheated by recuperators.

For the efficient operation of oil-fired furnaces, there are several important requirements that merit brief mention. In the first place, the burner or burners must thoroughly atomize the oil and the atomized oil must be thoroughly mixed with the proper amount of air for complete combustion. This requirement can be met by using properly designed burner equipment. Further, a high furnace temperature must be maintained to

sustain combustion and the combustion space must be large enough for the gases to burn completely before they are chilled. Also, the flame action must not be localized on either the material being heated or the furnace brickwork. These requirements can best be met by having ample combustion space, proper direction of the burner flame, and sufficient radiating surface to maintain high-combustion space temperatures.

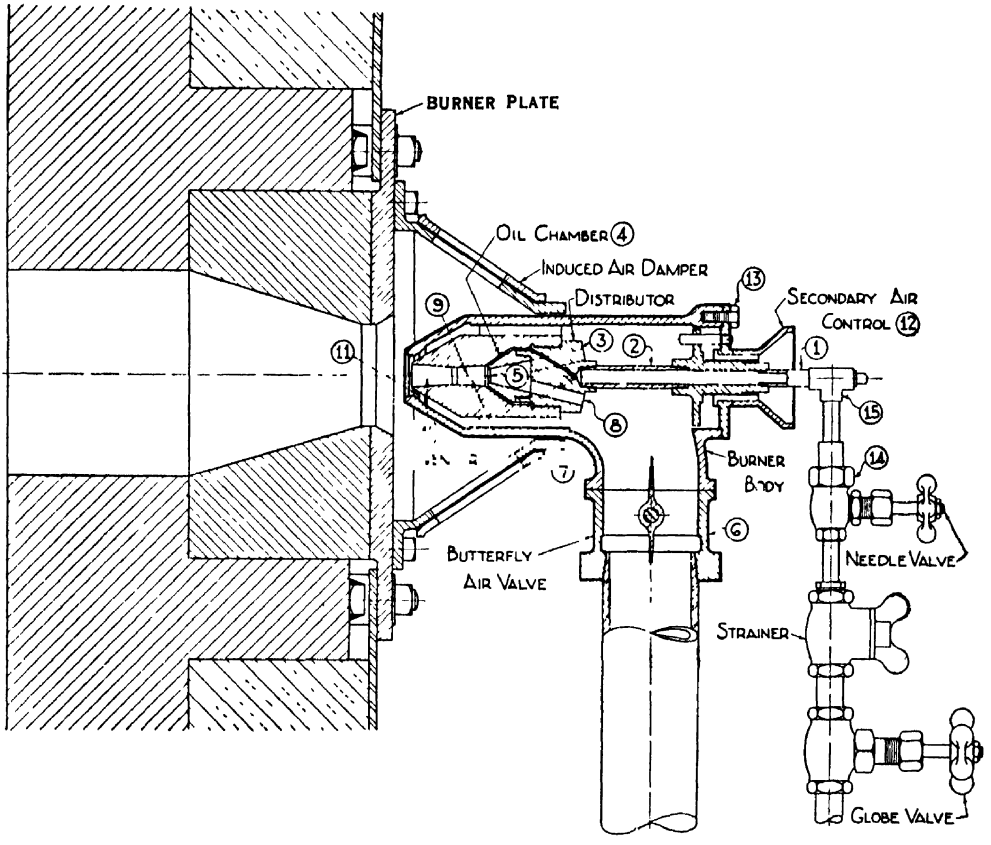


FIG. 9-VII.—Cross-sectional view of an oil burner. (*Courtesy of The Philadelphia Drying Machinery Company.*)

A cross-sectional drawing of an oil burner, designed for heat-treating furnaces, is shown in Fig. 9-VII. A large advantage of this burner lies in the fact that its minimum capacity can be made as low as ⅛ gal. of oil per hour. A big objection to many types of oil burners has been that they could not be throttled down enough for some operations. Oil enters the burner through the nipple (1) at the back, then passes through the central oil tube (2) to the distributor (3), where the oil is directed into the oil chamber (4) around the primary air orifice (5). Air enters the burner through the butterfly valve (6)

attached to the burner body (7). The butterfly valve is machined to shut tightly when the valve is closed. A stuffing box around the handle prevents air leakage and allows the valve to be held in any desired position. The inlet side of the butterfly valve is threaded for standard pipe. Part of the air enters the distributor head (3) through holes (8), then passes through the primary air orifice (5), and then through the venturi (9). As the air passes through the venturi (9), a partial vacuum is created in the oil chamber (4), so that the oil is withdrawn in a thin film around the primary air. The oil film is broken up into a fine mist and is intimately mixed with the primary air as it passes through the mixing tube (9). The secondary stream of air flows between the burner body and the outside of the venturi mixer (10), where it is given a whirling motion, and then discharged from the orifice (11) at the tip of the burner, where it acts upon the primary mixture, causing further atomization and mixing.

A variable capacity is obtained by turning the handwheel (12) at the back of the burner, which causes the venturi body to travel longitudinally, varying the secondary air opening (11). It can readily be seen that by this method of varying the air flow a constant discharge pressure is maintained over a wide range in burner capacity. This method of adjustment is also more convenient than adjusting a hot nozzle. Another advantage is the fixed relation between the burner orifice and the burner tile.

The advantages of oil as a fuel may be summarized as follows: (1) It weighs 30 per cent less and occupies 50 per cent less space than coal containing equivalent B.t.u. (2) There is no trouble from spontaneous combustion (as with coal) and no deterioration during storage. (3) It is much easier to handle than coal and its labor and handling costs are low. (4) The furnace can be run with practically no smoke and there is no ash problem. (5) High efficiencies, due to the low excess air required, are possible and easily maintained (see Table 9-VII). The disadvantages of oil as a fuel are the initial cost of the handling equipment and the cost of the oil itself.

Combustion of Gaseous Fuels.—The heating value of industrial gases ranges all the way from about 90 B.t.u. to over 2,400 B.t.u. per cubic foot, depending upon the composition. When

a gas is richer than 300 to 325 B.t.u. per cu. ft., the gas contains appreciable quantities of hydrocarbons in amounts depending upon the heating value of the gas. If the heating value is

TABLE 9-VII.—EXCESS AIR IN EFFICIENTLY OPERATED FURNACES OF VARIOUS TYPES*

Furnace	Per Cent Excess Air
Oil fired	15–25
Powdered coal fired	15–30
Chain-grate stoker fired	35–70
Hand fired	50–150

* HASLAM and RUSSELL, "Fuels and Their Combustion," McGraw-Hill Book Company, Inc., New York, 1926.

below 300 to 325 B.t.u., the gas contains inert materials (N_2, CO_2, H_2O) and the lower the heating value the greater the percentage of inerts present.

The principal problems in the combustion of gaseous fuels consists in getting the fuel to the furnaces, proportioning the gas and air properly, and then mixing them thoroughly just before combustion. The first problem is relatively simple as it can be taken care of by pumps and pipe lines, while the others are met by a properly designed and operated gas burner.

The burners are of three general types with regard to the method of admitting and mixing the gas and air: (1) The *port* type, in which separate streams of gas and air are passed into and mix within the furnace, is used mainly with highly preheated gas and air which, if mixed outside the combustion chamber, would explode; or with gas that is dirty and would clog other types of burners. (2) The *aspirator* type mixes the gas and air by the momentum of one or the other of the streams. One or both of the streams is under pressure and the momentum of one stream is sufficient to draw in the required quantity of the other. In this type, enough primary air may be introduced to make the theoretical mixture, or the momentum of an incomplete mixture may be used to induce the remainder of the necessary air. (3) In the third type, *proportioning machines* are used to mix all the air for combustion with the gas and the resulting mixture is delivered as a blast to the various furnaces. The choice and design of burners depend on the type of work the furnace is required to do and upon the heating value of the gas. The degree of mixing the gas and air is an important factor in con-

trolling the rapidity and completeness of combustion. If all the heat must be liberated quickly in a confined space, the gas and air must be thoroughly mixed. On the other hand, if a long, soft flame is required, combustion of the gas must extend over a considerable distance and mixing of the gas and air must be retarded. The larger the ratio of primary air to gas, the shorter will be the flame.

There is one further method by which gas can be burned with air—the method known as *surface combustion*. The method is based upon the principle that gaseous combustion is accelerated or catalyzed by solid surfaces. In the commercial applications of surface combustion, an explosive gas-air mixture in the theoretical proportions for complete combustion (or with slight excess air) is burned *without flame* in contact with an incandescent solid. The advantages claimed for this system are as follows: (1) Combustion is greatly accelerated and may be concentrated where heat is desired. (2) Combustion is perfect with a minimum of excess air. (3) Very high temperatures can be attained without the use of elaborate devices for preheating the gas and air. (4) Heat transmission is very rapid because of the large amount of radiant energy developed. The surface-combustion method is used to a considerable extent in heating and muffle type furnaces. In such cases, air and gas, mixed in the correct proportions, are admitted at both sides of the furnace and the mixture plays directly on piles of refractory material which become incandescent and on which surface combustion takes place.

The chief advantages of gaseous fuels in general are as follows: (1) Coal may be gasified at one point and the gas cheaply and easily conveyed to furnaces over a wide area. (2) Combustion permits easy control as to variation in temperature, in oxidizing or reducing character of the furnace atmosphere, and in length of flame. (3) When high temperatures are desired, gaseous fuels permit greater thermal efficiency, since the heat in the stack gases may be utilized to preheat the fuel and air. (4) Smoke and ash, often harmful to the material being heated, are eliminated. (5) Low-grade fuels can be gasified and burned more efficiently than by burning the low-grade fuels directly.

The chief disadvantage of gaseous fuels lies in their fire and explosion hazard. Certain mixtures of gas and air are explosive and must be handled with care in order to avoid an explosion.

Table 10-VII shows the limits of flammability (ability to burn) of certain gases in air at ordinary temperature and atmospheric pressure. Mixtures within these limits will burn if ignited, while mixtures above or below these limits will not ignite and continue

TABLE 10-VII.—LIMITS OF FLAMMABILITY OF GASES IN AIR*

Gas	Limits as per cent by volume in air	
	Per cent lower limit mixtures	Per cent upper limit mixtures
Hydrogen	6 2	71 4
Carbon monoxide	16 3	71 2
Coal gas	7	21
Coke-oven gas	7	21
Blue water gas	12	67
Blast-furnace gas	36	65
Methane	5 8	13 3
Ethane	3 3	10 6
Ethylene	3 4	14 1

* HASLAM and RUSSELL, "Fuels and Their Combustion," McGraw-Hill Book Company, Inc., New York, 1926.

to burn of their own accord (without continuous external application of heat).

Combustion Calculations.—In this section we are concerned with the quantitative relations accompanying the combustion of fuels. The methods of calculation are equally applicable to all kinds of furnaces, burning all classes of fuels. Before turning to the actual calculations, however, several general considerations will be taken up.

The *pound mol*—the molecular weight of the substance in pounds—is the unit of quantity most generally used in combustion calculations. It is a very convenient unit because a mol of any one gas is exactly equivalent to a mol of any other gas since they both contain the same numbers of molecules and, at the same temperature and pressure, will occupy equal volumes (Avogadro's hypothesis). The *mol fraction* of a substance in a mixture of several substances is the number of mols of the substance divided by the total number of mols in the mixture. From Dalton's law of partial pressures we know that the pressure

exerted by each component in a mixture of gases is proportional to its concentration in the mixture and the total pressure of the mixture is equal to the sum of those of its components. The pressure exerted by each component of the mixture divided by the total pressure is known as the *partial pressure* of that component. When dealing with gases, the following connection can be established between the above considerations by means of Avogadro's hypothesis:

$$\text{Volume per cent} = 100 \times (\text{mol fraction}) = \frac{100 \times \text{partial pressure}}{\text{total pressure}}$$

for any component of a gaseous mixture. We can, therefore, say that the volume per cent = the mol per cent = the partial pressure per cent for any component of a gaseous mixture. The pound-molecular volume, analogous to 22.4 liters in the metric system, is equal to 359 cu. ft. at 1 atm. pressure (29.92 in. of Hg.) and 32°F.

The B.t.u. is the common unit of heat in combustion calculations, although the centigrade heat unit (C.h.u.) is used to some extent. The C.h.u. is the amount of heat necessary to raise 1 lb. of water 1°C. and is equal to 1.8 B.t.u. The heat given up by a gas in cooling through a certain temperature interval is known as the *sensible heat* and is equal to the mean or average specific heat of the gas over that temperature range multiplied by the amount of the gas involved.

Table 11-VII gives the total heat above 32°F. contained in the common gases at various temperatures, *i.e.*, if a pound mol (44 lb.) of CO_2 is cooled from 1000 to 32°F., 10,000 B.t.u. are liberated. If a pound mol of CO_2 is cooled from 1000 to 100°F., however, the heat liberated is equal to 10,000 − 610 = 9390 B.t.u.

In solving combustion problems, the laws of conservation of matter and energy hold true and are a distinct aid in computation. For instance, the weight of coal and air going into a furnace over a definite time interval must equal the sum of the weights of the products of combustion, the excess air, and the unburned refuse in the ash pit. Furthermore, the recoverable heat in the coal over this same time interval must equal the sum of the heat necessary to heat the incoming air, the heat loss up the stack in the products of combustion, the heat transferred to the material

being heated, and the heat lost by radiation and conduction through the furnace walls.

If pure carbon could be burned with the theoretical amount of air (composition by volume: 79 per cent N_2 and 21 per cent O_2)

TABLE 11-VII.—HEAT CONTENTS OF GASES IN B.T.U. PER POUND MOL

Temperature, °F.	CO_2	H_2O	Diatomics (O_2, N_2, CO, H_2, air)
40	73	70	55
50	160	150	120
55	200	190	155
60	250	233	190
65	298	278	225
70	340	320	258
75	388	366	295
80	433	408	328
90	520	490	398
100	610	575	463
150	1,070	990	815
200	1,520	1,410	1,170
250	1,980	1,750	1,500
300	2,500	2,300	1,850
350	2,950	2,730	2,200
400	3,400	3,120	2,510
450	3,950	3,600	2,890
500	4,420	3,950	3,200
550	4,920	4,350	3,560
600	5,450	4,750	3,920
650	6,000	5,200	4,300
700	6,600	5,600	4,600
750	7,100	6,000	5,000
800	7,650	6,500	5,350
850	8,200	6,850	5,700
900	8,750	7,300	6,100
950	9,300	7,700	6,450
1000	10,000	8,200	6,800

required for combustion, CO_2 would replace the O_2 in the air, mol for mol, and the analysis of the combustion gases would necessarily be 21 per cent CO_2 and 79 per cent N_2. This is true because carbon burns according to the equation $C + O_2 \rightarrow CO_2$. If 50 per cent excess air were used, however, only two-thirds of the O_2 in the air would be replaced by CO_2, causing the compo-

sition of the flue gas to be 14 per cent CO_2, 7 per cent O_2, and 79 per cent N_2. The formation of CO, due to incomplete combustion, causes an additional difficulty because the reaction, $2C + O_2 \rightarrow 2CO$, shows that 2 mols of CO are obtained for each mol of O_2 used. Suppose that coke (hydrogen-free) is burned under such conditions that 75 per cent of the carbon burns to CO, the remainder to CO_2, and no excess air is used. Taking 100 atoms of carbon as a basis, 75 mols of CO and 25 mols of CO_2 will be formed for every 100 atoms of carbon burned. The oxygen required to form the CO will be $\frac{75}{2}$ or 37.5 mols, while 25 mols of O_2 are required for the CO_2 formation, the total being $37.5 + 25 = 62.5$ mols of O_2. Now, for every 100 mols of air, 79 mols of inert N_2 must appear in the stack gases. On the basis of 100 mols of air, the amount of O_2 going to CO formation is in the proportion of 37.5:62.5, or

$$\text{Mols } O_2 \text{ forming CO per 100 mols air} = 21 \times \frac{37.5}{62.5} = 12.6 \text{ mols}$$

$$\text{Mols } O_2 \text{ forming } CO_2 \text{ per 100 mols air} = 21 \times \frac{25}{62.5} = 8.4 \text{ mols}$$

The mols of CO formed $= 2 \times 12.6 = 25.2$ mols while the mols CO_2 formed $= 8.4$ mols. These data, together with the percentage composition of the flue gas, are given in Table 12-VII.

TABLE 12-VII

Component	Mols per 100 of air	Fraction of total	Per cent of gas
N_2	79.0	79.0/112 6	70.15
CO	25 2	25.2/112 6	22.4
CO_2	8.4	8.4/112 6	7.45
Total combustion gases.....	112.6		100.00

The presence of hydrogen in the fuel involves still another point. Pure hydrogen, when burned with the theoretical amount of air, would remove the oxygen from the air as water, . . . to the equation $2H_2 + O_2 \rightarrow 2H_2O$. Since water condenses before and during a gas analysis, the analysis in the above case would show 100 per cent N_2. With excess air, the corresponding oxygen would appear in the gas, with a decrease in the percentage

of N_2. For example, when 1 mol of methane is burned with 100 per cent excess air, according to the equation

$$CH_2 + 2O_2 \rightarrow CO_2 + 2H_2O$$

the result of this combustion would be 1 mol of CO_2, 2 mols of H_2O, and as much O_2 as was used in combustion (2 mols). The total O_2 entering is 4 mols and this amount of O_2 brought $4 \times 79/21 = 15.05$ mols of N_2 with it. The total mols of gas is, therefore, $15.05 + 1 + 2 \times 2 = 20.05$ mols, but only 18.05 mols of dry gas, because of the condensation of the water vapor. On the dry basis, the composition of the stack gas can be calculated as follows:

$$\frac{1}{18.05}(100) = 5.54 \text{ per cent } CO_2$$

$$\frac{2}{18.05}(100) = 11.08 \text{ per cent } O_2$$

$$\frac{15.05}{18.05}(100) = 83.38 \text{ per cent } N_2$$

Suppose that 1 mol of a mixture of equal volumes of CO and H_2 are burned with 30 per cent excess air but with only 90 per cent of the CO being converted to CO_2. The 0.5 mol of CO and 0.5 mol of H_2 would each require 0.25 mol of O_2, a total of 0.5 mol of O_2 for theoretical combustion. Using 30 per cent excess, the total O_2 entering would be $(1 + 0.3) \times 0.5 = 0.65$ mol. The O_2 present in the flue gas may be considered as coming from two sources: (1) the 0.15 mol used in excess of the theoretically required amount and (2) 10 per cent of the 0.25 mol theoretically required by the CO but not used in the combustion. The calcu-

TABLE 13-VII

	Mols	Fraction of total	Per cent dry basis
90 per cent of 0.5 mol CO	0 45 CO_2	0.45/3.12	14.4 CO_2
10 per cent of 0 5 mol CO.....	0 05 CO	0 05/3.12	1 6 CO
0.15 + 0.10 (0.25)	0 175 O_2	0 175/3 12	5 6 O_2
0.65 (79/21)	2 445 N_2	2.445/3.12	78 4 N_2
Total water-free gas.....	3 12		100.0
0.5 mol H_2...	0 50 H_2O		
Total gas.....	3 62		

lation of the flue gas analysis can be easily followed in Table 13-VII.

Coal and fuel oil contain carbon and hydrogen in proportions that are not in simple molal ratios as above. For example, the analysis of a fuel oil shows it to contain 84.6 per cent C., 10.90 per cent H, and 2.87 per cent O by weight (the symbols H and O are used because hydrogen and oxygen are combined and not present as gaseous molecules). This oil is burned with 20 per cent excess air, 95 per cent of the carbon burns to CO_2, the remainder to CO, and all the hydrogen is burned to water. It is desired to calculate the flue gas composition.

The oil analysis is first converted to a molal basis as the stack gas will be calculated on that basis. On a basis of 100 lb. of oil, we have

$$\frac{84.6}{12} = 7.05 \text{ atoms C}$$

$$\frac{10.90}{2.02} = 5.40 \text{ mols } H_2$$

$$\frac{2.87}{16} = 0.18 \text{ atom O}$$

The 0.18 atom of O is equivalent to an equal number of mols of H_2, because of the equation $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$. Since the H_2 in the oil combines with the oxygen in the oil, $5.40 - 0.18 = 5.22$ mols of net H_2 are left to combine with O_2 in the air.

$$5.22 \div 2 = 2.61 \text{ mols}$$

of O_2 are required to burn the net H_2. Oxygen is needed to burn both C and H_2, the total necessary O_2 being

$$7.05 + 2.61 = 9.66 \text{ mols}$$

Since 20 per cent excess was admitted, the total O_2 admitted is $9.66 \times 1.2 = 11.59$ mols, and the nitrogen entering with this 11.59 mols O_2 is $11.59\ (79/21) = 43.6$ mols N_2. The O_2 appearing in the flue gas is the sum of the actual excess,

$$0.2 \times 9.66 = 1.93 \text{ mols}$$

and the amount unused by the carbon due to its burning only to CO, $0.05\ (7.05)/2 = 0.18$ mol. The total O_2 in the stack

gas is then 2.11 mols. The CO_2 is 95 per cent of the carbon ($0.95 \times 7.05 = 6.70$ mols) while the remainder (0.35 mols) is CO. The total mols of stack gas per 100 lb. of oil is, then, $6.70 + 0.35 + 2.11 + 43.6 = 52.76$ mols on a dry basis and the analysis of the stack gas is as follows:

$$\frac{6.70}{52.76} \times 100 = 12.7 \text{ per cent } CO_2$$

$$\frac{0.35}{52.76} \times 100 = 0.6 \text{ per cent CO}$$

$$\frac{2.11}{52.76} \times 100 = 4.0 \text{ per cent } O_2$$

$$\frac{43.6}{52.76} \times 100 = 82.7 \text{ per cent } N_2$$

The principles set forth in the foregoing examples are put together in the following illustration, the data for which follows: A furnace burns a coke containing, as fired, 3.5 per cent moisture and 14.5 per cent ash. The balance of the coke may be considered as carbon and hydrogen, while the moisture content of the air and the combustible matter left in the ash may be considered as negligible. The flue gases from the furnace contain (by volume) 16.3 per cent CO_2, 0.4 per cent CO, 3.3 per cent O_2 and, by difference 80.0 per cent N_2. The temperature at which the flue gases leave the furnace is 550°F. while the air and coke enter the furnace at 50°F. From these data we can calculate many important quantities.

First, let us analyze the data obtained on the flue gas. Taking 100 mols of dry flue gas as a basis, we place the data in tabular form (see Table 14-VII). The components are placed in the first column and the mols of each per 100 mols dry flue gas (equivalent to the volume per cent) in the second column. The atoms of carbon from which the CO_2 and CO were formed can then be set down because 1 atom of carbon forms 1 mol of CO or CO_2. Finally, we can determine the mols of oxygen necessary to produce the CO and CO_2 or appearing in it, the O_2 appearing in the flue gas being placed in this column also. It is evident that one-half the mols of CO is the amount of O_2 necessary to form it, or 0.2 mol. The total of O_2 accounted for can be seen to be 19.8 mols.

TABLE 14-VII

Component	Mols	Atoms C	Mols O_2
CO_2	16 3	16 3	16.3
CO	0 4	0.4	0.2
O_2	3 3	....	3.3
N_2	80 0		
Total.....	100.0	16 7	19.8

Now, we know that the oxygen brought in with the 80 mols of N_2 must be $80.0 \times {}^{21}\!/_{79} = 21.25$ mols. Therefore,

$$21.25 - 19.8 = 1.45 \text{ mols } O_2$$

unaccounted for and this amount of oxygen must be that necessary to burn the net hydrogen in the fuel. From the equation

$$2H_2 + O_2 \rightarrow 2H_2O$$

we see that twice the O_2 disappearance is equivalent to the net hydrogen burned, or $2 \times 1.45 = 2.9$ mols H_2. This same value, 2.9 mols, is also equivalent to the mols of water vapor produced by the reaction. From the data in Table 14-VII we can calculate the total weight of net combustible burned per 100 mols of dry flue gas, as follows:

Pounds carbon burned $= 16.7 \times 12 = 200.4$ lb.
Pounds hydrogen burned $= 2.9 \times 2.02 = 5.86$ lb.
Total weight net combustible burned/100 mols flue gas
$= 206.26$ lb.

From the foregoing data we can also calculate the percentage of excess air. In computing this figure, it should be remembered that the combustion reactions did not complete themselves, some unburned CO remaining. The term "excess air" is defined as the amount of air used above that theoretically needed for complete combustion, *i.e.*, to burn carbon and hydrogen and their compounds to CO_2 and water. The ratio of the excess air (or oxygen) to the amount of air (or oxygen) theoretically required, multiplied by 100, is the percentage of excess air. The oxygen present in the flue gas (3.3 mols) is not the true excess because, by definition, complete combustion of carbon to CO_2

is required. This amount of O_2 must be diminished by the amount necessary to burn the CO present to CO_2, or 0.2 mol. The excess O_2 is, then, $3.3 - 0.2 = 3.1$ mols. The oxygen necessary for combustion is 16.7 mols for the carbon ($C + O_2 \rightarrow CO_2$) and 1.45 mols for the hydrogen, a total of 18.15 mols. The total oxygen entering was calculated as 21.25 mols. The percentage of excess air or oxygen may be found in several different ways, all leading to the same result:

$$(100)\frac{\text{Unnecessary}}{\text{Total} - \text{unnecessary}} = \frac{100 \times 3.1}{21.25 - 3.1} = 17.1 \text{ per cent}$$

$$(100)\frac{\text{Unnecessary}}{\text{Necessary}} = \frac{100 \times 3.1}{16.7 + 1.45} = 17.1 \text{ per cent}$$

$$(100)\frac{\text{Total} - \text{necessary}}{\text{Necessary}} = \frac{100 \times (21.25 - 18.15)}{18.15} = 17.1 \text{ per cent}$$

Turning now to the coke, the analysis shows that the combustible in it is 82.0 per cent of the total, since $14.5 + 3.5 = 18$ per cent combined water and ash. This combustible is composed of carbon and hydrogen, since the combined oxygen was driven out in the coking operation. The flue gas analysis shows that the C:H ratio (by weight) in the combustible is 200.4:5.86, or the fraction of H in the total combustible is

$$\frac{5.86}{200.4 + 5.86} = \frac{5.86}{206.26}$$

Therefore, the hydrogen in the coke can be calculated because the fraction of H in the total combustible is equal to X over the total combustible (82.0 per cent), or

$$\frac{5.86}{206.26} = \frac{X}{82} \qquad \text{and} \qquad X = 2.32 \text{ per cent hydrogen}$$

and the carbon is $82.0 - 2.32 = 79.68$ per cent of the combustible. The fuel analysis can now be tabulated (Table 15-VII) on the basis of 100 lb. of coke as fired. The mols or atoms are obtained by dividing the weight in pounds by the molecular weight of the substance.

From the results obtained above, several more important quantities may be calculated, one being the cubic feet of air

used per pound of coke fired. It is obvious that all the carbon from the fuel is present as CO or CO_2 in the stack gases and, therefore, a connection exists between the atoms of carbon in the stack gases (16.7) and the atoms of carbon in the fuel (6.64), although they are on different bases. Likewise, the mols of nitrogen connect the amount of flue gas with the amount of air used since all the nitrogen enters with the air and goes through the furnace unchanged. The flue gas data (Table 14-VII) show that in the flue gas the ratio between the mols of nitrogen and

TABLE 15-VII

Component	Pounds	Mols or atoms
Moisture	3 5	0 195
Carbon	79 68	6 64
Hydrogen	2 32	1 15
Ash	14 5	
Total	100.0	

atoms of carbon is 80.0:16.7. If, therefore, the atoms of carbon per pound of fuel (0.0664) be multiplied by this ratio, the mols of nitrogen per pound of fuel are obtained. Since all this N_2 came from the air and makes up 79 per cent of the air, the mols of air can be computed by multiplying by $^{100}/_{79}$ and the result can be converted to cubic feet at standard conditions by multiplying by the pound mol volume. If it is desired to know the cubic feet of air used per pound of fuel fired at 50°F. and 29 in. of Hg., the computation may all be done as follows:

$$0.0664 \times \frac{80.0}{16.7} \times \frac{100}{79} \times 359 \times \frac{460 + 50}{460 + 32} \times \frac{29.92}{29} = 154.2 \text{ cu. ft.}$$

Another desired quantity that can be calculated from the above data is the cubic feet of flue gas per pound of coke fired. The *dry* flue gas per pound of coke fired is obtained by multiplying the atoms of carbon per pound of fuel fired by the ratio of the mols of dry flue gas to the atoms of carbon in it, or

$$0.0664 \times \frac{100}{16.7} = 0.398 \text{ mol dry flue gas per lb. coke fired}$$

This figure is obviously not the total flue gas because no account is taken of the water vapor it contains. The water vapor comes

from two sources: (1) from combustion of the net hydrogen in the fuel and (2) from the moisture in the fuel. The fuel analysis (Table 15-VII) shows that the coke contains water and carbon in the ratio 0.195:6.64 and if the carbon content of the flue gas, 16.7 atoms (the same quantity as 6.64 but on a different basis), be multiplied by this ratio, the water in the flue gas coming from the moisture in the coal is obtained.

$$\frac{0.195}{6.64} \times 16.7 = 0.49 \text{ mol } H_2O \text{ from moisture in fuel}$$

We have already found that the water vapor from combustion of net hydrogen is 2.9 mols, the total water vapor in the flue gas per 100 mols of *dry* flue gas being, therefore, 0.49 + 2.9 = 3.39 mols. The total amount of flue gas per pound of coke fired at the stack temperature (550°F.) and 28 in. of Hg. is

$$0.0664 \times \frac{100 + 3.39}{16.7} \times 359 \times \frac{460 + 550}{460 + 32} \times \frac{29.92}{28}$$

$$= 323.5 \text{ cu. ft.}$$

Finally, from the data above, the heat loss in the flue gases can be calculated. The heat loss is most easily found by multiplying the number of mols of each gas by the difference in their respective molal heat contents at 550 and 50°F. because, in order to recover all the available heat, the products of combustion must be cooled to the same temperature as the entering substances. The diatomic gases, CO, O_2, and N_2, are grouped together because their specific heats *per mol* are identical. The data are placed in tabular form as in Table 16-VII on the basis of 100 mols of dry flue gas and the molal heat contents at 550

TABLE 16-VII

Gas	Mols	Heat content, B.t.u.		Difference, heat loss per mol	Total loss, B.t.u.
		At 550°F.	At 50°F.		
CO_2	16 3	4,920	160	4,760	77,600
CO	0 4				
O_2	3 3	3,560	120	3,440	288,000
N_2	80 0				
H_2O	3 39	4,350	150	4,200	14,200
Total.....	103.39				379,800

and at 50°F. read from Table 16-VII. The difference between these values for any one gas is the heat loss per mol and this value, multiplied by the number of mols of the gas, gives the total heat loss in B.t.u. for that component. The total, 379,800 B.t.u., is the sensible heat retained per 100 mols of dry flue gas or 103.39 mols of wet flue gas, *i.e.*, by the total gas volume corresponding to 16.7 atoms of carbon burned. The heat loss per pound of coke fired is, therefore,

$$\frac{0.0664}{16.7} \times 379{,}800 = 1510 \text{ B.t.u. per lb. coke fired}$$

The percentage loss can be computed by finding the heating value of the fuel.

$$C + O_2 \rightarrow CO_2 + 174{,}600 \text{ B.t.u.}$$
$$H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O + 123{,}000 \text{ B.t.u.}$$

By knowing the fuel analysis, we can determine the gross heating value of the fuel per pound, as follows:

$$\begin{aligned} \text{Carbon: } 0.0664 \times 174{,}600 &= 11{,}593 \text{ B.t.u.} \\ \text{Hydrogen: } 0.0115 \times 123{,}100 &= \underline{1{,}416 \text{ B.t.u.}} \\ \text{Total} &= 13{,}009 \text{ B.t.u. per lb.} \end{aligned}$$

The percentage of the gross heating value of the coal as fired which escapes as sensible heat in the flue gas is, then,

$$\frac{1510}{13{,}015} \times 100 = 11.6 \text{ per cent}$$

From the analysis of the flue gas and its temperature and from a knowledge of the moisture and ash content of the coke, as well as the temperature of the entering air, we have been able to calculate the following:

1. The percentage of excess air.
2. The cubic feet of air per pound of fuel fired.
3. The cubic feet of flue gases per pound of fuel fired.
4. The analysis of the coke.
5. The percentage of heat lost up the stack.

With more data it would be possible to calculate many more important quantities but these suffice to show what knowledge can be gained through combustion calculations.

PRODUCER GAS MANUFACTURE

Producer gas is generated by blowing a mixture of air and steam up through a thick, hot bed of coal or coke. This process results in an oxygen-free gas containing a large proportion of the original heating value of the solid fuel in the form of CO and H_2. The coal or coke is fed into a brick-lined producer chamber and the producer gas, consisting of CO, H_2, N_2, volatile matter, tar, and soot, passes out through a discharge main near the top.

Producer gas is the cheapest form of industrial gas that can be manufactured and hence is widely used in industrial heating. It possesses all the general advantages of gaseous fuels and is used where a gaseous fuel is the most economical source of heat or where coal cannot be used and cheap gas is a necessity. In other words, producer gas is used either for economy or in order to improve the quality of the product. Gasifying the coal before combustion may increase the economy (1) when the fuel is to be used in many scattered furnaces, (2) when power is to be generated in isolated plants, and (3) when high temperatures are needed and it is advisable to preheat the air and fuel with the recoverable heat from the stack gases. The factor of effect on quality of product enters (1) when close control of temperature is necessary, (2) when the furnace atmosphere must be controlled (oxidizing, neutral, or reducing), (3) when long-flame combustion is necessary, and (4) when the ash or sulfur in the solid fuel would spoil the product.

The Gas Producer.—Many different types of gas producers are in operation in this country and vary so widely in detail that a description of them cannot be taken up here. Most of them are alike in essential features, however, and a description of one common type, the Wellman, will be sufficient for our purpose here.

Figure 10-VII shows a cutaway view of this producer. The brick-lined cylindrical shell is supported on rollers, one of which is shown, and rotated by gears and the mechanism supported on the foundation at the right. Both the bottom pan and the cover of the producer are stationary, and the revolving shell operates in a water seal at both the top and bottom. The coal is automatically and uniformly introduced from a hopper at the top

by means of the revolving feeder. The double bell arrangement permits the fuel to be introduced without loss of gas. The steam and air mixture enters through the central pipe at the bottom and the double apron distributes the gas mixture uni-

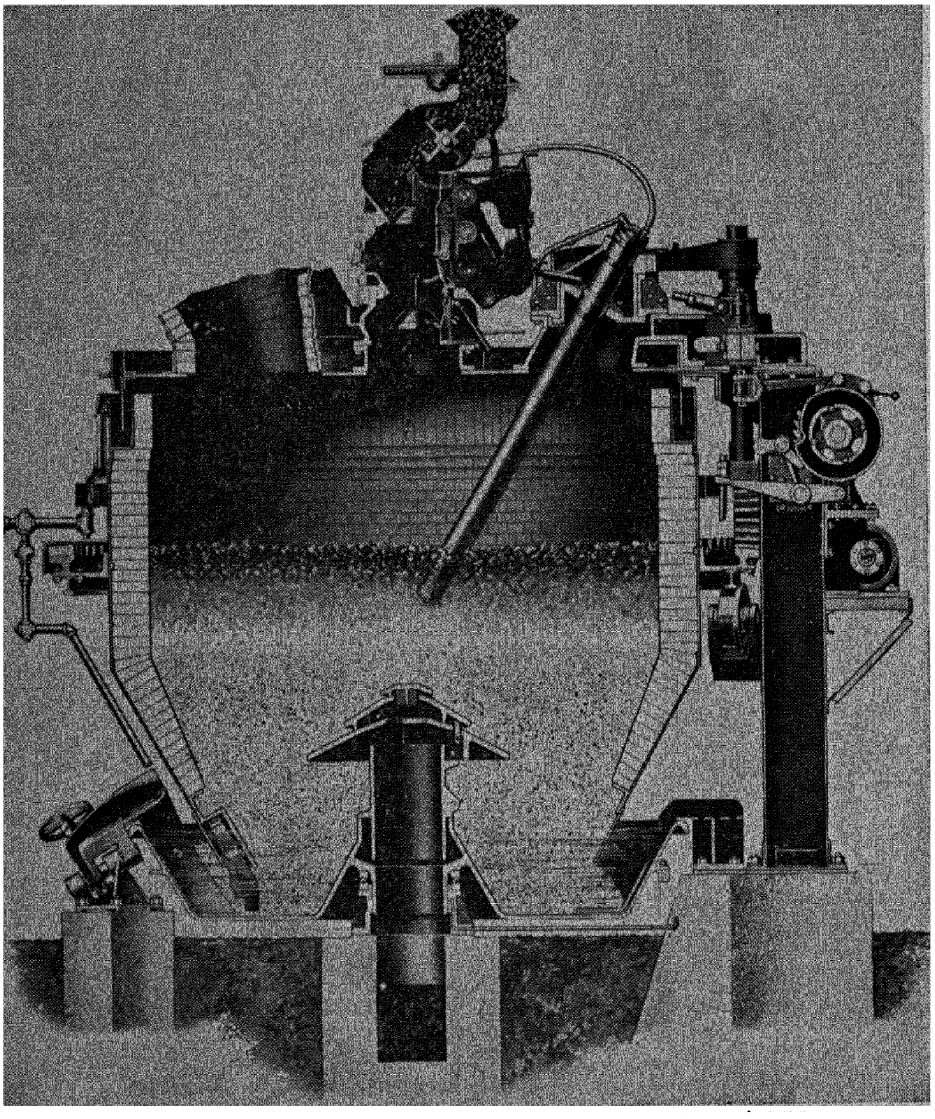


FIG. 10-VII.—Cutaway view of a gas producer. (*Courtesy of the Wellman Engineering Company.*)

formly through the bottom of the fuel bed. The automatic continuous ash remover is shown at the lower left. The water-cooled mechanical poker oscillates between the center and the side of the fuel bed as the producer body and its contents revolve. The producer body and the fuel bed make one revolution in about

8 min. and the entire top of the bed is stirred frequently, thus closing up any channels and keeping the fuel bed level. The producer gas escapes through the brick-lined flue at the upper left.

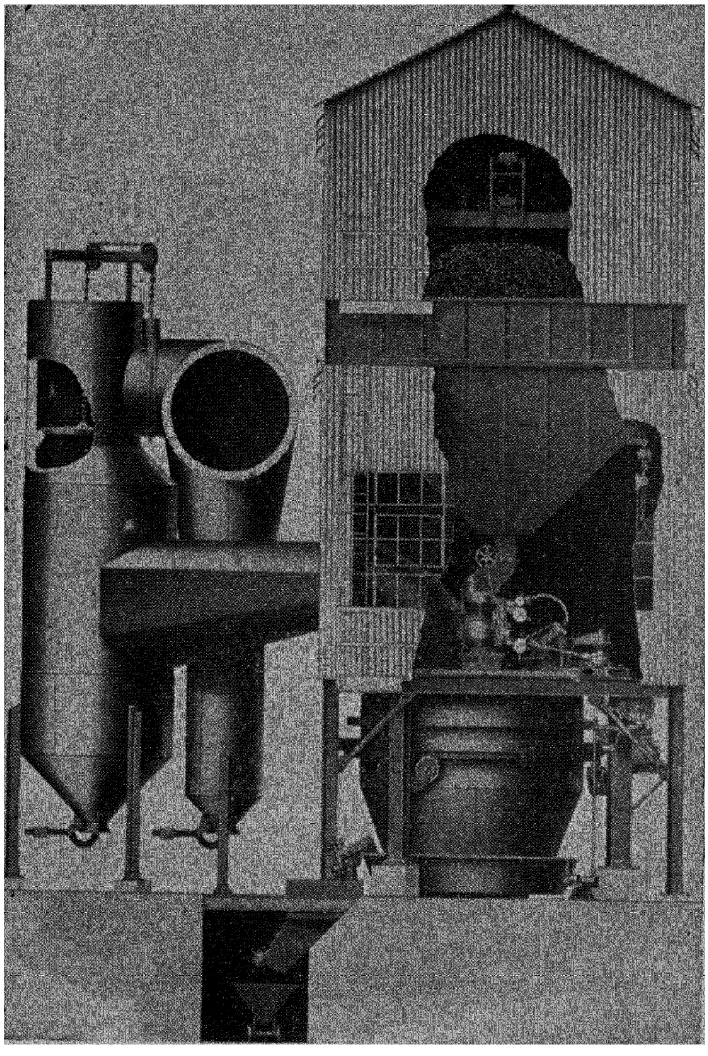


FIG. 11-VII. Producer gas set and auxiliaries. (*Courtesy of the Wellman Engineering Company.*)

Figure 11-VII shows the arrangement of the producer with regard to the auxiliary equipment. The gas from the producer passes to the dust catcher and then to the flue leading to the furnaces. The dust collects at the bottom of the vessels and is removed periodically. The equipment is placed as close to the furnaces as possible in order to save the sensible heat in the gas and prevent deposition of tar in the mains.

Mechanism of Gas Formation.—The fuel bed of a gas producer may be divided into four zones which, from the bottom up, are known as the ash, oxidation, reduction (primary and secondary), and distillation zones. The entering air-steam mixture does not undergo any change in composition in passing up through the ash zone but is only preheated. At the end of the ash zone, the mixture comes in contact with incandescent carbon (coke) and combustion begins. The oxygen in the air is entirely consumed in the next few inches, CO_2 being formed by the reaction.

$$C + O_2 \rightarrow CO_2 + 174{,}600 \text{ B.t.u.} \quad (1)$$

The formation of CO from CO_2 does not begin until all of the oxygen is gone. The same is true of the decomposition of water vapor. This zone, in which only the oxidation of carbon to CO_2 takes place, is known as the *oxidation* zone and is the hottest zone in the producer.

As the mixture of CO_2, H_2O, and N_2 rises farther, CO_2 and H_2O undergo the following reactions:

$$C + CO_2 \rightarrow 2CO - 70{,}200 \text{ B.t.u.} \quad (2)$$

$$C + H_2O \rightarrow CO + H_2 - 70{,}900 \text{ B.t.u.} \quad (3)$$

$$C + 2H_2O \rightarrow CO_2 + 2H_2 - 71{,}600 \text{ B.t.u.} \quad (4)$$

Water decomposition starts shortly after the beginning of CO formation and the hydrogen content increases rapidly at first and then increases only relatively slowly. This is called the *primary reduction zone*, because all of the reduction of steam by carbon and most of the reduction of CO_2 by carbon takes place in this zone, which is fairly thin.

Above the primary reduction zone, steam continues to be decomposed, but by the action of CO instead of carbon according to the equation

$$CO + H_2O \rightarrow CO_2 + H_2 - 700 \text{ B.t.u.} \quad (5)$$

In addition, reaction (2) takes place slowly in this zone, which is termed the *secondary reduction zone.* An important function of this zone is to act as a heat interchanger, the gases giving up some of their sensible heat to the incoming fuel.

In the *distillation zone,* the coal is distilled and its volatile matter is added to the gas, thereby increasing the heating value of the gas by as much as 40 per cent with the best producer

coals. In case anthracite coal or coke is used, this zone is necessarily absent. This zone is usually thin—under 1 ft. In the open space above the fuel bed, the gases change in composition with a decrease in heating value. Since the gas is no longer in contact with hot carbon, it is possible for the reaction

$$2CO \rightarrow CO_2 + C \qquad (6)$$

to take place. Also, a certain amount of CO_2 and undecomposed steam always is added to the gas at the top of the fuel bed, owing to leakage around the edge of the fuel bed and through channels. Figure 12-VII shows the changes in gas analyses through the fuel bed for a producer fired with coke, the analyses being calculated on the basis of 100 mols of N_2.

Operation of the Producer.—From a practical standpoint, the operation of the producer can best be controlled by judging the appearance of the gas and the producer bed and by complete gas analyses. Judging by appearance is quick and, to the trained eye, usually satisfactory. From this standpoint, the best gas is a slightly smoky yellow and the top of the fuel bed should be a dull red. A dark sooty gas usually indicates that the top temperature of the producer is too high because of blowholes or too thin a fuel bed. On the other hand, if the gas is free from all soot, the producer is usually being operated below capacity or with a very high steam-coal ratio. If channels exist in the fuel bed, they may be located by the appearance of bright spots due to localized high temperature.

In controlling a producer by analysis, it is best practice in most cases to aim for from 2 to 5 per cent CO_2. If the CO_2 content of the gas is over 5 per cent, the operation usually is at fault in one or more of the following ways: (1) Too much steam is being used, causing the temperature of the reduction zone to be too low and thereby decreasing the reduction of CO_2 to CO. (2) The fuel bed is too thin, reducing the time of contact of CO_2 with carbon. (3) The rate of gasification (pounds coal gasified per square foot grate area per hour) is too high, causing clinker formation in the oxidation zone, thus lessening the contact between the gas and fuel. (4) Air may be leaking in at the top of the producer and a portion of the CO thus burned to CO_2. (5) Channels cause the CO_2 to pass through the bed without

reduction. Table 17-VII presents the effects of method of operation on the characteristics of producer gas.

Practically any fuel from anthracite coal to wood can be successfully used in a gas producer, but bituminous coal is most widely used for this purpose. When the gas is used for heating furnaces, the highest heating value in the gas at the lowest cost is desired. It is advisable to strike an economic balance

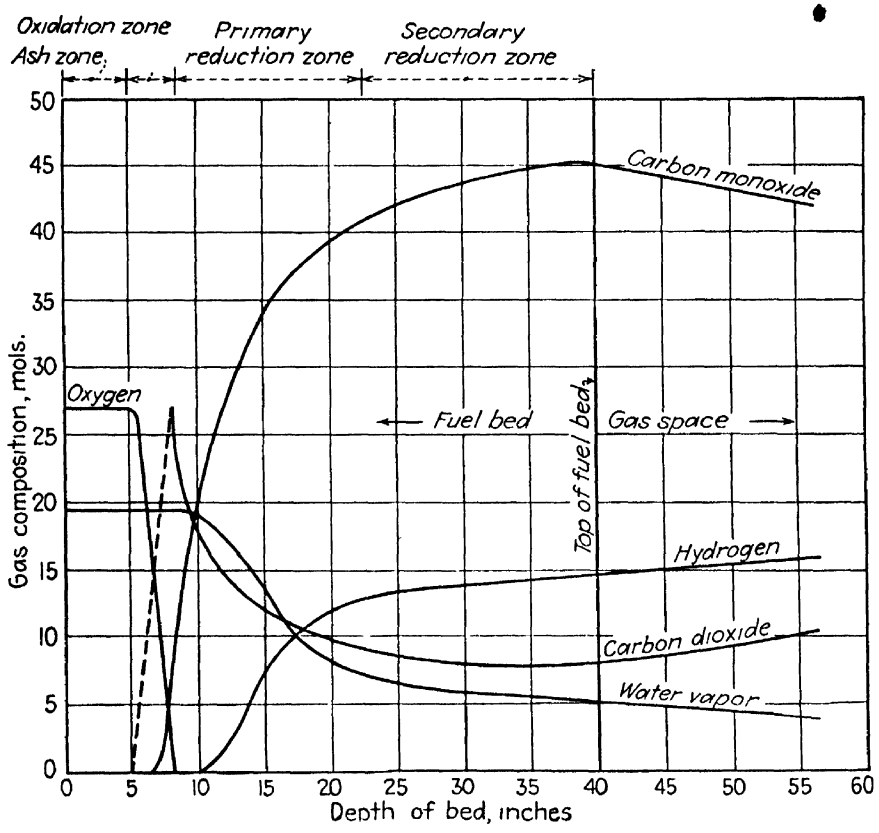


FIG. 12-VII.—Gas analyses at various depths in the fuel bed of a gas producer fired with coke. (*Haslam and Russell, Fuels and Their Combustion.*)

between the cost and heating value of the coal and the cost of gasification. The coal should be dust-free, all should pass through a 2-in. ring, should be noncaking, and should have a high V.C.M. content. The ash should have a high fusion point, and the coal should have a low moisture content to avoid loss of heat.

In order to maintain steady production of a good grade of producer gas, it is necessary to observe several important precautions: (1) Coal should be fed continuously and uniformly over the fire bed. (2) Channels should be kept closed. (3) When poking the bed to close channels, the ash must not be

TABLE 17-VII.—INFLUENCE OF METHOD OF OPERATION ON CHARACTERISTICS OF PRODUCER GAS*

Kind of operation	Gas analysis			Characteristics of gas		Appearance of fuel surface	Value of gas obtained and causes of poor operation
	Per cent CO_2	Per cent CO	Per cent H_2	Temperature °F.	Appearance		
Cold fire.....	Over 7	Below 20	13–17	1200–1300	Golden yellow; much tar	Dull red or pale cherry	Very bad; combustion too slow; upper part much hotter than lower; too much steam or grate choked
Good fire.....	3–5	About 24	About 15	1300–1500	Yellow; still much tar: often a little smoky from decomposed tar	Cherry to bright red	Excellent operation
Good fire with channels in bed	Over 5	Less than 24	15 or less	1300–1500	Smoky, tar decomposed	Cherry to bright red	Upper part much hotter than lower; poor operation, not enough poking, coke too sticky, or too much fusible ash
Hot fire	3–4	Over 25	5–10	Well above 1500	Smoky; tar entirely decomposed	Bright red to pale yellow	Not enough steam; operation passable, and sometimes to be recommended with rich or low-ash coals, channeling changes this to next type
Hot fire with channels in bed	Over 3 or 4	Less than 25	5–10	Well above 1500	Smoky; tar entirely decomposed	Bright red to pale yellow	Not enough steam; too much ash, ash too fusible; not enough poking; very poor gas, distinguished by low H_2

* HASLAM and RUSSELL, "Fuels and Their Combustion," McGraw-Hill Book Company, Inc., New York, 1926.

mixed with hot coal. (4) The ash should be removed uniformly and mechanically. (5) The air-steam mixture should be distributed evenly over the bottom of the fuel bed. (6) The air:steam ratio should be maintained constant with varying load.

Producer Gas Calculations.—The general principles of combustion calculations already discussed are applicable to gas producers but there are a few differences that merit brief mention. For example, let us consider a producer gas of the following composition and determine what quantities we can from the analysis alone: 9.84 per cent CO_2, 0.04 per cent O_2, 0.18 per cent C_2H_4, 18.28 per cent CO, 12.90 per cent H_2, 3.12 per cent CH_4, and 55.64 per cent N_2.

Taking 100 mols of dry producer gas as a basis, we can set up the data in tabular form (Table 18-VII). The total mols of each constituent are placed in the first column and the atoms of carbon contained in them in the second. Since there are two atoms of carbon to a molecule of C_2H_4, there is 0.36 atom of carbon per 0.18 mol of C_2H_4. The mols of hydrogen in C_2H_4 is also twice the number of mols of C_2H_4 and the same is true in the case of CH_4. Finally, the mols of oxygen that can be accounted for are computed, the total being 19.02 mols O_2. Assuming that all of the N_2 in the gas comes from the air, we can calculate the oxygen entering in the air to be

$$55.64 \times (21/79) = 14.80 \text{ mols } O_2$$

per 100 mols of dry producer gas. This is less than the total O_2 accounted for in the gas, the remainder being equivalent to decomposition of water since this is the only other possible source of oxygen. The mols of water decomposed and the hydrogen formed from the water are equal to twice the corresponding mols of oxygen. The hydrogen from the steam is less than the total present in the gas—the difference between the two must be the net hydrogen from the fuel. These calculations are summarized below:

Mols O_2 from decomposition of water

$$= 19.02 - 14.80 = 4.22 \text{ mols}$$

$$\text{Mols of water decomposed} = 8.44 \text{ mols}$$

$$H_2 \text{ from decomposition of water} = 4.22 \times 2 = 8.44 \text{ mols}$$

$$\text{Mols } H_2 \text{ from net } H_2 \text{ in fuel} = 19.50 - 8.44 = 11.06 \text{ mols}$$

on the basis of 100 mols of dry producer gas.

By multiplying the atoms of carbon by the atomic weight, the pounds of carbon gasified per 100 mols of dry producer gas can be found. A similar procedure on the net hydrogen in the gas and the water decomposed yields the following results:

$$\text{Pounds C in gas} = 31.60 \times 12 = 379.2$$
$$\text{Pounds net } H_2 \text{ in gas} = 11.06 \times 2.02 = 22.3$$
$$\text{Pounds } H_2O \text{ decomposed} = 8.44 \times 18.02 = 151.8$$

From these figures, the amount of dry gas produced, the amount

TABLE 18-VII

Gas	Mols	Atoms C	Mols H_2	Mols O_2
CO	9 84	9 84	. .	9 84
O_2	0 04	.		0.04
C_2H_4	0 18	0 36	0 36	
CO	18 28	18 28		9 14
H_2	12.90	. .	12 90	
CH_4	3 12	3 12	6 24	
N_2	55 64			
Total	100 00	31 60	19 50	19 02

of dry air used, and the amount of water decomposed per pound of carbon gasified can be calculated as follows:

$$\frac{151.8}{379.2} = 0.4 \text{ lb. } H_2O \text{ decomposed}$$

$$\left(\frac{100}{379.2}\right) \times 359 = 94.8 \text{ cu. ft. dry gas produced at standard conditions}$$

$$\frac{55.64}{379.2} \times \frac{100}{79} \times 359 = 66.8 \text{ cu. ft. dry air used at standard conditions}$$

If the coal analysis were known, as well as the steam consumption, we could calculate many more important quantities relative to the producer operation.

In order to run a complete test on a gas producer, the following data should be collected:

1. The steam consumption per hour and its gauge pressure.
2. The coal consumption in pounds per hour.

3. A complete analysis of the coal as fired and its heating value.
4. The temperature and water content of the entering air.
5. The temperature and analysis of the producer gas.
6. The water content of the producer gas.
7. A complete analysis of the refuse (ashes).
8. The barometric pressure.
9. The amount and analysis of the tar formed.

From these data, the following can be calculated:

1. The gas production per hour.
2. The amount of air used.
3. The steam decomposition.
4. A complete heat balance on the producer, including
   a. Heat input in the coal and steam.
   b. Heat output in the form of
      (1) Heat required to vaporize the water formed on combustion.
      (2) Sensible heat in the gas.
      (3) Heat of combustion of the gas.
      (4) Heat in the tar.
      (5) Heat of combustion of carbon in the refuse.

The actual computation is beyond the scope of this volume but anyone interested in such calculations is referred to "Industrial Stochiometry" by Lewis and Radasch, McGraw-Hill Book Company, from which much of the material on combustion calculations has been taken.

COKE MANUFACTURE

The destructive distillation of coal in the absence of air produces coke, coke-oven gas, tar, ammonia, and the benzol compounds. In the metallurgical industries coke is the principal product desired as it is essential for blast-furnace operation, although the gas is utilized and the by-products recovered. In the manufactured gas industry, the gas is the principal product desired, although the coke is sold for domestic consumption and the by-products are recovered and sold. In some chemical industries, other products are the principal material desired. For instance, in the Solvay process for the production of sodium

carbonate, the ammonia only is desired, the coke, gas, and tar being sold as by-products.

Metallurgical coke is made in both *beehive ovens* and *by-product ovens.* The beehive oven is a hemispherical brick structure about 7 ft. high with a door at the side for admittance of air and an opening at the top, which acts as a flue and through which the coal is charged. Air is admitted through a door at the side in order to burn the volatile products in the space above the fuel bed, about 2 ft. of coal being placed on the floor of the oven. This combustion heats the oven to a temperature high enough to distill off all the volatile matter in the course of two or three days. The coke is then removed, quenched outside the oven, and a new charge introduced. This method of making coke is very inefficient because the valuable volatile products are entirely wasted and from 10 to 15 per cent of the coke is burned by the air admitted. For this reason, as well as others, the beehive process has almost disappeared and will not be considered further in this section.

Coal for Metallurgical Coke.—We have already seen that certain coals soften or melt on heating, give off their volatile matter, and finally solidify into a solid cake, leaving a hard, cellular, coherent mass on further heating. The degree of fusion of the coal, the amount of gas evolved, and the strength and porosity of the resulting coke depend to a large extent on the coal used. The chemical analysis of the coal does not give a definite indication of its coking quality. For metallurgical uses, however, the ash content should not be above 8 per cent, the sulfur not more than 1.5 per cent, and the phosphorus content not more than 0.02 per cent. The best way to determine the coking quality of a bituminous coal is to conduct actual full-scale tests upon it. A large amount of chemical work has been done in attempting to determine coking quality by the study of complex organic compounds in the coal and, although much progress has been made toward a better understanding of the process, the evidence is still not conclusive. In other words, we still cannot predict exactly the coking quality of a coal from its chemical analysis.

The appearance and other properties of coke vary greatly with coals from different localities. For instance, coking coals from the Connellsville district of Pennsylvania produce a hard, dense coke while the Westmoreland coals yield a light, porous,

friable coke. If a coal that yields a porous coke on account of its excess of bonding or cementing material is mixed with a low-volatile, poor coking coal, a denser and stronger coke results. This fact gave rise to the prevalent practice of mixing coals to produce the desired structure of the coke. In general, 70 to 90 per cent of the high-volatile coal is mixed with from 10 to 30 per cent of low-volatile coal in order to produce a mixture containing about 30 per cent volatile matter. If a certain coal yields a desired grade of coke, however, mixing is dispensed with.

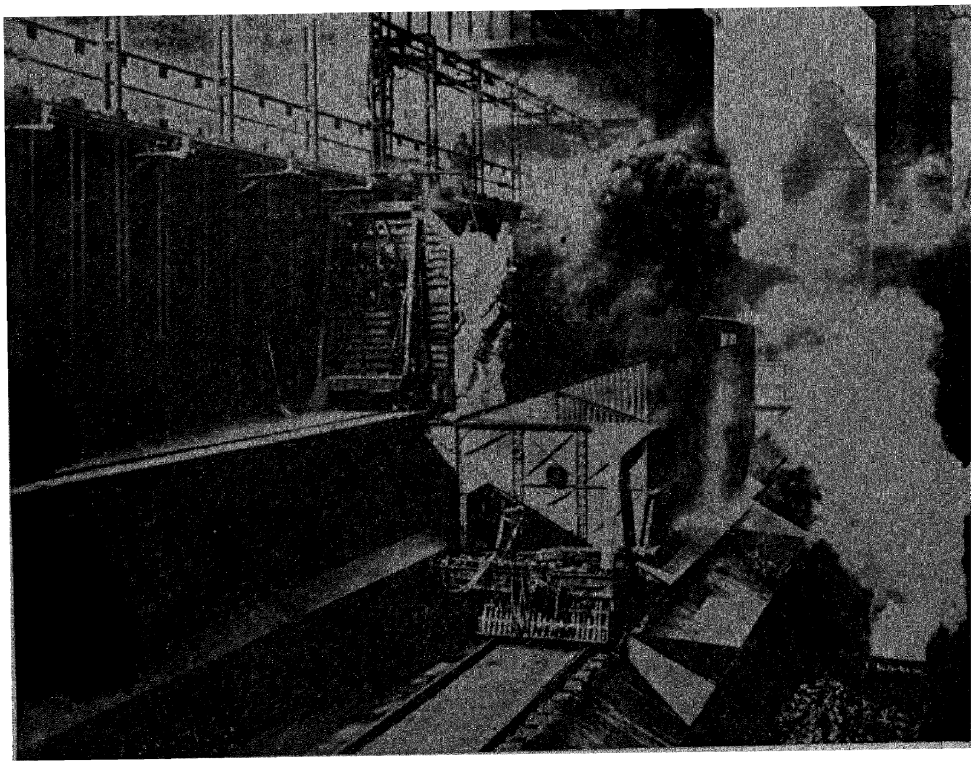


FIG. 13-VII.—A battery of by-product coke ovens in operation showing one oven in the process of being discharged. (*Courtesy of the Youngstown Sheet and Tube Company.*)

By-product Coke Ovens.—The modern by-product coke oven is a long, narrow, rectangular chamber lined with silica brick heated from without by gas passing through flues at the sides of the oven. This oven may be from 30 to 40 ft. long, from 11 to 22 in. wide, and from 6 to about 14 ft. high, the larger sizes predominating in recent large installations. Coal is charged through a series of holes in the top of the oven and the coke discharged 14 to 20 hr. later by means of a ram or pusher which ejects the coke from the end of the oven, the oven being tapered

slightly from the pusher to the discharge end in order to increase the ease of pushing. A large number of ovens, sometimes as many as 80 or more, are built side by side in a unit and called a battery. Figure 13-VII shows a battery of ovens in operation, one of which is in the process of being emptied.

Many different types of construction are used in by-product ovens—too many, in fact, for their descriptions to be included here. The Becker type Koppers oven is a prevalent type in this country and is selected for description; a cutaway view is shown in Fig. 14-VII. This oven is designed to be heated with either coke-oven gas, which does not require preheating, or blast furnace or producer gas, which does require preheating. One side of the oven wall is shown at *A* in Fig. 14-VII, the holes through which the coal is charged at *B* and the offtakes for the coke-oven gas at *C*. Regenerators are built under the ovens to preheat the entering gas and air to conserve the heat in the products of combustion. The dividing wall *D* separates the regenerators, which extend the length of the battery, into two parts. This wall also extends up through the heating flues, thus dividing the battery into two longitudinal sections. The flow of gases is, therefore, independent in each half but occurs in exactly the same manner on both sides of the dividing wall. The dividing walls between regenerators support the ovens, which are placed side by side and separated by vertical heating flues.

If producer gas is used to heat the ovens, it enters through the pipes *E*, while the air for combustion enters at *F*. During one-half of a cycle, for example, air is preheated in regenerator *G*, having entered from the main through the square duct at the bottom, while the gas is preheated in regenerator *H*. The preheated gases enter the series of vertical heating flues *I* through the ports, and combustion takes place in these flues. The gases then enter the horizontal flue and pass over the top of the oven through the crossover flues *J*, one of which serves several vertical flues. The hot gases are then distributed by the horizontal flue *K* to the vertical flues *L*, through which they pass down to the pair of regenerators, one of which is shown at *M*, the other one being cut away in the view shown. The gases divide at the ports, give up their heat to the two regenerators, and pass out through the flue ducts *N*. At the same time, producer gas is entering at *O* and air at *P*, burning up through

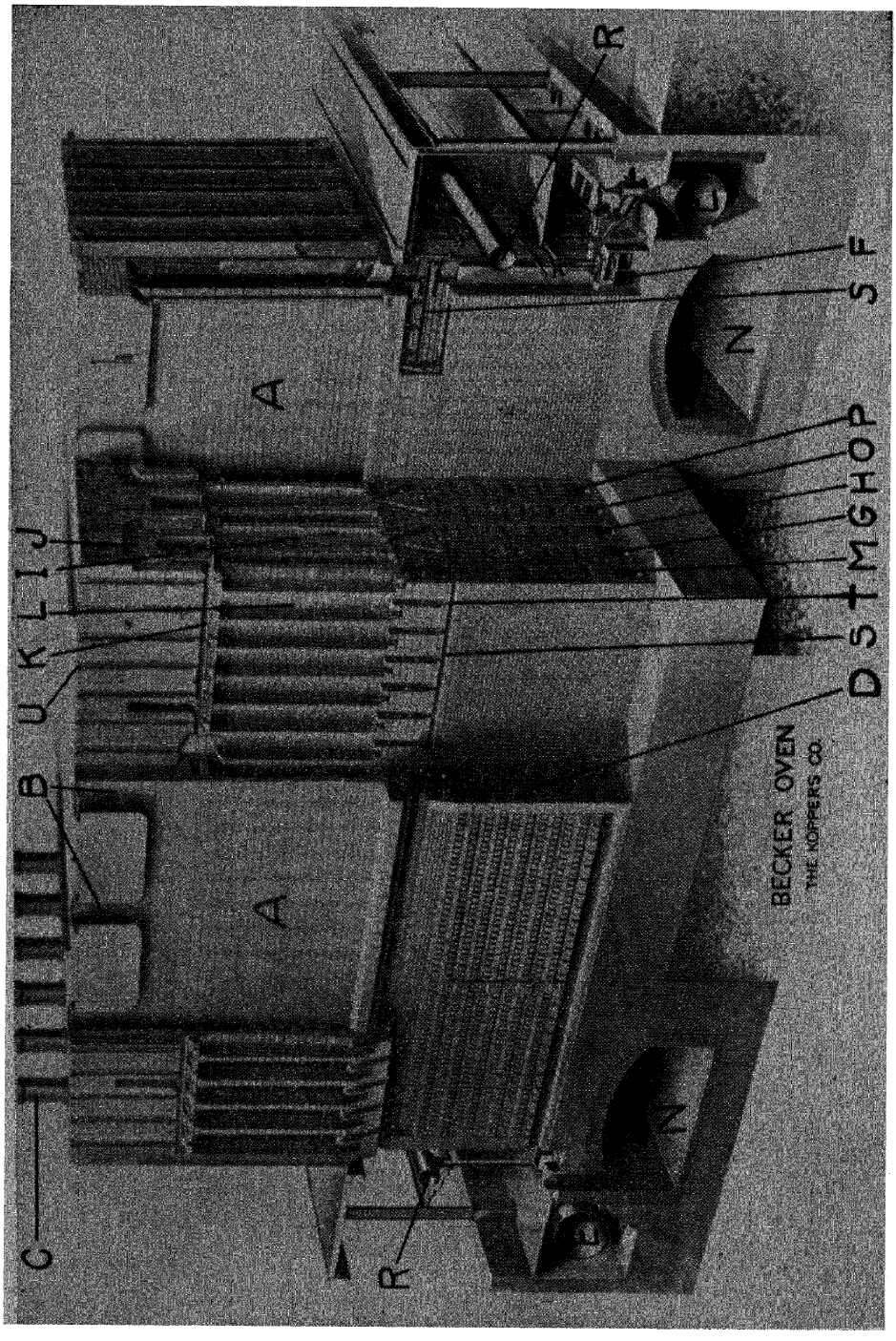


FIG. 14-VII.—Cutaway view of a Becker type Koppers by-product coke oven. (*Courtesy of the Koppers Construction Company.*)

the vertical flues, over the crossover flues to the right and down through the vertical flues and regenerators. In this way, combustion is taking place in the flues on both sides of every third oven, and the regenerators are used for the following purposes along the battery: 1 for air, 2 for producer gas, 1 for air, 4 for waste heat, 1 for air, 2 for producer gas, etc., in that sequence.

At intervals of from 20 to 30 min., the flow of gases is reversed over the entire battery to ensure even heating. In this way, the regenerators that preheated the gas and air become, upon reversal, the ones that receive the waste heat from the products of combustion. Likewise, the vertical flues in which combustion formerly took place now carry the waste gases to the regenerators connected to them, thus heating the ovens evenly. The reversal is accomplished by an endless cable which passes entirely around the battery and is connected to a motor. The cable is connected to all regenerator valves which are so placed that a movement of the cable opens one-half the total number of valves and closes the remainder at each reversal.

If the plant is located in an area in which coke-oven gas is in demand for domestic purposes, it is often advantageous to fire the ovens with producer gas and sell the entire gas output of the ovens. In some plants, particularly in isolated areas, the gas, after stripping the important by-products, is returned to the ovens as fuel. Under these conditions, the coke-oven gas enters through the pipes R and is distributed to the vertical heating flues by the ducts S, finally burning at the refractory nozzles T. Both regenerators preheat the air, so that four regenerators are preheating the air, the next four are handling the waste gases, and so forth down the line. The refractory nozzles often become clogged with soot, owing to cracking of the coke-oven gas, and the holes U are so placed that these nozzles can be replaced without interfering with the operation of the ovens. The holes are sealed at the top of the battery when repairs are not being conducted.

Mechanism of Coking.—When coal is placed in the hot oven, that portion of the coal charge in contact with the hot walls is heated very rapidly to a high temperature, which causes a thin layer to soften, become plastic, and finally melt. This layer of plastic material, called the fusion zone, travels toward the center of the oven as the temperature of the charge is raised. In the

fusion zone, as well as immediately on either side of it, destructive distillation of the coal takes place, and some of the gaseous products force their way out of the plastic material, thus forming

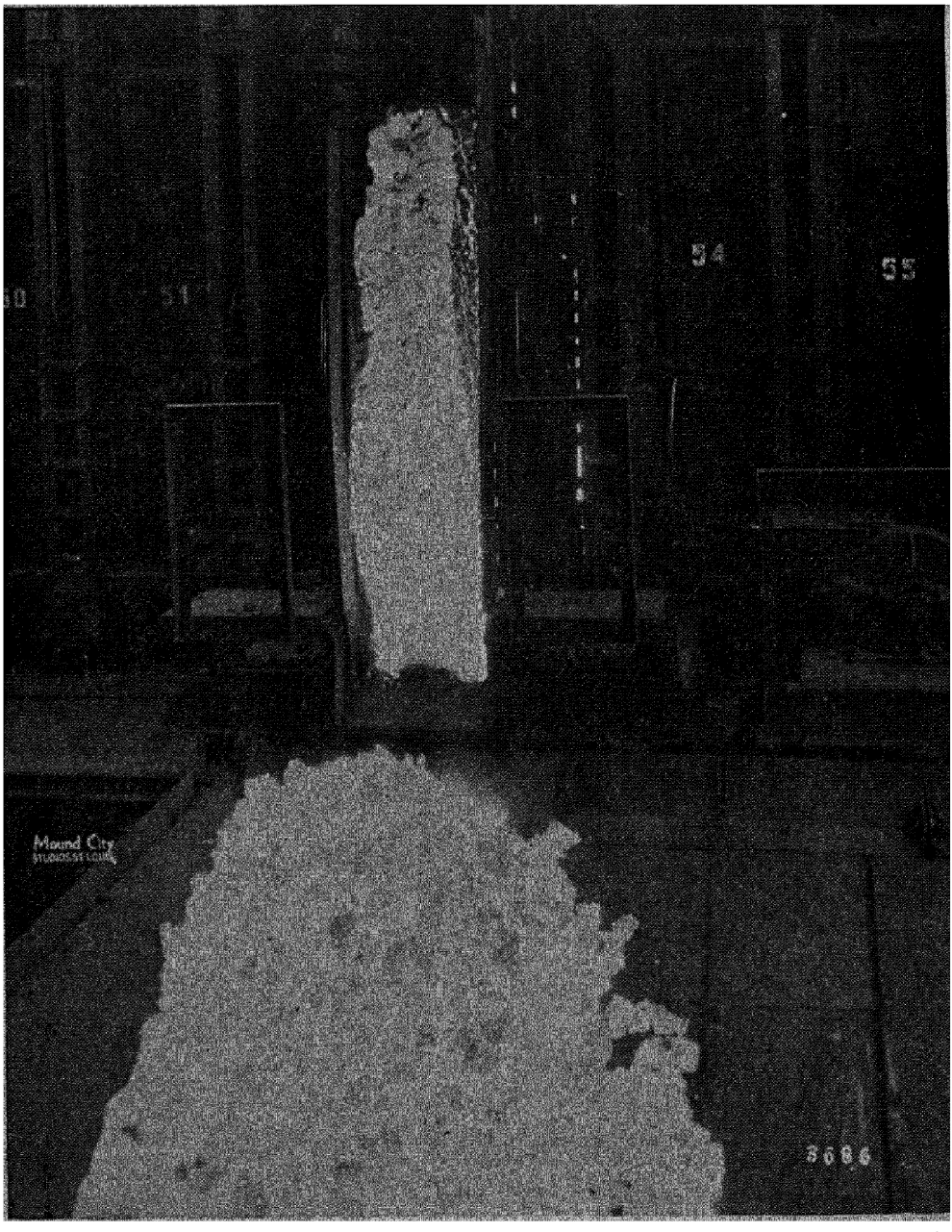


FIG. 15-VII.—The structure of the coke as it emerges from the oven. (*Courtesy of the Koppers Construction Company.*)

the cellular, porous structure of the final coke. On the side of the fusion zone next to the oven wall, the plastic layer finally hardens into a cellular residue, and the volatile matter left in the

coke is gradually driven off as the temperature rises during the remainder of the coking period. The gas evolved in this later period is rich in hydrogen, whereas the gas evolved in earlier stages of coking contains methane, ethane, ethylene, and benzols, which have high heating values. At the inner face of the fusion zone as it travels away from the hot oven wall, the relatively cool coal nearer the center of the charge is melted and coked. Finally, if the heating from both sides of the oven has been uniform, the fusion zones first formed at the walls will meet at the center, the junction showing up as a crack down the center of the mass of coke. The structure of the coke as it comes from the oven is shown in Fig. 15-VII.

The gases evolved from the fusion zone and the volatile constituents driven off at either side of it force their way either to the walls of the chamber or through the raw coal—predominantly the latter during the early stages of the process. The gases forcing their way through the hotter wall face of the fusion zone, however, have to pass through cracks in the coked coal, up along the hot oven walls, and finally through the hot free space above the charge. During this passage they are subjected to considerable thermal decomposition. During the latter portion of the coking period this process is intensified because the temperature of the charge is rising. Thus, thermal decomposition becomes more severe as coking proceeds, the hydrocarbon gases coming from the retort become less complex in structure, owing to cracking, the hydrogen content of the gas increases, and the coke becomes silvery-gray, owing to deposited particles of carbon formed by cracking of the hydrocarbons.

Control of the Process.—The coking process is usually carried out at final temperatures ranging from about 1600 to about 2100°F. With modern ovens, the coking is usually complete in 16 to 20 hr., although the coking time may be increased considerably if the demand for the coke is not sufficient to keep the ovens operating at capacity. Owing to the fact that it is dangerous to cool the ovens because of the dangers of cracking the silica refractories, it is better to increase the coking time and run the battery continuously than to shut it down periodically. During slack periods coke has been held as long as 60 to 70 hr. after coking to avoid large accumulations. A good yield is .68 per cent furnace coke, 7 per cent fines unsuitable for the blast

furnace, and 25 per cent gases and vapors, all on the basis of the original charge of coal.

It has been found, among other things, that the size of the coal has an important effect upon the coke obtained. If the coal charge is pulverized so that 50 per cent will pass through a ⅛-in. mesh screen, a denser and stronger coke is obtained than if it were pulverized so that 70 per cent would pass through the screen. However, when a mixture of coals is charged, finer pulverization has been shown to be advantageous in producing coke of uniform strength and porosity.

Coking temperature is also important in its effect on the coke. When too high a temperature is used, the coke tends to break up easily during and before screening, while coke produced at too low a temperature usually possesses too low a resistance to abrasion. The amount of moisture in the coal has an effect upon the density of the coke. A coal of high moisture produces a more open or a less dense coke than a coal of low moisture content. Also, the coking time has an effect upon the size of the resultant coke. A rapid rate of coking tends to produce coke of smaller size than a longer coking time. The coking time may be said to be directly proportional to the cross-sectional area of the oven and inversely proportional to the temperature at which the process is carried out.

Products Obtained from the Process.—The products normally obtained from the coking process are coke, gas, ammonia liquor, ammonium sulfate, and also light oil which may be further refined to produce benzol, toluol, xylol, and solvent naphtha. A few other substances that can be recovered and purified are phenol, naphthalene, sulfuric acid (from S in the gas), ethylene, and sodium ferrocyanide. The recovery plant will be very briefly described.

The gas evolved during the carbonizing period passes from each oven through an opening provided for this purpose, into the ascension pipe connected to the collecting main. The gas is sprayed by liquor as it enters the collecting main. This cools the gas and condenses the heavy tar and part of the ammonia contained in the gas. The collecting main slopes toward the center where it connects to the suction main, through which the gas and condensates flow. The condensates drop into the hot

drain tank provided for this purpose, while the gas under suction continues to the primary cooler where it is further cooled. Here, most of the tar and part of the ammonia are condensed and washed out. Approximately 20 per cent of the ammonia collects here in water solution. The gas is then drawn by exhausters through the tar extractors, where any remaining tar is removed. From the tar extractors the gas passes through the reheaters and thence is forced by the exhausters through saturators, where the ammonia is removed in the form of ammonium sulfate. The gas bubbles through a sulfuric acid bath in the saturator and the ammonium sulfate precipitates as a solid salt. The reaction is complete and all of the ammonia is recovered. The ammonium sulfate formed in the saturator is dried in a centrifugal drier and is then carried to the storage pile.

The ammonia liquor condensed in the primary coolers, together with tar from the coolers and tar extractors, is drained to a tank where, by taking advantage of their differences in specific gravity, the two liquors are separated by decantation. The tar is pumped to a storage tank and is ready for sale or use. The ammonia liquor also is pumped to a storage tank and from there it is taken to stills where the ammonia vapors are released. These vapors are piped into the stream of coke-oven gas just before the saturators, and are converted into ammonium sulfate along with the ammonia in the gas. This completes the recovery of all the ammonia produced. After leaving the saturator, the gas passes through an acid separator where any acid from the saturator is removed, then into a final cooler where the gas is cooled to a proper temperature.

If it is desired to recover the benzol, the gas is then washed with a straw oil which absorbs the benzol vapors in the gas. This straw oil is then distilled to recover the absorbed vapors in the form of crude light oil, after which it is cooled and recirculated. The crude light oil is treated with acid and alkalies and is then distilled, and pure noncorrosive benzol, toluol, xylol, and solvent naphtha are taken off.

The coke is tested for specific gravity (true and apparent), porosity, resistance to breakage (shatter test), and resistance to abrasion (tumbler test), as all of these have a bearing upon the durability of the coke.

The following material balance (Table 19-VII) was obtained at one plant over a period of eight months and shows the distribution of the materials with relation to the coal charged.

TABLE 19-VII.—MATERIAL BALANCE ON A BY-PRODUCT COKE PLANT

Dry coal charged	316,802 0 tons
Blast-furnace coke (dry)	214,928.7 tons
Breeze (dry)	23,037.5 tons
Ammonia	1,032.7 tons
Gas	53,755.0 tons
Tar	19,357.7 tons
Light oil	4,117.3 tons
Total recovery	316,228 9 tons
Loss	573 1 tons
Percentage loss	0.18 per cent

Metallurgical Coke.—To meet blast-furnace conditions, coke should be strong enough to withstand handling and the crushing weight of the stock and be porous enough to burn rapidly at the tuyères and yet be not too vulnerable to the chemical action of the gases in the upper part of the furnace. It should be uniform in size for good distribution in the furnace and also uniform in analysis. A uniform coke with well-developed cell structure, that is porous and of light weight, but with strong cell walls and surfaces, seems to be ideal blast-furnace coke. Good by-product coke for blast-furnace use is from 2 to 4 in. in size and will weigh from 28 to 32 lb. per cu. ft.

Coke larger than 4 in. will result in too much coke rolling to the center of the furnace, thereby allowing too much ore to lie along the walls, resulting in the ore being insufficiently reduced on arriving at the zone of fusion, and causing a cold-working and inefficient furnace. On the other hand, coke too fine, which is easily broken up, packs together with the ore too tightly and offers too much resistance to the upward flow of gas. The blast must then force its way through, giving rise to slips.

TABLE 20-VII

	H_2O	Volatile matter	Fixed carbon	Ash	Sulfur
Coal	8 04	45 67	57 86	6.47	1.17
Coke	4.07	0 90	89.53	9.57	0.92

Chemically, a coke with uniformly low ash, low sulfur, and high fixed carbon is desired, but cannot be made unless coal of the proper analysis is used. A typical coal analysis for good coking coal and the resultant coke is shown in Table 20-VII. This coal has been mixed and blended, has had the slate removed, and, finally, has been washed.

Suggested Questions and Problems for Study and Class Discussion

1. Classify fuels as to physical characteristics and method of production. Give illustrations of each class.

2. Describe the formation of coal. What is the effect of thrust pressure on coal formation?

3. What methods of analysis are used on coals? What are the advantages of each?

4. Give a classification of coals and a predominant property of the coals in each class.

5. Describe the origin and formation of petroleum.

6. What methods are in use for the production of fuel oil from crude petroleum?

7. List the general specifications for fuel oil and give the purpose for each specification.

8. What are the so-called elementary fuels? Show by an example how a complex fuel is decomposed into its elementary fuels before combustion starts.

9. Of the reactions listed in Table 8-VII, which are of great importance in producer gas manufacture? Why?

10. Divide the fuel bed of a coal-fired furnace into zones and discuss the process of combustion.

11. What are the drawbacks of hand firing of coal and to what extent are these disadvantages overcome by the use of stokers?

12. What are the general advantages and disadvantages of powdered coal as a fuel? Describe the equipment necessary for its preparation and combustion.

13. Describe the equipment necessary for the efficient use of oil as a fuel. Describe one type of oil burner.

14. Discuss briefly the principles underlying the construction of the various types of gas burners. Which type would you recommend for a small, isolated furnace?

15. What is the surface-combustion principle? How is it utilized in furnaces?

16. Discuss the advantages or disadvantages of lump coal, powdered coal, fuel oil, and coke-oven gas as fuels from the following standpoints:

a. Ease of handling.

b. Amount of excess air necessary for efficient combustion.

c. Ash-handling costs.

d. Completeness of combustion.

e. Storage difficulties.

f. Fire hazard.

17. If dry hydrogen gas at atmospheric pressure is burned completely in a furnace with 32 per cent excess air, calculate the gas analysis of the flue gas (dry basis) from this furnace. How much water vapor is formed?

18. An annealing furnace uses a fuel oil containing 16.4 per cent H and 83.6 per cent C. It is proposed to fire this furnace with 25 per cent excess air. Calculate the flue gas analysis (dry basis), assuming that 10 per cent of the total carbon is burned to CO, the remainder to CO_2. Calculate the amount of water formed per pound of oil fired.

19. The flue gases from a furnace fired with hydrogen-free coke contain 13.9 per cent CO_2, 1.0 per cent CO, and 6.4 per cent O_2. These gases leave the furnace at 750°F. The air used for combustion is substantially dry and enters the furnace at 70°F. Calculate:

a. The volume in cubic feet of the flue gases leaving the furnace per pound of carbon burned.

b. The volume of air in cubic feet entering the furnace per pound of carbon burned.

c. The percentage of excess air.

d. The percentage of the heating value of the coke which leaves the furnace with the stack gases.

20. Discuss the advantages and disadvantages of gasifying coal in a gas producer and burning the gaseous fuel in a furnace, as compared to burning the coal directly in the furnace.

21. Describe the construction and operation of a gas producer. What auxiliary equipment is necessary?

22. Discuss in detail what takes place in the fuel bed of a gas producer. Consider both the gas rising through the bed and the coal descending in it.

23. If a gas analysis of a producer shows 10 per cent CO_2, 15 per cent CO, and 15 per cent H_2, the surface of the fuel bed is a very dull red and the temperature is 1220°F., what is wrong with the operation and what should be done in order to correct the defects?

24. Why are beehive coke ovens only used at times of great demand for coke?

25. What are the requirements of coal for by-product coke ovens?

26. Describe briefly the construction and operation of a battery of by-product coke ovens.

27. Describe the mechanism of coking.

28. What is the effect of size of raw coal on the structure and properties of the coke produced? What are the effects of temperature and time of coking?

29. List the products that can be recovered from the destructive distillation of coal and give one commercial use of each.

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CHAPTER VIII

REFRACTORIES, FLUXES, AND SLAGS

The reactions between substances in contact with one another at high temperatures differ to some extent from the same substances dissolved in water at room temperature. At least, a slightly different perspective is needed in studying these reactions. Reactions between substances in the absence of water are known as reactions "in the dry way," and are of utmost importance in metallurgy as the purification of iron ore in the blast furnace and the subsequent refining of pig iron in the manufacture of steel depend entirely upon them.

REFRACTORIES

A refractory may be incompletely defined as any substance that is infusible at the highest temperature it may be required to withstand in service. This definition is not complete because many other properties are required of a refractory in service, as will be seen later, but the property of infusibility is probably the most important one.

Refractories are essential to metallurgical operations and processes. This statement can be appreciated when one stops to consider that refractories are the principal material of construction used in all furnaces and retaining vessels as well as flues, regenerators, and stacks through which hot gases are conducted. The problem of obtaining refractory materials suitable for metallurgical operations is an important and difficult one because of the widely varying conditions that exist and the severity of the service in most cases. Furthermore, refractories are expensive and any failure results in a loss of time, equipment, product, and, sometimes, loss of life.

General Properties.—The general requirements of a refractory are

1. Infusibility.
2. Resistance to spalling (cracking or crumbling).
3. Minimum coefficient of expansion.

4. Minimum coefficient of thermal conductivity.
5. Minimum permeability.
6. Good physical properties.
7. Resistance to chemical attack.

A perfect refractory would possess all these properties to the highest degree but all known refractory materials have shortcomings in one or more of them. The factor of cost must always be taken into account because, although better refractories are known than the ones used in commercial installations in some cases, the better refractory is invariably much more expensive and the inferior material must be used because it is cheaper.

All metallurgical refractories possess the property of infusibility (resistance to softening or melting) to quite a high degree. In any one type of refractory, this factor depends chiefly upon its composition. Most commercial refractories are made up mainly of a single chemical compound of high melting point, the remainder being made up of impurities which, in general,

TABLE 1-VIII.—MELTING POINTS OF MINERALS AND OXIDES PRESENT IN REFRACTORIES

	°C.	°F.
Alumina, Al_2O_3	2050	3722
Chromite, $FeO \cdot Cr_2O_3$	2180	3956
Chromium oxide, Cr_2O_3	1990	3614
Ferric oxide, Fe_2O_3	1548	2808
Ferrous oxide, FeO	1360	2480
Ferro-ferric oxide, Fe_3O_4	1538	2818
Kaolinite	1755	3191
Lime, CaO	2570	4658
Magnesia, MgO	2800	5072
Rutile, TiO_2	1700	3092
Silica (cristobalite), SiO_2	1713	3115
Zirconia, ZrO_2	2720	4928

lower the melting point of the material as a whole. The melting points of some pure compounds present in refractories are given in Table 1-VIII. (It should be remembered, however, that the melting point of a mixture of two or more substances of high melting point is, in most cases, considerably lower than the melting point of any of the components.

Spalling may be defined as the breaking or cracking of refractory brick in service to such an extent that pieces are separated or fall away, thus leaving new surfaces of the brick exposed. Four types of spalling are recognized: (1) Thermal spalling, in which the cracking is caused wholly or mainly by rapid expansion or contraction of the brick as a result of rapid temperature fluctuations. (2) Textural spalling is due to changes in the mineral constitution of the hot part of the brick. This may be caused by the action of heat or by the absorption of slags or fluxes, both of which may result in the formation of different zones between the inner and outer brick surfaces. The physical properties of these zones may differ not only from those of the

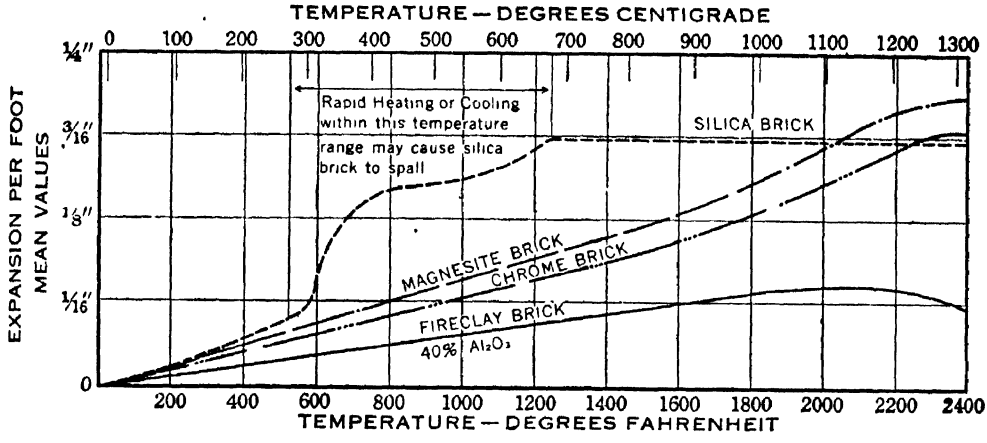


FIG. 1-VIII.—Thermal expansion of some refractory materials. (*Courtesy of the Harbison-Walker Refractories Company.*)

original brick but also from each other. The inner ends of the bricks may tend to crack or fall off for various reasons, such as the development of shrinkage cracks, differences in thermal expansion between zones, or increased sensitiveness to rapid temperature changes caused by internal changes or slag absorption at the hot end of the brick. (3) Mechanical spalling is often due to such influences as abuse in removal of slag, "pinching" caused by thermal expansion, and other causes. "Pinch spalling" in sprung arches is frequently observed and results from the thermal expansion of the heated portions of the brick and the consequent transfer of the stresses in the arch to a relatively small bearing surface at the hot end. (4) Structural spalling is due to improper design of the brick shapes, faulty design or construction of the furnace, or excessive insulation which unnecessarily increases the severity of the furnace conditions.

The effect of temperature on the volume changes of refractory materials is of considerable importance in the design and construction of furnaces. The effect of temperature on the mean expansion per foot of length of four typical refractories is shown in Fig. 1-VIII. In addition to the normal effect of temperature on expansion, some refractory materials undergo internal changes in structure which cause abrupt and important changes in volume. Silica brick is of this type and the volume change over a short temperature interval is so great that rapid heating or cooling between about 525 and 1225°F. may readily cause spalling. It is obvious that silica brick would cause trouble when placed in contact with chrome brick in a furnace which is heated and cooled, owing to their differences in rate of expansion.

TABLE 2-VIII.—APPROXIMATE THERMAL CONDUCTIVITY OF REFRACTORIES
(B.t.u. per hr. per in. per sq. ft. per °F.)

Temperature, °F.	Magnesite brick	Silica brick	Fire clay brick
0	39 5	6.0	5 0
200	37 2	6.8	5.6
400	35 4	7.5	6 1
600	33 3	8.3	6.7
800	31 5	9.0	7.3
1000	30 0	9 8	7.8
1200	28 3	10 5	8.4
1400	26 9	11.3	9 0
1600	25 9	12.0	9 6
1800	25 0	12 8	10 1
2000	24 0	13 5	10 7
2200	23 5	14 3	11.3
2400	23 2	15.0	11.8
2600	23.0	15.8	12.4

Since a large part of the heat losses from a furnace is due to heat being conducted away by the furnace walls, the refractory in use should possess a very low coefficient of heat conductivity. The approximate thermal conductivities of three common refractories at different temperatures are given in Table 2-VIII. The values are expressed in B.t.u. per hour, per inch of thickness, per square foot of wall area, per degree Fahrenheit temperature difference. It can be seen from this table that the conductivity of magnesite brick decreases with increase in temperature but is

much higher than that of the other two, even though their conductivities increase with increase in temperature.

The resistance of refractory materials to the penetration of gases and liquids into them decreases with increase in temperature. Commercial refractories that are used to hold liquids are impermeable to them if they are not subject to chemical attack by the liquid. On the other hand, it is difficult to prevent penetration of gases through refractory materials at high temperatures. In most commercial work, this is not important but must be considered in some laboratory investigations and in the recent work done in the field of vacuum melting of steel in commercial quantities.

Of the physical property requirements of refractories, one of the most important is resistance to abrasion. Abrasion is defined as the wearing away of a refractory at its surface through the cutting action of solids. Refractories are often subjected to the abrasive action of tools, moving charges as in a blast furnace, or dust-laden gases. This resistance usually decreases with increase in temperature. Refractories have practically no resistance to tensile stresses at any temperature but do have considerable resistance to compression even at elevated temperatures. It is obvious that refractories must be able to withstand their own weight in compression at operating temperatures or the furnace walls will sag. They should also possess resistance to mechanical shock or impact caused by entering charges, working of the charge in the furnace, etc.

Finally, refractories should show a minimum of reactivity with materials that come in contact with them. This is of utmost importance and is the first consideration in determining whether a refractory can be used under a given set of conditions. Acidic oxides in the form of refractories cannot be placed in contact with basic oxides (and vice versa) at high temperatures because of the formation of compounds of the two substances, the result being either an eating away of the refractory or a lowering of the melting point of the refractory owing to the formation of the compound or compounds. This action of promoting fusion of a solid material by chemical action is known as *fluxing* and enters into many metallurgical processes. For example, the ash of many coals acts as a flux on refractories, the acid furnace lining is acted upon by FeO (base) in the acid open-

hearth furnace, and mill scale, essentially FeO, acts on the bottoms of heating furnaces unless they are protected by basic materials.

The type of chemical reactivity of refractories forms a basis for their classification: acid, basic, and neutral refractories. The refractory to be used for a given purpose must always belong to the class that will not react chemically with its surroundings under the conditions of service. Of the possible refractories in the class, the final choice will depend upon their other suitable properties, uniformity of composition, and cost.

Acid Refractories.—Acid refractories owe their acid character only to silica, SiO_2, and are of two kinds: those composed mainly of silica and those composed mainly of aluminum silicate or clay. Silica, itself, occurs in several forms. Quartz and chalcedony are common silica minerals while quartzite, sandstone, and sand are composed largely of free silica in the form of quartz. Ganister is another name for quartzite. In the pure state, silica fuses at a very high temperature (see Table 1-VIII), but when heated in contact with basic substances, it forms silicates, some of which are easily fused. In refractories composed mainly of silica, therefore, the presence of impurities, alumina, as well as the stronger bases, must be guarded against. As a refractory, silica is used in the natural forms of sand and cut stone and in the prepared form of brick. Sand contains from 90 to 99.5 per cent silica, depending upon its origin, and is used to make up the bottoms of acid open-hearth furnaces and in some types of heating furnaces. A mixture of either crushed firebrick or silica rock and clay, often called ganister, is used in tamped linings, particularly in acid Bessemer converters. The term ganister is incorrectly used in the foregoing connection because ganister is actually a dense, high-silica rock suitable for the manufacture of silica brick.

Silica bricks are prepared from quartzite rock found in Pennsylvania, Wisconsin, and Alabama. Quartzite is a rock consisting essentially of quartz (SiO_2) grains so strongly bonded together that when the rock is broken the fracture will pass through both grains and bonding material, instead of between the grains. In other words, the bonding material is as strong as the grains. The rock is first crushed to a fine size and then intimately mixed with about 2 per cent of lime, CaO, in the form

of milk of lime, which acts as a cement or binding material to hold the particles of silica together and to give the brick the necessary strength. This moist mixture is compressed and molded in the desired shapes and allowed to dry slowly. The bricks are finally heated at about 1500°C. (2732°F.) in large kilns, held there for several days, and allowed to cool very slowly. The brick contains lime and small quantities of iron oxide, alumina, and alkalies as impurities. In service, silica brick must be heated very slowly between atmospheric temperature and a dull red heat or spalling will result, owing to rapid expansion in this temperature range (see Fig. 1-VIII). Quartzite brick are made in approximately the same manner as silica brick except that clay is used as the binding material.

Clay is defined as an earthy or stony mineral aggregate consisting essentially of hydrated silicates of alumina, plastic when sufficiently pulverized and wetted, rigid when dry and vitreous (glassy appearing) when fired at a sufficiently high temperature. The principal mineral constituent of most fire clays is called kaolinite, which consists theoretically of 39.8 per cent alumina, 46.3 per cent silica, and 13.9 per cent combined water. The chemical formula is $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$. The ordinary varieties of clay are formed by the decomposition or weathering of certain rocks, are more or less impure, and contain 10 to 15 per cent of combined water. Fire clays (refractory clays) are of two varieties: plastic and flint clays. The latter is very hard and rigid, even when ground, but is very refractory. The best refractory clays are associated with the coal measures in Pennsylvania. The impurities in clays are alkalies; sand; gravel; iron oxides, silicates, and sulfides; calcium and magnesium silicates or carbonates; titania, TiO_2; and organic matter. Of these impurities, the basic oxides Na_2O, K_2O, CaO, MgO, and FeO are the most harmful as they lower the fusion point of the clay, owing to the fact that aluminum silicate combines with bases at high temperatures, forming complex silicates.

In making *fire clay brick*, often called simply *firebrick*, the clay, in a finely crushed condition, is moistened with a definite amount of water and thoroughly mixed. When flint clay is being used, some plastic clay is used as a binder. Upon being dried, clay begins to shrink and continues to do so during the burning, when the combined water is driven off and the brick

becomes hard. Allowance for this shrinkage must be made when the brick is molded, while calcined or burned clay is employed in the mixture to control the shrinkage. Once burned, the brick ceases to shrink and permanently loses the property of plasticity. The refractory properties of fire clay brick depend upon the nature and amount of impurities and on the ratio of silica to alumina. Besides its use as a brick, clay is important as a refractory mortar used in laying bricks in furnaces and ladles and as a plaster where seamless linings are required.

Basic Refractories.—*Magnesia*, MgO, with a melting point of 2800°C., is the most satisfactory basic refractory. It is obtained by calcining the mineral magnesite, $MgCO_3$, which contains, when pure, 47.6 per cent MgO and 52.4 per cent CO_2. The known deposits contain small amounts of iron oxide, lime, and silica. Owing to the comparative rarity of the deposits, magnesia is an expensive refractory and is used only where conditions require its use. It has a further disadvantage of not possessing much mechanical strength at high temperatures.

The raw magnesite is hand-picked at the quarries, calcined at a sufficiently high temperature (about 1500°C.) to drive off all the CO_2, to effect full shrinkage of the material, and to produce hard, dense nodules which are inert to atmospheric moisture and carbon dioxide. It is finally screened into sizes depending upon its future use. Magnesia is furnished in crushed form and as brick. The brick is universally used for the bottoms and lower side walls of basic steel melting furnaces, and dead burned magnesite in crushed form, mixed with about 25 per cent of basic slag, is widely used in making up sintered bottoms of basic furnaces.

At high temperatures, magnesia enters into chemical combination with fire clay or silica refractories. At about 2650°F., a violent chemical reaction occurs between dead burned magnesite and first-quality fire clay brick with the formation of a thin liquid slag. The reaction is weaker between dead-burned magnesite and silica brick and begins to take place at about 2750°F. Magnesite brick should always be separated from fire clay brick and usually separated from silica brick by a course of neutral chrome brick. Although dead-burned magnesite does not absorb moisture or carbon dioxide from the air to an appreciable extent, it slakes readily when acted upon by steam.

TABLE 3-VIII.—TYPICAL CHEMICAL ANALYSES OF REFRACTORIES

Refractory	Silica, SiO_2	Iron oxides	Alumina, Al_2O_3	Lime, CaO	Magnesia, MgO	Alkalies, Na_2O and K_2O	Water, H_2O	Titania, TiO_2	Carbon dioxide, CO_2, or ignition loss
Acid:									
Gannister	93–99	0 1–1 0	0 2–4 5	0 1–1 0		Trace–0 5			
Silica sand	90–99	0 3–3 5	0 2–3 0	0 1–1 0	Trace–0 1	Trace–0 5			
Silica brick	94–96	0 5–1 5	0 5–1 5	1 5–2 0	0 1–0.5	0 25 max.			
Fire clay (plastic)	48–73	0 5–8 0	15–45	0 1–1 2	0 1–1 5	0 2–3 0	6–14	0 1–2 5	
Fire clay (flint)	40–63	0 1–3 0	21–47	0 1–1 0	0 1–0.5	0 5–3 0	6–14	0 1–1 5	
Fire clay brick	Mixture of plastic clays, or plastic and flint clays								
Basic:									
Magnesite, raw	1–5	0 3–4 0	0 2–3 0	0 5–3 0	38–45	0 2–1 0	0 5–1 5		43–51
Magnesite, burned	2–9	0 5–8 0	0 5–5 0	1 0–6 0	76–91	0 5–2 0	0 1–0 5		0 1–0 5
Dolomite, raw	0 3–1 0	0 5–2 0	0 5–3 0	30–34	20–23	0 2–1 0	0.5–1.0		46–48
Dolomite, burned	1–2	1 0–4 0	1 0–6 0	52–55	33–36	0 5–2 0			1–3
Dolomite, synthetic.	1–6	1 5–8 0	1–5	45–55	28–38	0 5–2 0			0 4–1 0
Magnesite brick	1–5	1.0–7 0	1–4	0 2–1 0	85–94	0 2–1 0			0 1–0 3
Neutral:									
Graphite, natural.	4–12	0 2–4 0	2–10	0–0 3	0.1–1.0	0.1–0 6		0 1–0 4	Vol. C. 1–5 Graphite C 70–92
Graphite, tar-coke	0 1–4 0	0 1–2 0	0 1–3 0						Graphite C 90–99
Chromite, chrome ore	2–10	10–22	8–30	1–3	8–20				2–3 Chromium oxide 30–56
Chrome brick	2–6	11–17	15–33	1–5	10–18				Chromium oxide 30–45
Forstarite	40–43	1 5–4 5	0–1	0–2	50–58				
Olivine	39–43	5–17	0–1	0–2	44–52				

Another basic oxide, CaO, possesses a melting point almost as high as that of MgO but the pure substance cannot be used as a refractory because it slakes readily with water [reacts with H_2O to produce $Ca(OH)_2$]. When mixed with MgO, it gives fairly satisfactory results if used properly. Dolomite, a naturally occurring mixed carbonate of calcium and magnesium, is found in large quantities in this country and, after calcining, is commonly used as a cheaper substitute for MgO. A typical composition is shown in Table 3-VIII. It is not so good a refractory as magnesia but is widely used for making up the banks of basic open-hearth furnaces and in patching the sintered magnesite bottom between heats.

Neutral Refractories.—The ideal furnace lining is, of course, a neutral material that will not react chemically with either acid or basic substances at any temperature. Two such substances are well known but the conditions of natural deposits are such that the substances are expensive and are used only in restricted quantities. The two materials are graphite and chromite.

Graphite is a naturally occurring form of carbon although it can be prepared artificially in small quantities. In this country it is found in New York and requires extensive purification before use. It is infusible even at the temperature of the electric arc but burns at that and lower temperatures forming CO and/or CO_2. Mixed with clay as a binding material, it is used in making special brick, crucibles, etc. It is an excellent refractory in that it possesses relatively good compressive strength at elevated temperatures and is insensible to thermal shock (rapid heating and cooling). It burns only very slowly at open-hearth furnace temperatures.

Chromite most nearly approaches the ideal refractory from the chemical standpoint as it can be used satisfactorily under both acid and basic conditions. It is also the principal ore from which chromium is produced. The fusion point of pure chromite, $FeO \cdot Cr_2O_3$, is well above the highest temperatures normally employed in iron or steel making but, owing to this fusion point, it is difficult to set or sinter together in crushed form. Chromite brick is made by mixing the crushed ore with lime, or clay and lime, as a binder and is widely used as the dividing courses between acid and basic brick and in the bottoms of soaking pits as it also is inert to molten iron oxide. The ground ore, mixed

with ground slag, is used to patch the walls of open-hearth furnaces near the slag line.

Testing of Refractories.[1]—The best test for a refractory is a trial test in which the material is put in service under the most severe conditions it is expected to withstand in service. As this method of testing is expensive if the material does not come up to expectations and is furthermore often impossible, laboratory tests are often resorted to in obtaining data on the relative value of different materials for a specified type of service. Such tests are not always conclusive because of the difficulty of obtaining laboratory conditions identical with service conditions. Laboratory tests have the advantages, however, of being rapid and relatively inexpensive. Furthermore, laboratory tests are of great importance in determining the uniformity of a certain type of refractory.

These tests are both chemical and physical in nature. From the chemical analysis the composition of the material, its uniformity of composition from specimen to specimen, and its quality are judged. Physical tests are used to supplement the chemical analysis because the method of manufacture of the refractory and the care with which it is carried out affect the quality of the material. The most important physical tests are fusion point, crushing strength, expansion and contraction, slagging, porosity, density, resistance to compression, impact, abrasion, and spalling tests. Most of these tests will not give absolute values of the properties desired but, under carefully controlled conditions, are very valuable in comparing different refractories for a certain type of service.

The *fusion temperature* of a refractory is determined either with the aid of an optical pyrometer or by the use of Seger cones. These cones are small triangular pyramids, 6 cm. high with a base of 2 cm., and are composed mainly of aluminum silicates of various compositions. By varying the ratio of alumina to silica, the melting points of successive cones can be varied through wide ranges of temperature. For low-temperature melting points, varying amounts of lime or Na_2O are added. In this way, a series of cones can be prepared with melting points ranging between

[1] Details of tests are from those used by the Carnegie-Illinois Steel Corp., as given by Camp and Francis in "The Making, Shaping, and Treating of Steel," 5th ed., 2d impression, Carnegie-Illinois Steel Corp., 1940.

1040 and 2015°C. (1922 to 3659°F.). Upon being gradually heated, the cones will soften and slowly bend until their tops touch the base plate upon which they are resting. This point is taken as the fusion point of the cone. In testing the fusion point of an unknown refractory, a pyramid of the same dimensions as the standard cones is made and placed in a furnace with several standard cones which have melting points suspected to be near that of the unknown refractory. The furnace is then gradually heated until the unknown substance fuses. If, for example, cone 28, which melts at 2939°F., fuses just before the unknown substance and cone 29, which melts at 2984°F., is still standing when the unknown substance has melted, the fusion points of the unknown refractory can be estimated accurately enough for most purposes. Since the fusion point taken in this manner is not a finite value, but is, rather, expressed in terms of the cone of nearest fusion point, the term "pyrometric cone equivalent," or P.C.E. value, is now standard nomenclature for this test.

The resistance of a brick to *compression* is often measured on a modified form of a machine which is used to measure the hardness of metals (the Brinell machine). A round steel ball, 2½ in. in diameter, is so mounted that it can be placed in contact with the brick and a pressure applied to the ball by a load bearing on the ball from above. This pressure forces the ball into the brick, making a measurable indentation. In making the test, the brick is slowly heated to 1350°C. (2462°F.), held at that temperature for at least 3 hr., and quickly removed to the testing machine. A pressure of 850 lb. is immediately applied to one flat surface by means of the ball and this load gradually increased to 1,600 lb. at the end of 5 min. The depth of the depression made by the ball is taken as the measurement of the resistance of the brick to compression.

A brick is prepared for an *expansion* and *contraction* test by grinding the ends so that they will be parallel to each other and perpendicular to the sides. Its length is then measured by means of a special type of micrometer. The brick is heated to the temperature at which it is to be used in service, removed from the furnace, and immediately measured with the microm-

eter. The expansion is expressed in inches per foot of original length.

By means of the *slagging* test, the penetration of slag into the brick is determined. The brick is prepared by drilling two circular holes, 2½ in. in diameter, in the brick to such a depth that the area of the greatest cross section is 1.7 in. These holes are placed at the centers of each half of one flat face of the brick. The brick is then heated to 1350°C. and 35 g. of a pulverized blast-furnace slag placed in one hole and the same amount of a heating furnace slag in the other. The brick is held at that temperature for 2 hr., cooled to room temperature, and cut lengthwise so that both cavities are bisected. The area penetrated by the slag is readily visible on this cross section and is measured and expressed in square inches.

The density of the brick is determined by weighing it in air, determining its size by measurement, and calculating the density in pounds per cubic foot. This value is the apparent and not the true specific gravity of the substance of which the brick is made because the brick always contains pore spaces, the size and number of which are greatly dependent upon the method and details of manufacture. The apparent specific gravity is lower than the true specific gravity in proportion to the amount of space taken up by the pores. The value of the apparent specific gravity is of more importance from a construction standpoint than the true specific gravity because it has to do with the weight-volume relationship of the brick itself.

The resistance of a brick to *thermal spalling* is often determined in the following manner: The brick is dried at 100°C. for 5 hr. or longer, weighed, and placed in the door of a furnace so that only one end is directly subjected to the heat. The brick is held at furnace temperature of 1350°C. for 1 hr., removed, and dipped into 2 gal. of water at 20°C. to a depth of 4 in. and held there for 3 min. It is then withdrawn from the water, allowed to dry 3 min., and replaced in the furnace door. This cycle of operations is repeated until the brick has been quenched 10 times, after which it is dried at 100°C. for 5 hr. or more and again weighed. The percentage loss in weight is taken as a measure of the spalling. This test is a measure of the spalling due to rapid temperature changes only and is not indicative of

the resistance to spalling under service conditions where many other factors enter in as has already been discussed.

The *abrasion* test attempts to determine the wearing qualities of the brick at the temperature at which it is to be used in service. The brick is first ground to a uniform thickness and a preliminary cut made in the end by a carborundum grinding wheel. The brick is then heated to the desired temperature, quickly transferred to the grinding wheel, and the preliminary cut deepened by contact with the wheel for a given time at a definite pressure. The depth of cut made on the hot brick is taken as a measure of resistance to abrasion. The test is affected by the pressure applied, the width of the cutting wheel, and the speed at which it revolves, as well as the particle size of the carborundum. All these factors, in addition to the time of contact, must be kept constant in order to get results from which comparisons can be made.

The *impact* test is of importance in the case of brick subjected to mechanical shock or blows, particularly brick placed in blast-furnace tops where they are struck by the entering charge. In fact, this particular service is so severe in this regard that metal linings are in use at the tops of many furnaces. The resistance to impact of refractory brick is greatly affected by the temperature, being, in some cases, as much as 40 per cent weaker at 600°C. (1112°F.) than at room temperature. In testing brick for use in blast-furnace tops, the following procedure is often used: The brick is heated to 260°C. (500°F.) over a period of 1 hr., removed to the testing machine, and placed in it with one end up. The machine drops a steel ball, 2½ in. in diameter and weighing 2.34 lb., upon the end of the brick from heights successively increased by 2 in. until the brick breaks. The height in inches of the ball in the last test is taken as the measure of the resistance of the brick to impact.

FLUXES

When metal is separated in the molten state from the impurities with which it may be chemically combined or physically mixed, the operation is known as *smelting*. Because of the fact that the metal in most ores is both chemically combined and physically mixed with undesirable impurities, the operation of smelting combines two processes: the reduction of the metal

from its compounds and its subsequent separation from the mechanical mixture. A flux is necessary in almost all smelting operations in order to effect this double separation. In the first place, many of the impurities have melting points above the operating temperature of the furnace, and their presence in the solid state would choke up the furnace and render the separation of the metal a very slow if not impossible procedure. The first function of the flux, then, is to render the impurities more easily fusible by combining chemically with them. In the second place, some elements, being reduced at the same time as the metal, combine chemically with it while other elements and some radicals, chemically combined with the metal in the raw materials, refuse to be separated from it, except when another substance is present for which they have a greater chemical affinity than the metal itself. The second function of the flux is to combine chemically with the impurities and remove them from combination with the metal. We say that the impurities are "fluxed out."

The choice of a flux for a given smelting operation depends upon the chemical composition of the materials entering, the melting points of the various compounds it is possible to form with the flux, and the fact that an acidic material will combine chemically with a basic substance quite readily at high temperatures. In general, if the substance to be fluxed is basic in character (lime, magnesia, etc.), an acid flux is used, while if the impurities to be fluxed are mainly acid (silica, phosphoric acid, etc.), a basic flux is required. In most ores, the impurities present belong to both classes, with one class or the other, usually the acids, predominating. In a few iron ores, the impurities are so well balanced that the ore is self-fluxing, *i.e.*, the impurities combine with each other and flux themselves out. In a few other cases, judicious mixing of two or more ores will bring about the same effect. In these cases, however, it is generally necessary to add a neutral flux or both acidic and basic fluxes in order to have a slag volume large enough for good operation. In order to control the fusibility, a low-melting-point neutral flux is required in many metallurgical smelting operations.

Acid Fluxes.—*Silica*, SiO_2, is the only natural substance that may be classed as a strictly acid flux, and it is readily available in the form of sand, gravel, and quartz. Since the impurities

in iron ores are largely acidic in nature, an acid flux is not generally needed in blast-furnace practice. When it is necessary to increase the acid content of the furnace charge, however, acid open-hearth or Bessemer slags are used since they are distinctly acid and, at the same time, contain iron oxides that can be recovered.

Silica sand will have an analysis range as follows:

	Per Cent
Silica, SiO_2	95–98
Oxides of Fe and Al	1 5–4 0
Lime, CaO, and magnesia, MgO	0.25–0.50
Alkalies	0.25

Alumina, Al_2O_3, can function as either an acid or a basic flux, depending upon conditions; for that reason, it is known chemically as an *amphoteric* substance. Thus, it forms aluminum silicate with silica and, with a strong base such as sodium hydroxide, it forms sodium aluminate. Alumina is seldom used intentionally as a flux but, as it is present in nearly all raw materials used in iron and steel manufacture, its presence and action are unavoidable.

Basic Fluxes.—The principal natural basic fluxes are limestone and dolomite. In addition, iron and manganese oxides act as basic fluxes in certain processes such as the acid open-hearth process. Both limestone and dolomite are used as fluxes in the blast furnace and there is not a great deal to choose between them for this service. A high percentage of magnesia (over 3 per cent) in blast-furnace slag makes it undesirable for cement, but this grade is satisfactory for concrete, ballast, etc., as it makes the slag harder. Aside from this unimportant one, the main factor governing the choice between limestone and dolomite is the cost per ton of available base.

By "available base" is meant the amount of basic substance left in the raw flux after the acids present in it have been satisfied. In Table 4-VIII are given typical analyses of several grades of limestone, the results of which do not add up to 100 per cent because of the CO_2 driven off during the analysis. The available base in the limestone given can be determined. The iron and phosphorus are completely reduced in the blast furnace and the moisture is driven off. The silica and alumina will require

TABLE 4-VIII.—REPRESENTATIVE ANALYSES OF LIMESTONES*

Use	Open hearth	Blast-furnace, Bessemer pig operation	Blast-furnace, basic open-hearth pig operation
Silica	0.80	3.43	1.20
Iron	0.10	0.30	0.60
Phosphorus	0.005	0.006	0.033
Moisture	0.10	0.60	0.60
Alumina	0.16	0.86	0.70
Lime	54.90	51.45	53.88
Magnesia	0.47	1.66	0.68

* CAMP and FRANCIS, "The Making, Shaping, and Treating of Steel," 5th ed., 2d impression, Carnegie-Illinois Steel Corp., 1940.

an equivalent amount of lime and magnesia to flux them and some lime will be needed to flux the sulfur. The resulting value will be used later in calculating blast-furnace burdens.

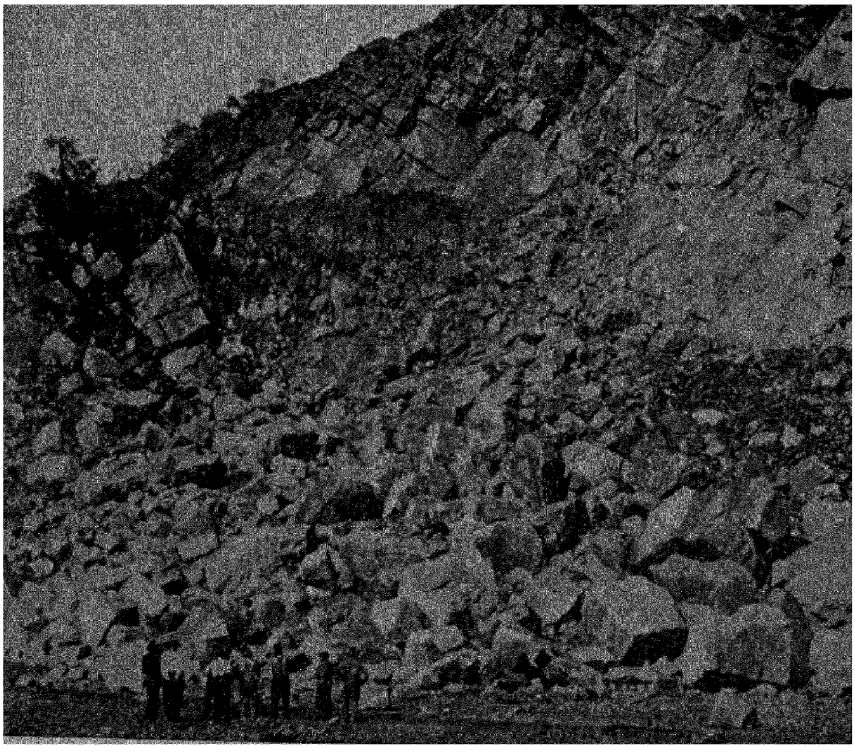


FIG. 2-VIII.—A limestone quarry. (*Courtesy of the Jones and Laughlin Steel Corporation.*)

Limestone, a term that also includes dolomite for our purpose here, is found throughout the area drained by the Ohio and Mississippi rivers in immense beds. The stone is quarried by blasting, and the broken stone is crushed and screened and, in some cases, washed. A view of a limestone quarry is shown in Fig. 2-VIII. Care should be taken to keep the stone free from clay as its presence disturbs blast-furnace operation. Ordinarily, about one-half ton of limestone is needed in the blast furnace per ton of pig iron produced. Limestone with the lowest silica content is usually reserved for basic open-hearth furnaces, that with the lowest phosphorus for blast furnaces making Bessemer pig iron, while limestone with higher phosphorus content is used in furnaces making pig iron for the basic open-hearth process.

Neutral Fluxes.—Neutral fluxes are used for the purpose of making slags more fusible without changing the ratio of acids to bases in them, a practice common in open-hearth operation. Fluorspar is the substance generally used although calcium chloride can be substituted.

Fluorspar will have an analysis range as follows:

	Per Cent
Calcium fluoride, CaF_2	85 00 min.
Silica, SiO_2	5.00 max.
Calcium and magnesium carbonates, barium sulfate, etc.	10.00

SLAGS

Slag is the name used for the molten product formed by the action of the flux upon the impurities (gangue) in the ore and fuel or upon the oxidizable impurities in the metal. It results principally from the neutralization of acids and bases, therefore corresponding to the salts in "wet" chemistry. The word *cinder* is often used to denote slag in solid form.

The slag in the iron- and steelmaking processes performs many important functions:

1. It separates most of the impurities from the metal because of its low melting point, chemical activity, dissolving power, and low density. The average fusion points of slags are given in Table 5-VIII.

2. It protects the metal from the injurious effect of hot gases because it lies on top of the metal.

3. It prevents overheating of the metal because it possesses low thermal conductivity. This is especially important in electric arc furnaces.

4. It conserves the heat in the bath by the same means.

5. Since it holds in solution oxides that rise from the metal and are insoluble in the metal, it serves to keep the metal clean.

TABLE 5-VIII.—AVERAGE FUSION POINTS OF SLAGS

	°C.	°F.
Acid open-hearth slag	1250	2280
Basic open-hearth slag	1250	2280
Blast-furnace slag	1170	2140
Heating furnace slag	1165	2130

Blast-furnace Slags.—The blast-furnace slag is an important aid in controlling the analysis of the pig iron produced. It is the only positive means of removing sulfur from the metal and is one means by which the hearth temperature can be regulated, since its fusion temperature varies with its composition. The slag is composed mainly of calcium silicate, the magnesia being combined with part of it as a double salt. The small amounts of iron, manganese, and alkali oxides present act the same as magnesia in forming double silicates with lime. The sulfur is dissolved in the slag in the form of CaS. The 12 per cent or more of alumina in the slag may be considered to be either acidic or basic as indicated before. In a highly siliceous (acid) slag it may form double silicates with lime, while in a strongly basic slag it may take the place of silica in neutralizing lime and magnesia. It is considered as an acid in ordinary blast-furnace practice, however, as in calculating the available base in a limestone, for example.

A typical analysis of a blast-furnace slag from a furnace making basic open-hearth pig iron is given in Table 6-VIII. The sum of alumina and silica is about 50 per cent or a little less. After deducting enough lime to satisfy the sulfur (CaS), the sum of the remaining lime and magnesia is about 45 to 48 per cent. The remainder is made up of CaS and small amounts of iron and manganese oxides. Blast-furnace slags are, therefore, close to neutrality and usually do not vary more than from 2 to

3 per cent on either the acid or basic side. The ratio of CaO to MgO may vary quite widely without affecting the slag properties. If the Al_2O_3 content becomes too high, the slag has a tendency to become viscous at operating temperatures.

TABLE 6-VIII.—TYPICAL ANALYSIS OF SLAGS

Substance	Blast-furnace	Basic open-hearth (finishing slag)	Acid open-hearth (finishing slag)	Acid Bessemer
Silica, SiO_2	35.0	16 0	61.0	64 0
Lime, CaO	44 0	46 0	8.2	7.5
Ferrous oxide, FeO	1.15	12 0	13.6	14 0
Ferric oxide, Fe_2O_3	.....	4.5		
Manganese oxide, MnO	1 10	6 0	12.8	12 8
Alumina, Al_2O_3	15.0	3 5	2.2	5.5
Magnesia, MgO	2 75	6 0	....	0.5
Oxide of phosphorus, P_2O_5	.....	2.5		
Metallic iron	0.30	2 7	....	2 5
Total sulfur	1 35	0 09		

Open-hearth Slags.—Final basic open-hearth slags contain a much higher percentage of bases than blast-furnace slags. In fact, the lime and magnesia are nearly always more than twice the sum of silica and alumina (see Table 6-VIII). This large excess of bases is necessary for the removal of phosphorus and the small and variable amount of sulfur. If the lime content of the slag becomes too high, the working of the heat is retarded because of increased viscosity.

The slag in the acid open hearth consists essentially of oxides of iron and manganese silicates. The silica content varies from 50 to about 58 per cent while the remainder consists of FeO, MnO, CaO, MgO, and combined phosphorus and sulfur. FeO and MnO make up the vast majority of this remainder.

Suggested Questions for Study and Class Discussion

1. List the general requirements of a refractory, giving at least one reason for each requirement.

2. Give an example of a service in which each type of spalling occurs alone or predominates in producing spalling.

3. Why must silica brick be carefully heated between room temperature and a low red heat? What is the result of carelessness in this regard?

4. How do we classify refractories? List the important refractories in each class.

5. Describe briefly how silica brick is manufactured.

6. What is kaolinite? How do we classify clays? What are the principal uses of fire clay?

7. Describe briefly the processing necessary to prepare magnesia refractories.

8. What precautions should be observed in using magnesia refractories?

9. What are the advantages and disadvantages of laboratory tests of refractories? Describe briefly at least three such tests.

10. What is a flux? What are the functions of a flux? Upon what factors does the choice of a flux depend?

11. Classify fluxes and list the commercial fluxes under each class name.

12. Why are different grades of limestone used in open-hearth and blast-furnace practice? Illustrate.

13. What is a slag? List its most important functions in iron- and steel-making.

14. Why is the ratio of bases to acids so high in basic open-hearth slags and not in blast-furnace slags?

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CHAPTER IX

THE MANUFACTURE OF PIG IRON IN THE BLAST FURNACE

THE ORES OF IRON

Iron is one of the most abundant elements found in the earth, since over 200 minerals contain it in some form. Iron is rarely found in the native state; a small amount in Greenland and that occurring in meteorites are the only known deposits. Of the many minerals containing iron, deposits of only four of them are of any economic importance as ores in this country. An ore, then, is a mineral or a mixture of minerals from which one or more elements may be extracted with profit. These are listed in Table 1-IX, together with their properties and other data. This table requires little explanation. The impurities listed do not represent all the impurities associated with the respective ores but only the ones present in the greatest percentages. Phosphorus and sulfur, which are present in all of them, are taken up separately later on. The colors listed in the column designated by "Color on streak test" are produced by drawing a piece of the mineral across a piece of unglazed pottery and observing the color of the streak left on the pottery. In other words, the color of the streak is the color of the powdered mineral, which is often different from that of the mineral in massive form.

From Table 1-IX it can be seen that the hematites in the Lake Superior region and in Alabama, and the magnetite deposits in New York, New Jersey, and Pennsylvania include about all the ore smelted in this country. The Lake Superior ores are relatively pure while those in Alabama are not of such high grade, being higher in phosphorus. There are many other places in the country where iron ores are found but in many of them the deposit is of such a low grade that their mining is not economically practicable at present prices. As the richer deposits now being used become depleted, the low-grade ores will become increasingly important. Other deposits of com-

TABLE 1-IX.—DATA CONCERNING THE ORES OF IRON

Name of mineral	Common names of ore	Chemical formula of mineral	Fe content when pure, %	Principal impurities associated with it	Color of mineral	Color on streak test	Specific gravity and other properties	1928 production, %	Chief producing areas in U.S.
Hematite	Specular, fossil oölitic, or kidney ore	Fe_2O_3	70	Water, silica, alumina, manganese, phosphorus, sulfur	Red or steel gray to black	Red	About 5	95 2	Lake Superior region, Birmingham, Ala., Chattanooga, Tenn., Hartville, Wyo.
Magnetite	Magnetite or lodestone	Fe_3O_4	72 4	Ordinary, including phosphorus and titanium	Black	Black	About 5, strongly magnetic	3.5	New York, New Jersey, Pennsylvania
Limonite	Limonite or yellow ocher	$2Fe_2O_3 \cdot 3H_2O$	59 9	Silica, alumina, lime, manganese	Yellow to brown	Yellow-brown	3.4–4 0	1.3	Alabama, Tennessee, Virginia, Georgia
Siderite	Blackband, clay-iron-stone, or spathic iron ore	$FeCO_3$	48.2	Silica, alumina, lime, manganese	Gray to brown	Gray	3.8	Very low	Ohio, Kentucky

mercial size and grade are so far from centers of consumption that the cost of transportation becomes prohibitive.

The most important deposit in the United States is the group of large beds of hematite in the Lake Superior district (Minnesota, Wisconsin, Michigan). Owing to the purity of the deposit, the ease of mining, and the low cost of water transportation, this region produced over 92,000,000 long tons of ore in 1941. The average iron content of this enormous production was 51.2 per cent—considerably below the theoretical figure given in Table 1-IX. This is due, of course, to the impurities associated with the mineral, the principal ones being silica, alumina, lime, magnesia, manganese, titanium, sulfur, and phosphorus. Most of these are removed, to a greater or less degree, by subsequent metallurgical treatment. Phosphorus and sulfur are, however, particularly undesirable because of their effect on steel and cast iron and the difficulties involved in their removal. These effects will be covered in detail in a later chapter.

One may wonder why the ores are shipped all the way from this district to Pittsburgh for smelting, and why the blast furnaces are not located near the ore mines. The reason for this is that coal and limestone are also needed in the smelting operation and it is very difficult, if not impossible, to ship coal or coke long distances with the accompanying handling because of their friability and the large amount of fines produced. Consequently, the furnaces are built near the coal deposits and the ore transported the longer distance. In the Alabama district, coal, ore, and limestone are found in close proximity to each other, an ideal arrangement. The low transportation charges account for the fact that Alabama producers can use an ore of lower grade and still compete with other producers who use the Lake Superior ores.

The important iron ore deposits now being mined in the world are in England, Scandinavia, and France, besides those in the United States. There are several deposits in the British Isles, some of which are of high grade (rich in iron) while others are rather impure, being high in phosphorus. The ore of the Minette district in Lorraine, France, is also high in phosphorus and produces, on smelting, a pig iron suitable for the basic Bessemer process. It is of low grade (30 to 40 per cent iron) but contains limestone as a gangue and is, therefore, self-fluxing,

which makes it as good an ore as if it contained a much higher iron content. In contrast to the above-mentioned deposits which are hematites, the ores of Norway, Sweden, and Finland are magnetities, most of them being of high purity. They are very large deposits and most of the ore production of this region is exported because of the scarcity of coal.

Three types of iron ore have been mined in Pennsylvania: magnetite, hematite, and limonite. Prior to the development of the Lake Superior beds, all three of these ores were mined in Pennsylvania. The carbonate deposits have never been worked. The abandonment of the mining of limonite and hematite and the limitation of the mining of magnetite to one mine were not due to the exhaustion of these ores, but simply to the fact that the deposits were not rich enough to be mined in competition with the high-grade Lake Superior ores mentioned above. The only iron ore being mined in Pennsylvania at present is a magnetic iron ore deposit at Cornwall. The Cornwall deposit has a low iron content, averaging 35 to 40 per cent, but it is profitable to mine it because it can be beneficiated very cheaply. This mine produced over 2,900,000 tons of ore in 1940.

Mining of the Ores.—Two methods of mining iron ore are in use: open-pit mining and underground mining. An ore body that lies near enough to the surface and is sufficiently thick to pay to strip off the overburden is mined by open-pit methods. A considerable proportion of the Lake Superior hematites are soft, fine, and earthy in character and lie close to the surface in large, deep beds. They are, therefore, well suited to open-cut methods of mining. The overlying material is stripped off with large steam shovels and the ore mined by means of the shovels. Railroad cars are run into the pit on tracks, as shown in Fig. 1-IX. The ore is loaded directly into the cars and taken to the concentrating plant or the ore docks. The Alabama deposits as well as the magnetite deposits at Cornwall, Pa., are mined largely by this method. The advantages of this method of mining are that an enormous annual production is possible, the mining costs are very low, the saving in labor is large, and, with the exception of the steam shovel operators, skilled labor is not necessary. For these reasons, as large a percentage as possible of these soft ores are used in the blast furnace in order to avoid the necessity of underground mining. The limit of the use of

fine ores is reached when they begin to choke up the furnace and impede the blast, and the cost of cleaning the top gases becomes too great.

Some of the Lake Superior deposits are hard and rocky in character and lie at depths from 300 to 5,000 ft. below the surface. These ores are mined by standard shaft methods of underground mining and, owing to the greater difficulties involved, are more expensive.

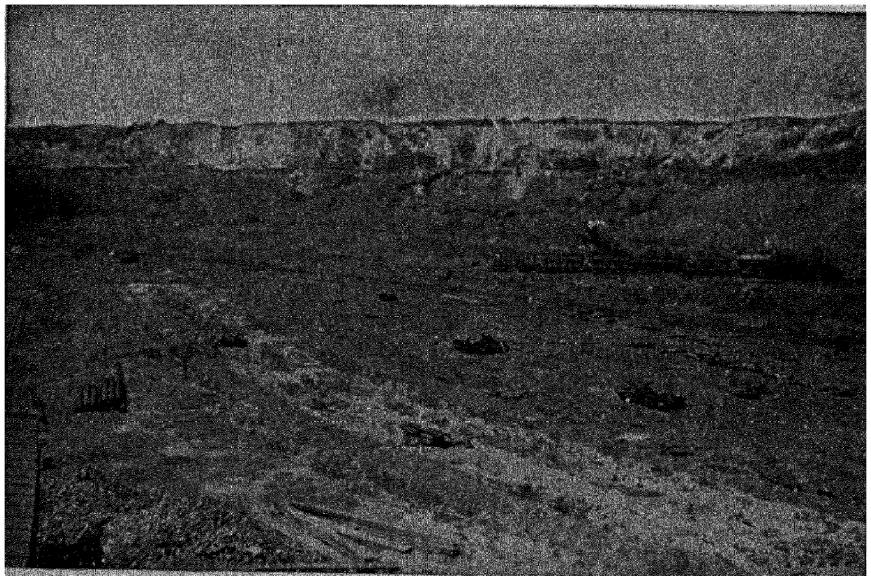


FIG. 1-IX.—Open-cut mining on the Mesabi range. (*Courtesy of the Jones and Laughlin Steel Corporation.*)

Valuation and Grading.—The important factors to be considered in the valuation of iron ores are richness (iron content), chemical composition, and accessibility. It is obvious that as high an iron content as possible is desired of the ore as the transportation of gangue is costly and represents a loss. Of the impurities present in Lake Superior ores, some are detrimental to furnace operation and some are not. Analyses of three typical ores from two ranges of the Lake Superior district are given in Table 2-IX on both the natural and dry basis. Analyses at the mine are reported on a dry basis, *i.e.*, the samples are dried at 212°F. before analysis, thus removing the free water and at least a small part of the water of crystallization. The "natural" analyses are on the basis of the ore as shipped. From these figures it can easily be seen that ores containing the same iron content on the dry basis can vary widely in amounts of impurities,

particularly in water content. It should be remembered that the theoretical iron content of a hematite ore, Fe_2O_3, is only 70 per cent, the rest being oxygen.

Of these impurities, CaO and MgO are desirable as fluxes while the alkalies Na_2O and K_2O are not detrimental. Up to about 5 per cent, Al_2O_3 is beneficial as it aids in regulating the blast furnace. It is generally conceded that from 5 to 7 per cent silica is necessary for blast-furnace operation in order to produce a sufficient slag volume, but above about 10 to 12 per cent the

TABLE 2-IX.—ANALYSES OF TYPICAL LAKE SUPERIOR HEMATITES*

Ore	State	Fe, %	P, %	SiO_2, %	Mn, %	Al_2O_3, %	CaO, %	MgO, %	S, %	H_2O, %	Ignition loss, %
Marquette..	Dry	57 36	0 137	15 62	0 08	1 26	0 68	0 33	0 007	. .	0 03
	Natural	56 82	0.135	15 47	0 08	1 25	0 67	0 327	0 007	0 94	0 03
Mesabi.....	Dry	57 03	0 042	12 48	0 56	1 69	0 21	0 32	0 010		2 80
	Natural	52 54	0 039	11 50	0 52	1 56	0 19	0 29	0 009	7 87	2 58
Mesabi... .	Dry	57 06	0 081	7 33	1 72	1 00	0 30	0 40	0 010		2 00
	Natural	47 47	0 067	6 09	1 43	0 83	0 25	0 32	0 008	16 80	1 66

* CAMP and FRANCIS, "The Making, Shaping, and Treating of Steel," 5th ed., 2d impression, Carnegie-Illinois Steel Corp., 1940.

amount of limestone necessary to flux the silica becomes excessive for economical furnace operation. Because the amount of *silica* reduced to *silicon* in the blast furnaces is controllable and, in former years, the amount of silica was never very high, this factor was not particularly troublesome. With the depletion of the low silica ores and the consequent advent of beneficiation methods, however, this factor has received considerable attention. The increase in silica content of the annual average analyses of Lake Superior ores is given in Table 3-IX and illustrates this point very well.

An ore is available for the manufacture of the ordinary grades of pig iron when its manganese content does not exceed 2 per cent of the iron content; between 2 and 10 per cent (same basis) it is necessary to mix the ore with others containing little of this element. If the manganese content is above 15 per cent of the iron content, the ore is suitable for the manufacture of spiegeleisen. The lowest possible water content is desired of iron

ores because of the added cost of transportation and the added burden on the blast furnace.

The impurities sulfur and phosphorus receive considerable attention in evaluating iron ores because both are detrimental to the properties of iron and steel. Since the average blast-furnace slag will hold less than 5 per cent sulfur (as CaS) and the actual sulfur content of the slag should not even approach this figure, the sulfur content of the ore should be as low as possible. The phosphorus content of the ore forms a basis for classification of the ore into *Bessemer* and *basic* grades. Phosphorus is not removed from the pig in acid steelmaking processes and should not be present in amounts greater than 0.110 per cent

TABLE 3-IX.—YEARLY AVERAGE ANALYSES OF LAKE SUPERIOR ORES*

Year	Fe natural, %	SiO_2 natural, %	Moisture, %	SiO_2 dry, %	Total % SiO_2 + moisture natural
1902	55.39	5 69	8.71	6 23	14 40
1905	54.14	5 72	10.20	6 37	15 92
1910	51.68	7.09	11 06	7 97	18 15
1915	51.49	7 22	11 29	8 14	18.51
1920	51 69	7.23	11.09	8 13	18 32
1925	51 74	7.53	10.58	8 42	18 11
1930	51.33	7.75	10 92	8 70	18 67
1935	51 44	8 93	10 75	7.98	19 68
1937	51 53	8 27	11 31	7.18	19.58

* "Lake Superior Iron Ores," Lake Superior Iron Ore Association, 1938.

in acid Bessemer steel except in certain cases. There must, therefore, be a relation between the iron and phosphorus contents of the ore in order to fulfill this specification. The phosphorus content of the coke and limestone should also be taken into account. For example, if the iron content of an ore is 60 per cent and the phosphorus content is 0.045 per cent, the per cent P in the pig, acquired from the ore, is 0.045/0.60 = 0.075 per cent. If the estimated phosphorus pickup from the coke and limestone is 0.020 per cent, the total per cent phosphorus expected in the pig iron is 0.075 + 0.02 = 0.095 per cent. The ore in question is, therefore, of Bessemer grade. In order to qualify in this class,

the total should not be above 0.100 per cent, because an allowance of 0.01 per cent P must be allowed for iron loss during purification. Ores containing more than the maximum P content as calculated above are classed as basic ores because the phosphorus can be reduced during purification by basic steelmaking methods. In evaluating ores, all these factors should be taken into account as well as accessibility, already discussed.

Owing to the wide variation in the analysis of Lake Superior ores, they are classified by analysis into certain grades and different analyses mixed, when necessary, in order to produce these grades.

The grading is done by sampling the ore in the cars as quickly as possible and rapidly analyzing the samples for SiO_2, Fe, P, and sometimes Mn. From these data, the car of ore can be put into a certain grade, mixed with other suitable ores if necessary, and the consumer's specifications met.

Beneficiation of the Ores.—By beneficiation is meant a treatment of the ore that will increase the iron content of the ore shipped, with a consequent reduction in the amount of gangue (inert material)—silica, in particular. The beneficiation of iron ores, as well as the methods used for improving them, has lagged far behind the methods used for the improvement of the ores of other metals. There have been two main reasons for this: (1) In the early days, the reserves of ore in the Lake Superior region that could be used in the blast furnace without treatment were so large as to seem almost limitless. (2) The selling price of the ore was so low that elaborate treatment of the ore was economically impossible. With the rapid depletion of the highest grade deposits in later years, steps had to be taken toward concentrating leaner ores to a marketable grade.

In many cases, the silica content of the ore shipped can still be kept within the desired limits (8 to 10 per cent) by mixing high-grade ore with ores of lower grade, with or without beneficiation of the leaner ores. The beneficiation of Lake Superior ores is, however, increasing year by year. In 1930, of the total ore shipped from that district, about 13½ per cent was beneficiated by washing, drying, and sintering and 25½ per cent by crushing and screening.[1]

[1] CLYDE E. WILLIAMS, Iron Ore Beneficiation, *Mining and Met.*, **12**, 186 (1931).

A washing plant was first installed in the Mesabi range in 1910 and the method used was quite successful on wash ores for about fifteen years. The wash ores are composed of hematite and fine silica sand and were improved by screening, followed by hand picking and treatment in log washers, turbos, and concentrating tables. A log washer is essentially a wooden or metal shaft, about 25 ft. long, to the outside of which are fastened spiral blades. The shaft rotates in an inclined trough with a clearance between it and the trough about equal to the size of the largest particles in the feed. The feed is introduced about one-third of the distance up from the lower end of the inclined trough and the revolving blades force the hematite up the incline against a descending stream of water which is introduced at the top. The blades agitate the material and free a portion of the gangue which is carried over the tailboard at the lower end of the trough, the concentrate being removed at the top. A turbo is a log washer that is equipped with additional water inlets along the bottom of the trough. Water is forced in through these inlets and further aids in agitation and separation. Concentrating tables are specially designed machines that effect separation on the basis of size and difference in specific gravity between the silica and the hematite and are particularly designed to separate the finer sizes.

The developments in washing in recent years have brought about the replacement of the turbos and tables by the much more efficient bowl classifiers and Dorr washers. Figure 2-IX is a flow sheet of a washing plant put into operation in the Lake Superior district. The details of operation are beyond the scope of this volume and the interested student should consult a textbook on ore dressing. At the present time, pilot plants are in operation and experiments are being conducted on the use of the Rheolaveur system (adapted from coal classification) on these wash ores, which seems to show a great deal of promise.

In many of the leaner types of ores in the Lake Superior region, the silica adheres to the hematite in such a way that coarse crushing and, in some cases, fine grinding are necessary to free the hematite from the silica so that the latter may be washed out. Coarse and intermediate crushing is used at the present time in some cases, but fine grinding has not proved to be economically possible at the present price of ore. The present

limitation on the finer sizes of ore has also precluded the use of fine grinding.

It is evident to the producers of iron ore that more elaborate concentrating plants will be needed in the near future since the ores that can be concentrated to a point where they contain only 6 or 8 per cent of silica by the foregoing washing methods are rapidly diminishing and many washing plants are now producing concentrates from leaner ores assaying 10 to 12 per cent silica. The chief difficulty standing in the way of introducing more elaborate methods is that the first cost and operating costs of

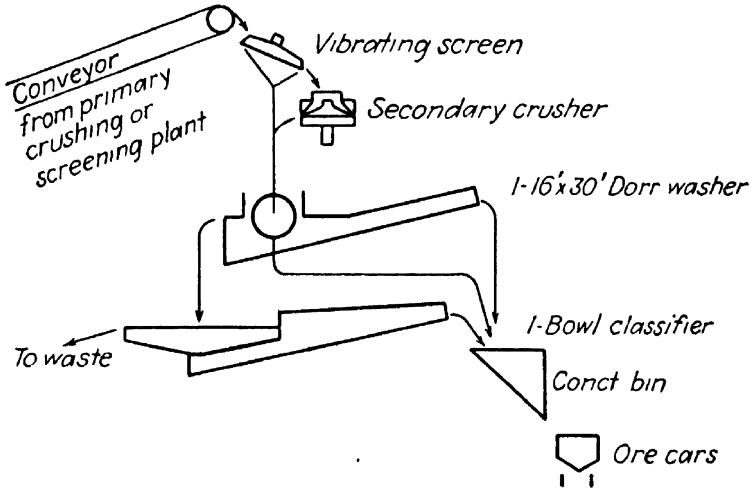


FIG. 2-IX.—Flow sheet of a recent washing plant. (*Mahon and Counselman, "Developments in Washing Mesabi Iron Ores."*)

such a plant are too high to be economically possible at the present selling price of the ore.

Nevertheless, a considerable amount of research work and experimentation with pilot plants is going on at the present time in an attempt to adapt concentration methods now used for the ores of other metals to iron ores. The use of jigs and other highly specialized equipment to handle the fine sizes, followed by drying and sintering of the fine concentrate, is receiving considerable attention.

Sintering is conducted by mixing the fine ore with about 10 per cent of coal, igniting a thin layer of this mixture and burning the coal by drawing air through this layer. Either a Dwight-Lloyd or a Greenawalt sintering machine is used for this operation. The temperature thus produced is sufficient partly to melt some of the minerals in the ore and produce a

strong cellular cake of excellent physical characteristics for introduction into the blast furnace. In this way, a large amount of high-grade fines are saved because the particle size would otherwise be too small for blast-furnace use. Also, experiments are being conducted in regard to magnetic roasting. The partly concentrated ore is heated to a red heat, passed into a reducing atmosphere which reduces the Fe_2O_3 to Fe_3O_4, and cooled in this atmosphere to prevent oxidation. The resulting Fe_3O_4 (being strongly magnetic) is separated by up-to-date wet magnetic separators in essentially the same manner as the magnetite ores of New York, New Jersey, and Pennsylvania are concentrated at the present time.

The following ideal qualifications for a beneficiation plant, taken from a paper by W. E. Davis,[1] presents a fair picture of the direction in which iron ore concentration methods must develop in the future:

1. The concentrate produced should contain 9 per cent or less of silica and 60 per cent or more of iron.
2. The recovery of iron should be above 85 per cent.
3. At least one-half of the concentrate should require no sintering.
4. Radical changes in structure and analysis of the ore should not seriously affect the grade of concentrate produced.
5. The plant should be located at some central point so that its ore supply will come from a number of mines with a long total operating life.
6. The plant should be capable of expansion in size to produce at least 1,000,000 tons of concentrate during a shipping season.
7. The total cost of treatment cannot greatly exceed $1.00 per ton of beneficiated ore normally shipped, with iron ore at its present price.

Transportation.—The importance of Lake Superior hematite deposits rests, to a large extent, upon the cheap transportation facilities that exist by virtue of the chain of Great Lakes. If the ore had to be transported to the smelting centers entirely by rail, the cost of the ore at the furnaces would be prohibitive in the Pittsburgh district. The methods of handling and transporting the ore that have been developed are capable of handling large

[1] DAVIS, W. E.: Concentration of Mesabi Hematites, *Mining and Met.*, **11, 518 (1930).**

amounts of the material at a very low cost. In many cases the entire operation of handling the ore from its position in the ore bed to the stock pile at the blast furnace is carried out entirely by mechanical means.

From the mines, the cars of ore are drawn by locomotives to docks on the lake shore where they are dumped by gravity into immense hoppers. The positions of the openings in the bottoms of these hoppers correspond exactly to the hatches of large ore-carrying steamers so that, by locating the steamer under these hoppers, a full cargo of from 10,000 to 20,000 tons can be loaded

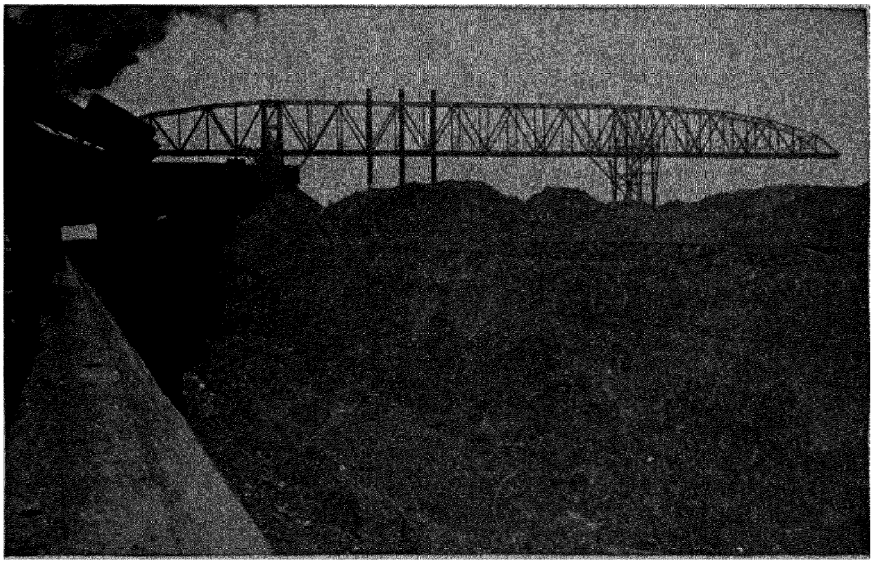


FIG. 3-IX.—View of iron ore unloading docks. (*Courtesy of the Jones and Laughlin Steel Corporation.*)

in a very few minutes. The ore carriers then proceed down the chain of lakes to their destination where the unloading is rapidly accomplished by means of large, electrically operated unloading machines (see Fig. 4-IX). As much as 15,000 tons of ore can be unloaded and piled on the docks (Fig. 3-IX) in about 4 hr. At the same time, another large machine picks up whole cars of coal and dumps their contents into chutes leading to the coal bunkers of the vessel so that the boat may start on its return journey to the mines as soon as the ore is removed.

If the blast furnaces are not located on the lake shore, the ore is loaded into cars and hauled by rail to the furnaces where it is stored in a large pile known as an ore yard. A large storage pile at the furnaces is necessary since navigation on the lakes is closed from November to April because of the ice and enough

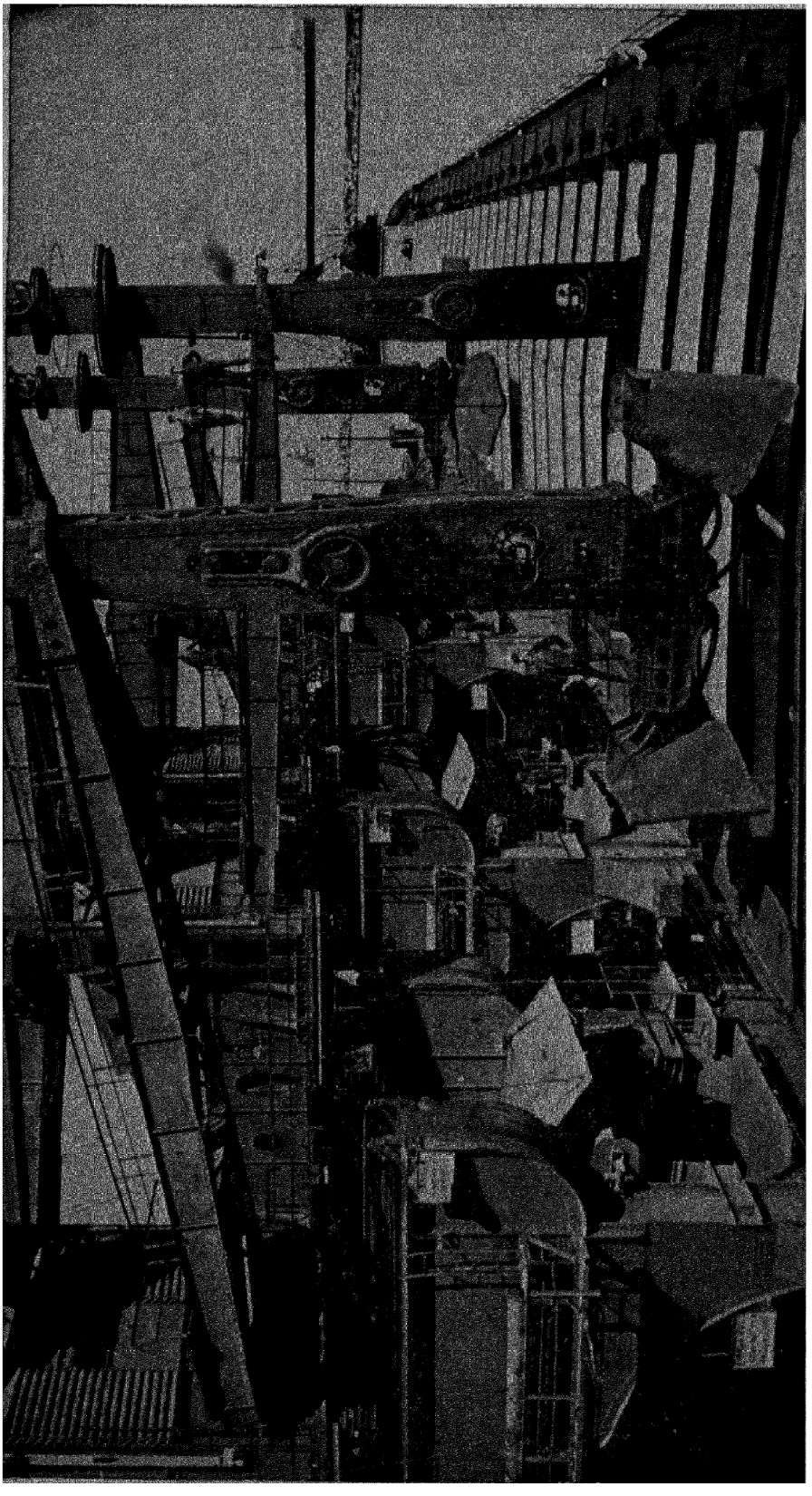


FIG. 4-IX.—Unloading an ore boat with Hulett electric unloaders. (*Courtesy of the Youngstown Sheet and Tube Company.*)

ore must be on hand to run the furnaces through the winter. The operations of loading, unloading, and piling the ore have the beneficial effect of thoroughly mixing the ore, if ores of different analyses are mixed to produce a certain grade.

THE MANUFACTURE OF PIG IRON

Historical.—The history of the use of metals by man dates well back before the dawn of civilization. It is a fascinating subject and a lot of data have been gathered in regard to it by the study of metal specimens found in the ruins of ancient civilizations and very old mine workings.

Probably the first metals used by man were gold, silver, and copper, which were found in the native or metallic state and used principally as ornaments. As man evolved from the Stone Age, the use of metallic implements and weapons grew slowly. According to many archaeologists, the use of bronze followed the use of the native metals by the ancients. Most modern metallurgists who have delved into the subject disagree with this belief because of the difficulties involved in smelting copper-tin alloys. The belief today is that iron antedated the use of bronze by a considerable period of time, but the easy corrodibility of iron implements and weapons has wiped out all traces of its early use and left bronze as the earliest remains of smelted metals. Although this assertion has never been proved, it is quite probable that it is true, since iron can be reduced from its ores much more readily and by cruder methods than can copper or tin. Also, the ores of iron are considerably more widespread than those of other metals, particularly tin.

There is some evidence that iron was used by the Egyptians in building the pyramids about 4000 B.C. but there can be no doubt that it was used by the ancient Hebrews, by the Assyrians about 1400 B.C., and, more recently, by the Greeks. Although there are no records (except on some Egyptian monuments) of how these early iron implements were made from the ore, it was probably very much like the methods employed by uncivilized tribes in Africa and India today. Easily reducible ore, mixed with charcoal, was smelted in shallow pits in the ground. The blast was furnished by bellows made from goatskins and was introduced through bamboo tuyères. The product was an impure mixture of spongy iron, slag, and unreduced ore. This

was again mixed with charcoal and resmelted, and the hot waxy mixture of iron and slag was hammered into various shapes. This type of iron was produced commercially about 1000 B.C.

A very old method of iron production was practiced before Roman times in India, and the same method is in use in that locality today. The furnace is round and of open construction, built of clay, is 2 to 4 ft. high, about 9 in. in diameter at the bottom, and 6 in. at the top. It has two openings near the bottom, one for working the furnace and the other for inserting the bamboo blast pipe which is connected to goatskin bellows. The ore is fed in alternate layers with charcoal and, after several hours of blowing, a pasty mass of iron is withdrawn and pounded to free it partly from slag. Wootz steel, the first known type of steel, was produced from this type of iron (after repeated smelting) by cutting it into small pieces, mixing it with a particular wood, and fusing it in clay crucibles placed in a shallow pit fired by charcoal. This material was highly prized by the Romans, although it was not homogeneous and was quite undependable as to properties. These crude methods continued to supply the iron of the world until the beginning of the fifteenth century.

The next improvement in the manufacture of iron was stumbled upon quite accidentally and resulted in the making of cast iron. The use of these early Indian furnaces spread into Europe and they were gradually enlarged to increase production. Water power was introduced in the Rhine region of Germany in about A.D. 1450 to work the bellows. The increase in furnace temperature that resulted melted the iron and it ran from the furnace in fluid form for the first time—the beginning of the cast-iron industry. This new method spread rapidly although the old direct methods of making iron in Catalan forges persisted until quite recently, even in this country.

In the sixteenth century the furnaces producing cast iron, built of sandstone, were roughly rectangular in cross section, about 14 ft. high and yielded 200 lb. of iron every 2 hr. Later improvements resulted in a circular furnace, somewhat higher and provided with an external crucible or breast at the bottom, into which the iron and slag flowed from the furnace.

This early predecessor of the blast furnace was introduced into France and England about A.D. 1550 and was improved

slowly but steadily. Stone tuyères were replaced by copper tuyères, and later by iron tuyères in 1697. Efforts to replace charcoal as a fuel resulted in the use of coal in England, because the shaft of the furnace was increased in height to 30 ft. and charcoal was no longer strong enough to support the charge successfully. Coke was first used with success in 1742 by Richard Ford in England and he later applied the steam engine as a means of working the bellows. These furnaces would each produce about three tons of iron per day (1754). Smeaton, in 1768, invented the cylinder blast engine and in 1829 Nielson,

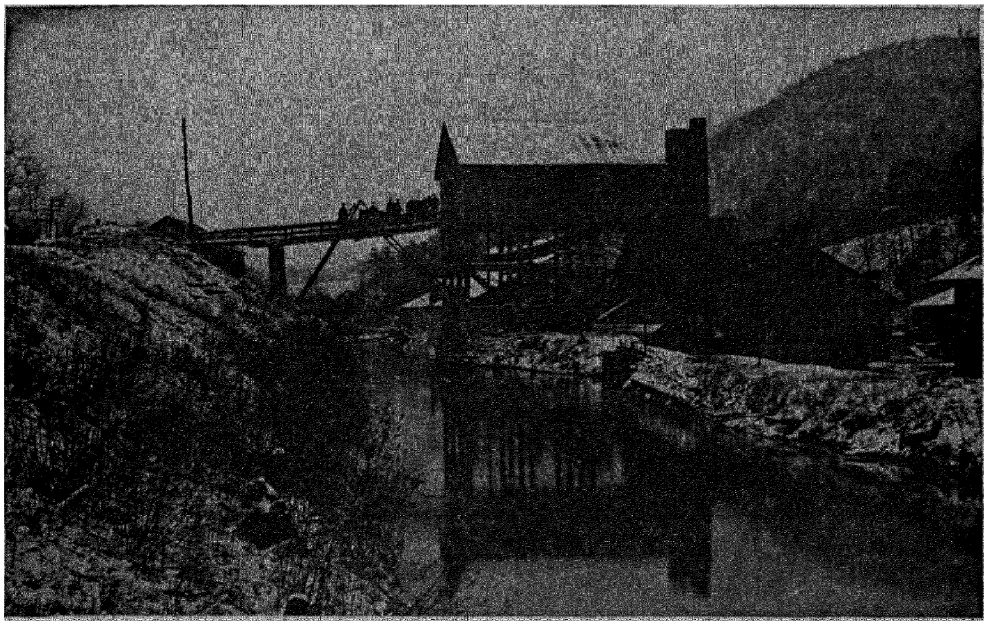


FIG. 5-IX.—A view of a cold-blast charcoal iron furnace.

at the Clyde Works, introduced the hot blast which greatly increased the furnace capacity. From this time on, improvements were rapidly made, until the present-day furnace is capable of producing 1,000 tons, or more, of pig iron in 24 hr.

The early smelting of iron in the state of Pennsylvania is worthy of mention. The furnaces in the central portion of the state made this region the principal iron-producing district of the country in the early half of the nineteenth century. These furnaces were constructed of heavy masonry in the outer form of a truncated rectangular pyramid, some 20 to 30 ft. on a side at the base and from 24 to 40 ft. high. The interior smelting chamber was circular and lined with ganister or sandstone. The

walls widened out below the mouth or charging opening until the bosh was reached, when they again contracted to form the crucible. Charcoal was used as fuel, near-by beds of easily reducible ore were available, and the cold blast was furnished by double bellows operated by water power.

In 1850 there were 48 of these furnaces in the four central counties in Pennsylvania and each produced from 1,000 to 1,600 tons of charcoal pig iron annually, which was marketed either on the seaboard or at Pittsburgh, being transported by canal-boats. The last of these furnaces, Eagle Furnace, was blown out in 1921, after being in operation over 100 years. A view of the Hecla Furnace, taken in 1913, is shown in Fig. 5-IX.

The Blast Furnace.—Practically all of the iron ore mined in this country is put through the blast furnace to produce pig iron. This is one of the basic industries in the United States and its annual production is enormous. This can be readily realized when one stops to consider that iron is the basic metal of this metallic age. It is of particular interest to note that Pennsylvania is the leading state in the manufacture of iron and steel.

Ore, coke to furnish part of the heat and support the charge, limestone to flux the impurities, and hot air for combustion are charged into the furnace, and molten pig iron, molten slag, gases, and dust are withdrawn. The functions of the furnace are to reduce the oxides of iron present in the ore to metallic iron, flux off the major part of the impurities contained in the ore and coke, and to produce the iron, so reduced, in liquid form free from slag.

The modern blast furnace is a tall circular structure, about 100 ft. high, built of firebrick, and reinforced by a steel shell on the outside. The interior form is circular, but of varying diameter. Figure 6-IX shows a cross section of the furnace, charging mechanism, and stockhouse. Owing to the immense weight of the furnace and charge, a heavy concrete and brick foundation is built either on bedrock or upon heavy pilings driven deep into the earth, if bedrock is too far below the surface. The portion of the foundation directly under the furnace bottom is constructed of firebrick. An adequate foundation is essential, as any appreciable settling will cause considerable trouble and may ruin the furnace.

Directly on top of the foundation is placed the crucible or hearth which serves as a receptacle for the molten metal and slag. It is about 25 ft. in diameter and 10½ ft. deep (inside

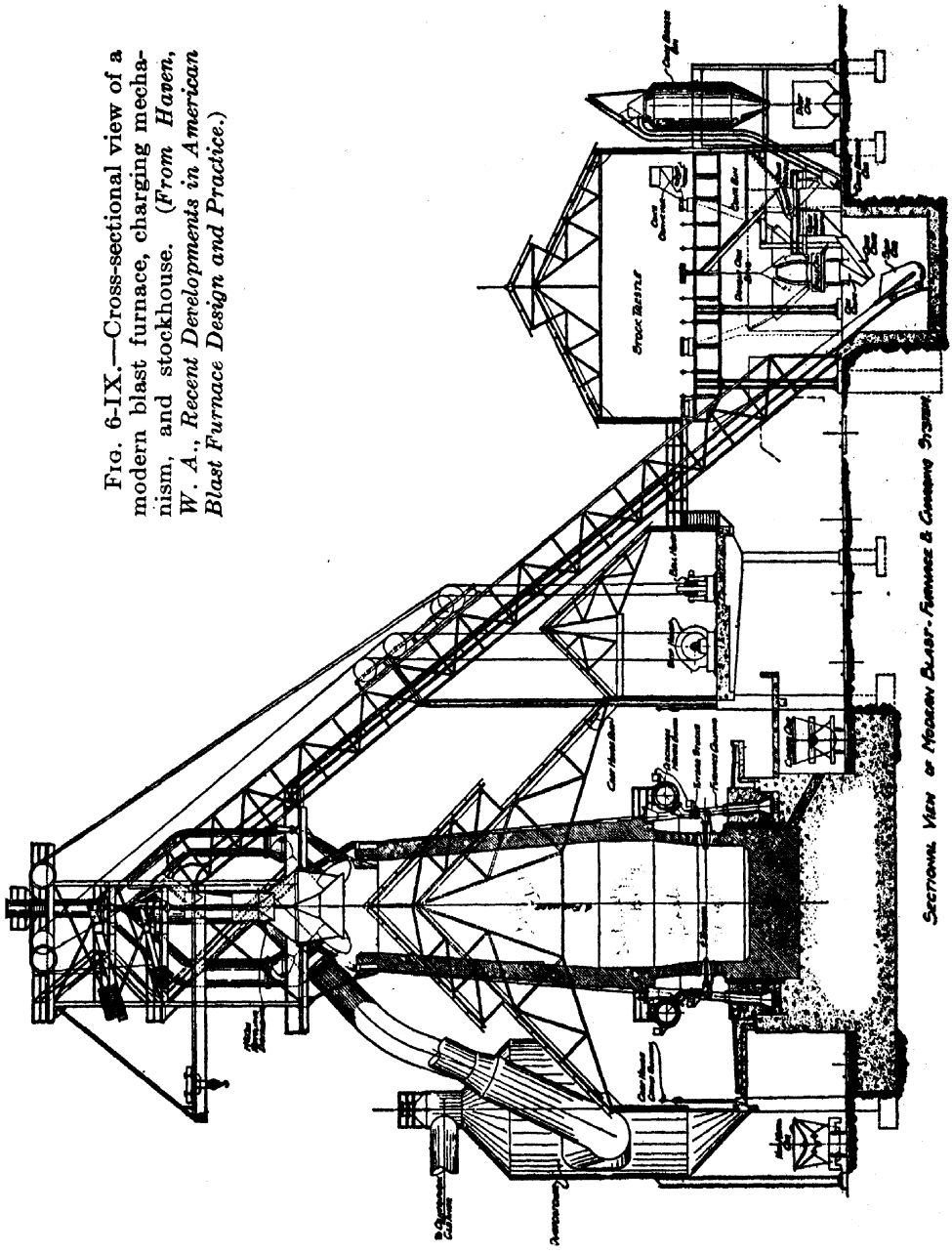


FIG. 6-IX.—Cross-sectional view of a modern blast furnace, charging mechanism, and stockhouse. (*From Haven, W. A., Recent Developments in American Blast Furnace Design and Practice.*)

dimensions) in the larger furnaces. The walls are constructed of the best quality of firebrick and are about 5 ft. thick. Inset water-cooled plates help to protect the brick from the high temperature in this part of the furnace. A heavy water-cooled

jacket, constructed either of steel or cast iron, reinforces the brickwork. At the bottom, the walls of the hearth are sometimes stepped out into the interior of the crucible (the lower 4 or 5 courses of brick), giving the bottom part a basin form. The furnace bottom proper is constructed of heavy blocks of firebrick and is 6 to 12 ft. thick.

Directly above the stepped-in portion of brick an 8- by 8-in. hole is provided in the crucible, called the *tapping hole* or *iron notch.* This hole enlarges slightly toward the outside and the hearth jacket is protected from iron splashings by water-cooled plates. About 6 ft. above the tapping hole and about one-quarter of the way around the furnace from it, another hole is situated, called the *cinder notch.* The vertical distance between these notches limits the amount of iron that may be allowed to collect in the crucible. The cinder notch is larger than the iron notch and is lined with water-cooled bronze castings to protect the brickwork from the destructive action of the molten slag.

The metal and slag are carried away from the furnace in deep metal troughs, called *runners.* The metal runner is sunk flush with the floor of the cast house and has inserted in it a skimmer to separate the metal from the slag which comes out with the metal near the end of the cast. The skimmer is a vertical brick baffle that extends nearly to the bottom of the runner and separates the metal from the lighter slag floating on top by diverting the slag into another channel. The metal flows from the runner into large brick-lined ladles. The slag runner is elevated and leads to the slag ladle or the granulating pit.

Symmetrically distributed around the upper circumference of the hearth are placed the tuyères, 10 to 12 in number, which conduct the hot blast of air into the furnace. They are placed about 4 ft. above the cinder notch and, therefore, limit the height to which the slag can be allowed to rise, since molten slag obviously must not flow into the tuyères. A circular water-cooled jacket is fitted into the brick with fire clay and the bronze water-cooled tuyère fits into it snugly and projects several inches into the furnace. Figure 7-IX, a half cross section of the furnace from foundation to mantle, shows the general shape and placement of the tuyère with respect to its connections and the rest of the furnace. The hot air is brought to the furnace through

the brick-lined *hot blast main*, and enters the *bustle pipe*, a large brick-lined pipe that encircles the furnace several feet above the tuyères and distributes the blast to them through the tuyère stocks, which are connected in turn to the blowpipes. The details of this installation cannot be gone into here, but notice should be made of a ball-and-socket valve through which a bar of steel can be inserted to punch out the tuyère nozzle, if necessary, without shutting off the blast. This arrangement also serves as an eye sight. Recent improvements in tuyère construction have resulted in the diverging nozzle tuyère which is designed to aid in initially directing the air into the furnace.

On top of the crucible and directly above the tuyère openings is placed the bosh, as the widening portion of the furnace is called. The bosh is about 10 ft. in height and its diameter increases (upward from the crucible) about 3 in. for each foot of height. The angle that the bosh wall makes with the horizontal varies considerably in different furnaces, depending upon the type of ore used and the size of the furnace. With the soft, fine Lake Superior hematites, better operation is obtained by using a steep bosh—angles of over 80 deg. from the horizontal being usual. This widening is obtained by stepping out the brickwork, which is about 30 in. thick, and supporting each step-out by heavy steel bands. The outside of the bosh is not usually jacketed, but the brickwork is protected by wedge-shaped, water-cooled hollow bronze castings set between the brick and extending almost entirely through the furnace wall. These bosh coolers, shown in cross section in Fig. 7-IX, are laid in rows all the way around the furnace, and the coolers in each row are staggered with respect to the adjacent rows above and below so that each cooler has only a small section of brickwork to cool. The *mantle*, which is made of heavy steel plates and angles and upon which rests the weight of the stack, is independently supported by 8 to 12 structural steel members embedded in the furnace foundation. With this type of construction, the bosh and crucible may be removed without disturbing the stack.

The portion of the furnace above the bosh, about 70 ft. in height, is called the *stack*, or *shaft*. It is constructed of firebrick and is jacketed by a heavy, riveted, steel shell. In interior shape it is, of course, circular. In the 1,000-ton furnaces, the

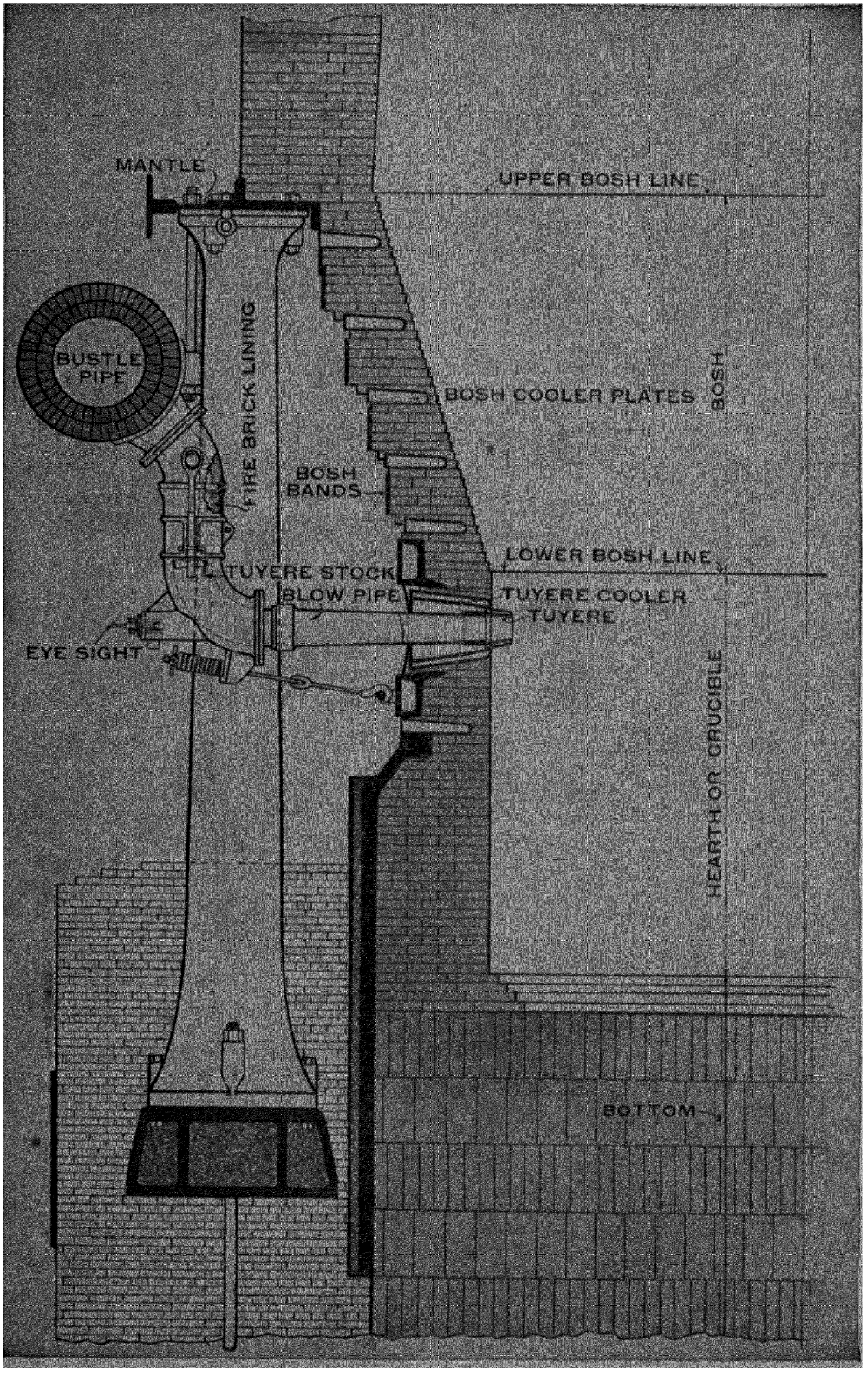


FIG. 7-IX.—Cross-sectional view of furnace from foundation to mantle. (*Courtesy of the Harbison-Walker Refractories Company.*)

inwalls rise vertically above the mantle for about 12 ft., then converge gradually to a point about 10 ft. below the stock line where they again become vertical. The diameter of the shaft is usually just under 28 ft. at the top of the bosh and about 18 to 20 ft. at the stock line. The thickness of the walls of the shaft varies in different furnaces from 5 ft. to less than 1 ft. In the thin wall types, the top of the furnace must be supported by structural steel work. If thick walls are used, no cooling plates are usually necessary above the mantle. This is the usual type of stack construction used. With the intermediate wall thicknesses, cooling plates part way up the stack are necessary. Thin stack walls are not used much in this country but, when used, they are cooled by spraying the steel jacket with water. It is interesting to note in this connection that the large modern blast furnace requires from 5,000,000 to 7,000,000 gal. of cooling water per day, of which amount about one-half is required by the tuyère coolers.

¶ The brickwork used in the interior construction of the entire furnace is of the best fire-clay refractory brick obtainable. The bosh and hearth brick are selected to resist very high temperatures as well as the corrosive action of the flux and slag; the inwall brick must have the properties of withstanding moderately high temperatures and the abrasive action of the stock; while the top brick are selected to withstand the impact of the entering charge and the accompanying abrasion. The properties of the brick used are of utmost importance since the life of the furnace is, in reality, the life of its masonry. Reconstruction of the brickwork is, of course, a very expensive proposition and is avoided as long as possible.

The top of a blast furnace is rather complicated in construction, the details of which vary widely from one furnace to another. Only a general description will be attempted here. The present-day furnace has an arrangement, called the *double bell and hopper*, which permits the introduction of raw materials into the top of the furnace without the escape of top gases. This mechanism is illustrated in Fig. 8-IX. A small hopper at the top of the furnace terminates in the small bell which can be lowered to allow the stock to fall into the larger conical hopper below. The bottom of this larger hopper is closed by a larger bell which, upon being lowered, allows the stock to fall into the

furnace. Since the upper bell is closed during this operation, the escape of gas is prevented. The bells are made of cast steel, in one piece, and are of a sufficient slope so that the stock will slide off of them readily when they are lowered. These bells form

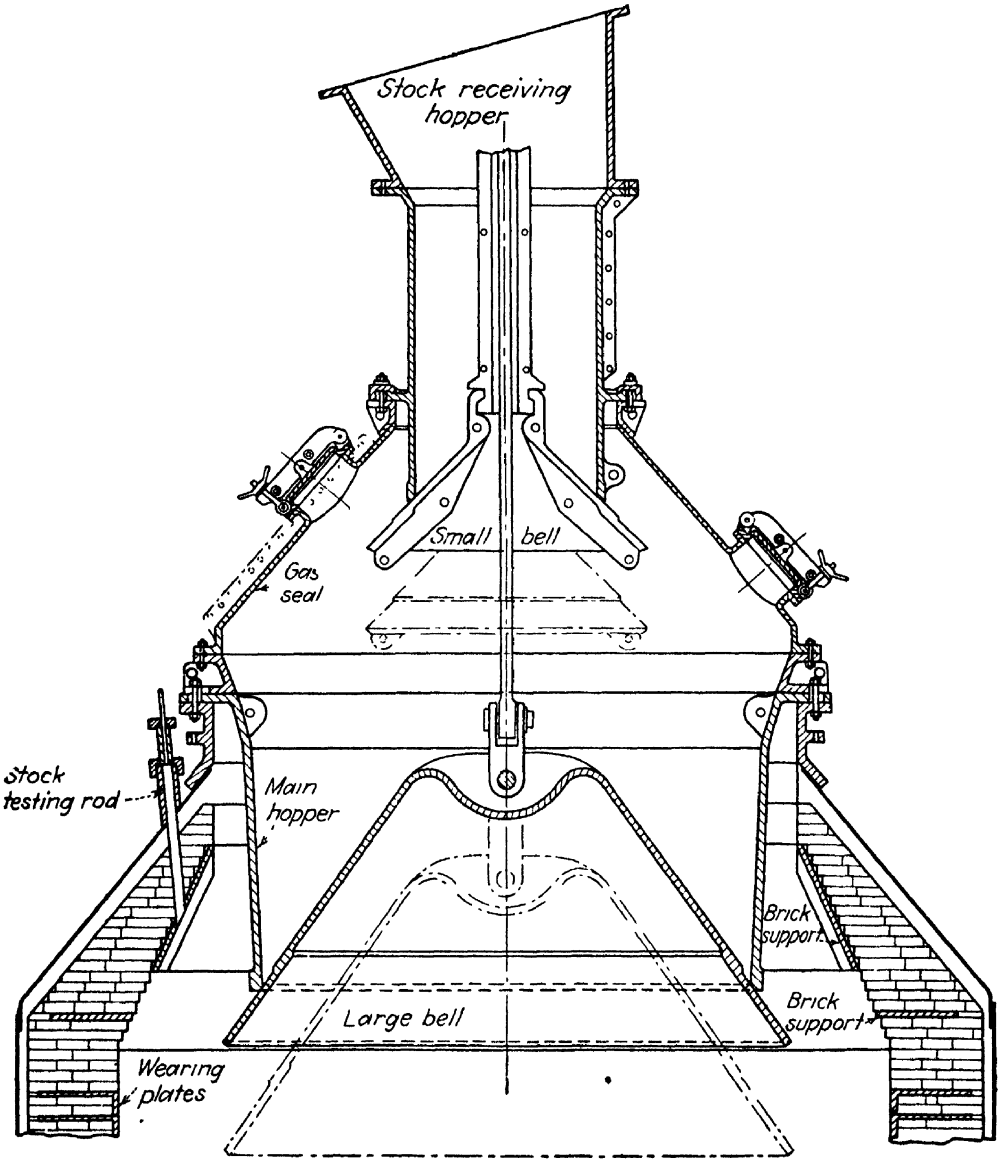


FIG. 8-IX.—Sectional view of a blast furnace top.

a practically gastight seal with the bottom of the hoppers when raised against them and they are supported at their top centers by a rod and sleeve arrangement. The bells are operated independently by means of counter-balanced levers actuated by electric motors, the control being from the stockhouse so that no men are required to work on the furnace top.

There are two types of mechanical charging mechanisms in use, the skip hoist and the bucket hoist, the former being the more common. In the skip hoist type of construction, a double-track steeply inclined runway is built and two skip buckets are so spaced upon it that when one is automatically dumping its load into the upper hopper at the top of the furnace, the other is situated directly beneath the chute, at the bottom of the

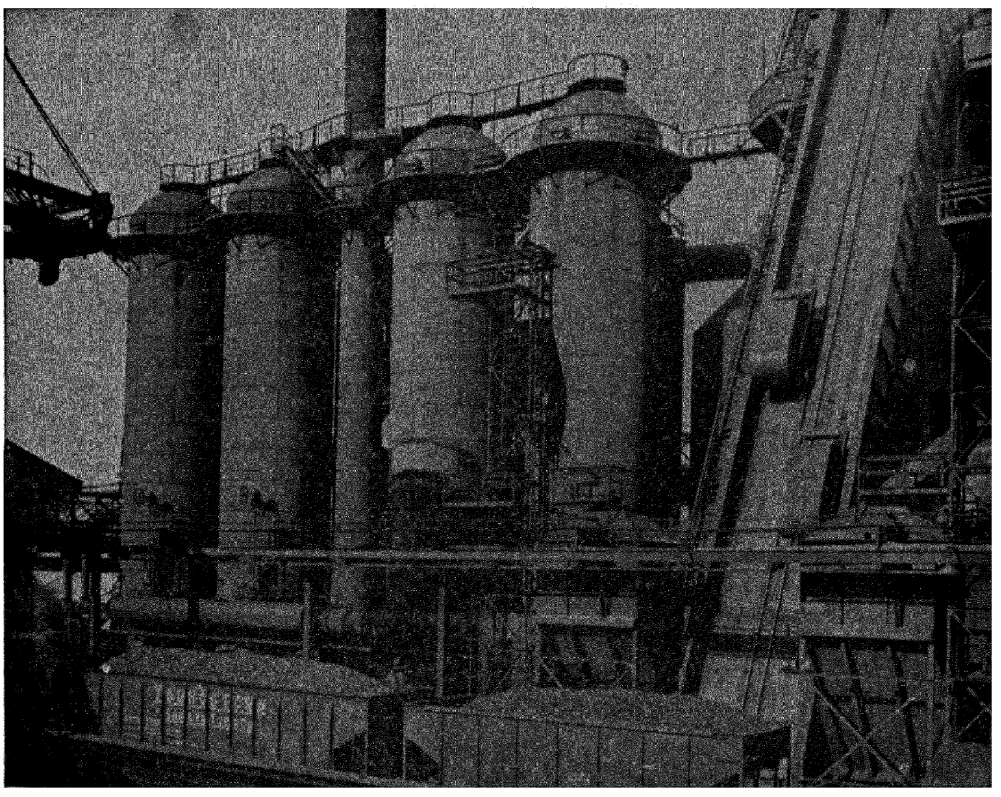


FIG. 9-IX.—A view of blast furnace skip hoist and stoves. (*Courtesy of the Youngstown Sheet and Tube Company.*)

stockhouse. Figure 9-IX shows a modern skip hoist in operation, while the details of the mechanism are shown in the sketch of Fig. 6-IX. In the bucket hoist, the charge is conveyed to the top of the furnace in a large bucket suspended from a carriage which runs on an inclined runway somewhat like that for the skip hoist. The bucket drops the charge directly into the space above the large bell and since the bucket itself is provided with a small bell, it takes the place of the upper bell.

When the charge to the furnace, composed of lumps of all sizes, is dumped on the large bell from the small bell there is a natural tendency for the large lumps to roll farther than the

small ones and for the large pieces to segregate into certain areas. The same situation occurs when the load on the large bell is dropped into the furnace, thus producing segregated areas in the furnace itself. The result of segregation is the channeling of the gases since the larger pieces offer less resistance to the blast,

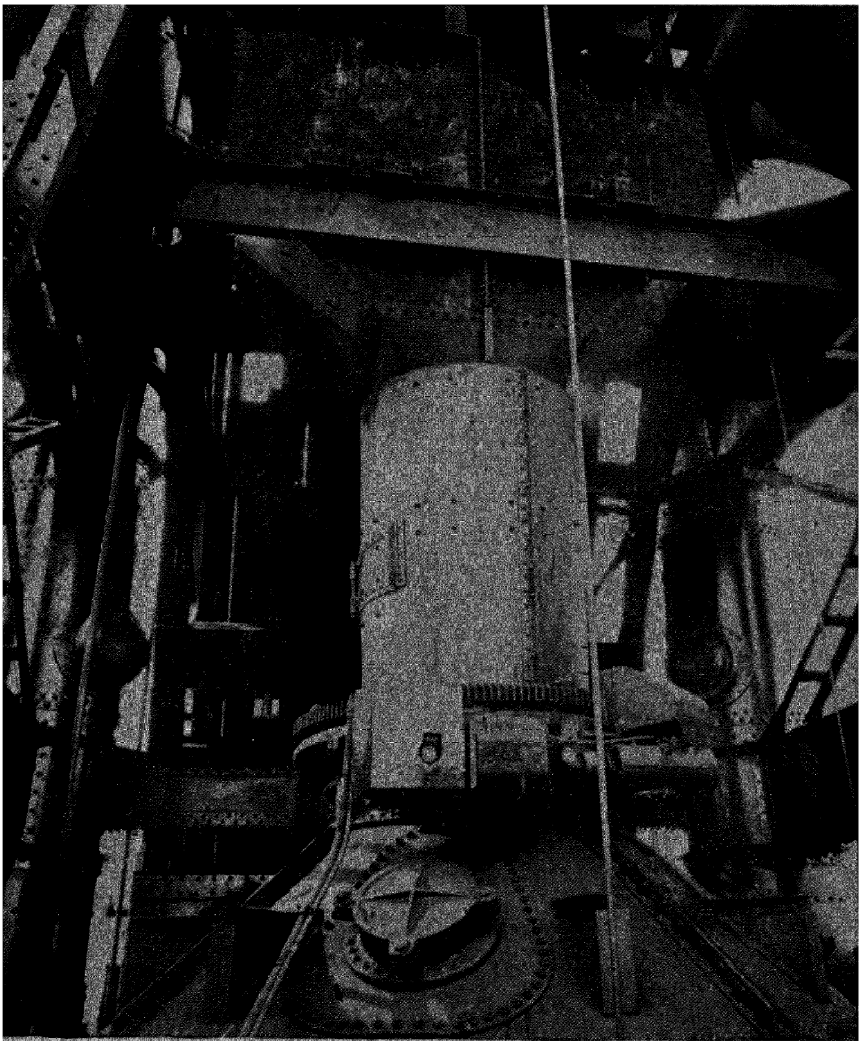


FIG. 10-IX.—The McKee revolving distributor. (*Courtesy of Arthur G. McKee and Company.*)

causing the larger portion of the gases to go up the shaft of the furnace through these regions. When these channels are near the walls, the high temperatures caused by the reactions resulting from the presence of the large volume of gases in these regions cause severe cutting away of the walls.

Several methods are in use for promoting an even distribution of coarse and fine particles in the furnace but the McKee revolv-

ing distributor, shown in Fig. 10-IX, is the most widely used. This device operates as follows: The skip dumps a load of material into the upper hopper, the bottom of which is the small bell. This load of material, together with the upper hopper and the small bell, is then revolved through a predetermined angle by the gear and motor arrangement. The small bell is then lowered, depositing the material into the large hopper. This process is repeated for every skip load until enough skip loads have been deposited and evenly distributed on the lower bell to make one "round," as it is called. Then this bell is lowered, depositing the material in the furnace. The cycle of operations is repeated except that during the next round the angle of rotation of the upper bell is changed, an even distribution of materials in the furnace being the result. This device is operated by remote control and performs its function almost automatically. In order that this device may function properly, the stock line (the level of the top of the material in the furnace) must be kept at a constant distance from the lower bell because a change in the distance of fall of the material from the large bell changes the distribution of the coarse and fine particles. In modern furnaces, a stock-line indicator automatically records the position of the stock line to the operator in control of the skip hoist and the McKee distributor.

The gas *offtakes*—usually four in number—are large, brick-lined steel pipes and are spaced equally around the circumference of the furnace just below the large bell. They lead into large vertical pipes, called *uptakes*, near the tops of which are placed explosion doors. These doors are, in reality, valves designed to open automatically at a certain pressure higher than the usual operating pressure. Where the uptakes converge, connections are made to the downcomers, usually two in number, which are large, brick-lined, steel pipes and lead the gases away from the furnace. The *bleeders*, two large vertical pipes, rise from the connections to the downcomers and afford means of escape of surplus gas when necessary. This arrangement for removing the gas minimizes the inclusion of dust in the gases and the ejection of solid material from the furnace in case of an explosion.

The Blast-furnace Plant.—Figure 11-IX is a schematic plan of a blast-furnace plant, complete with all accessory equipment

necessary to operate the furnace. It is not intended to be an actual plant layout as the actual placement of each piece of equipment relative to the plant is dependent upon the space available and a number of other factors. A single gas-cleaning plant and blower house usually serves a number of furnaces and

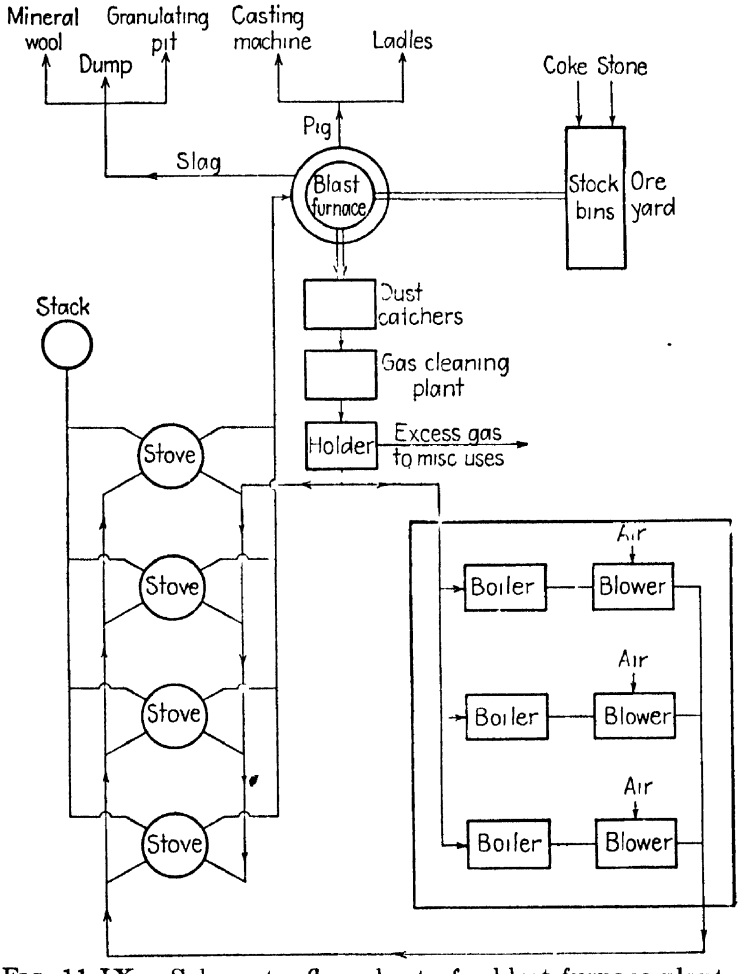


FIG. 11-IX.—Schematic flow sheet of a blast furnace plant.

sets of stoves, but only one furnace is shown here for the sake of simplicity.

The *stockhouse* is composed chiefly of bins which contain supplies of the solid materials charged into the furnace—coke, ore, and limestone. The position of the stockhouse with relation to the skip hoist and furnace is shown in Fig. 6-IX. The ore and limestone are brought to the stockhouse in bottom dumping cars. The tracks on which these cars run are situated directly above these bins and the cars dump their loads directly into the

bins. An electric larry car runs directly underneath the bins (Fig. 12-IX) and receives its loads from them, the operation being under the control of the operator. The larry has a weighing device, often automatic in operation, by means of which the correct amounts of limestone and ore can be obtained. The larry car conveys the material to a chute which leads directly into the skip car. The coke is brought from the coke works to two large bins at the stockhouse by means of a belt conveyer or by cars if the coke plant is too far away. The coke flows from these bins by gravity, over a screen through which the fines

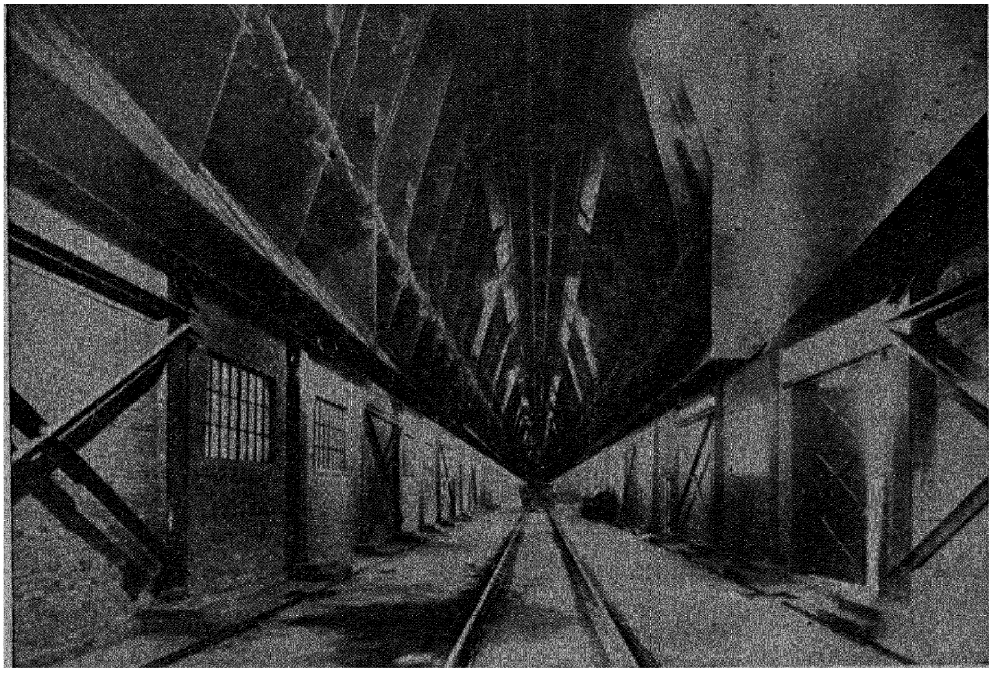


FIG. 12-IX.—Interior view of a modern stockhouse, showing larry car. (*Courtesy of Arthur G. McKee and Company.*)

(breeze) drop, and then into automatic weighing hoppers. From these hoppers, the coke drops down a chute into the skip car. The coke-weighing mechanism is shown in Fig. 13-IX. This device is electrically and automatically operated, its operation being synchronized with that of the bells and skip hoist. The apparatus automatically weighs a predetermined amount of coke and dumps it into the skip car. The apparatus is set in motion when the operator on the larry car presses a push-button switch.

The other substance charged into the furnace is air. It is supplied at a pressure of from 15 to 30 p.s.i. and at a temperature

ranging from 1200 to 1400°F., depending upon the type of operation. The furnace requires from 4 to 5 tons of air for every ton of pig iron produced, a figure which corresponds, for a furnace producing 1,200 tons of pig iron per day, to about 75,000 cu. ft. per min. The amount of moisture entering with this air is quite large and is a distinct loss in furnace operation, owing to the heat necessary to heat this water vapor. For a furnace using 75,000 cu. ft. per min. of air containing 1 grain of H_2O per cubic foot, the amount of water entering the furnace

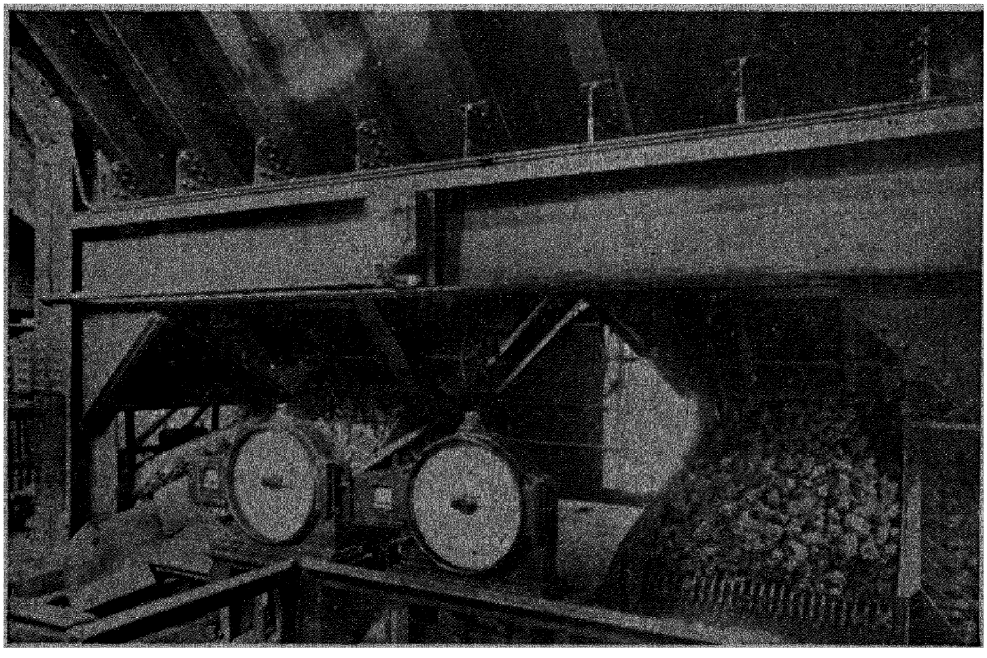


FIG. 13-IX.—Automatic coke-weighing mechanism in stockhouse. (*Courtesy of Arthur G. McKee and Company.*)

under these conditions amounts to 75 gal. per hr. or 1,800 gal. per day. If the air contains 8 grains of H_2O per cubic foot, 14,400 gal. of water enter with the air per day. Refrigerating methods have been tried as a means of removing the moisture from the air but the cost of the equipment for freezing the water out and the operating expenses are so high that the advantage of drying the blast is lost except at some Southern furnaces where the humidity is very high.

This blast of air, in passing through the furnace, undergoes certain chemical changes (to be considered later) and emerges at the furnace top as a mixture of nitrogen (N_2), carbon dioxide (CO_2), carbon monoxide (CO), hydrogen (H_2), water vapor

(H_2O), and dust. Owing to the carbon monoxide present (22 to 27 per cent), this waste gas can be burned to produce heat and is utilized for many heating operations around the plant. These uses may include the following:

1. Heating the air for the blast furnace in hot blast stoves.
2. Burning under boilers for steam-making purposes.
3. Burning in internal-combustion gas engines for power-producing purposes and for compressing the air for the blast.
4. Firing of coke ovens.
5. When mixed with coke-oven gas, it is often used to fire open-hearth furnaces and reheat furnaces in the steel mill.

For all of these uses, it is necessary to free the gas—more or less completely—from the large amount of dust it contains. This necessitates a gas-cleaning plant as an adjunct to the blast furnace. The gas flows through the downcomers to the dust catchers (usually two of them in series), which are large brick-lined steel chambers. These partly free the gas of dust by a sudden reduction in velocity on entering the chamber and by the impingement of the dust on baffle plates advantageously placed in the interior. The gas is drawn off at the top and is conducted through a large main to the gas-cleaning plant.

The necessity for cleaning blast-furnace gas becomes apparent when it is realized that about 50 per cent of the average Mesabi ores will pass a 20-mesh screen and about 11 per cent will pass a 100-mesh screen. Furthermore, 175 to 200 lb. of dust are carried out of the furnace with the top gases for every ton of pig iron produced. It is obvious that this large amount of dust would rapidly clog flues, regenerators, and furnaces through which it passed. The dust catchers act as a primary dry-cleaning unit and, if carefully designed, are capable of removing 65 to 75 per cent of this dust which consists of ore fines, coke breeze, and small limestone particles. Most of the remainder of the dust must be removed in the gas-cleaning plant. A value of 0.15 grain per cubic foot is about the maximum amount of dust that can be tolerated when the gas is to pass through furnace regenerators and blast-furnace stoves. If the gas is to be used in gas engines, it is necessary to clean it completely to 0.008 grain per cubic foot.

Within the last few years, a great deal of work has been done on developing gas-cleaning equipment in this country as blast-

furnace gas has been used more and more in the plant for firing coke ovens and open-hearth furnaces where quite a high degree of cleanliness is required. In the majority of cleaning plants, the gas first enters (coming from the dust catchers) at the bottom of a tall, cylindrical steel structure, called a *tower washer*, and passes upward through a spray of water which falls on screens through which the gas must pass. This treatment washes a considerable portion of the dust out of the gas and the entrained drops of water are taken out by giving the gas a rapid spiral motion in another chamber, called a *water separator*, the greater inertia of the water causing it to be deposited on the walls of the separator. Such a treatment usually reduces the dust content to about 0.3 grain per cubic foot so that treatment of the gas in two such units in series is sufficient when the gas is to be burned in stoves or in reheating furnaces.

For final cleaning, most American plants still use Theisen disintegrators, three or four being used in parallel as each has a capacity of about 15,000 to 30,000 cu. ft. of gas per minute. This unit has the approximate form of a large steel cylinder, mounted horizontally. The outer cylinder is stationary and encloses a similarly shaped but smaller revolving cylinder on the shell of which are riveted many steel vanes. These vanes project about a foot from the inner cylinder and extend longitudinally along it but in a slight spiral. At the receiving end of the cylinder the vanes act as a drawing fan and at the opposite end as a booster fan. Water is admitted at low pressure through several pipes halfway up the side of the outer shell. This water is dashed to a spray by the rapidly revolving vanes and, being propelled in a direction opposite to that of the gas, is thoroughly mixed with it, thus wetting the last small dust particles so that they will separate with the water. The entrained water is subsequently separated from the gas by a water separator.

All mechanical washers, such as the Theisen, McKee, and Feld types, have the disadvantages of high power costs and inability to dry the gas. Not much money can be afforded in cleaning the gas because it possesses only about 90 B.t.u. per cu. ft. All of its sensible heat is lost during cleaning and the cost of coal or oil is low enough that high-priced cleaning methods are not economical. Hence, a great deal of work has gone into the development of wet electrical precipitators, operating on the

principle first applied by Cottrell. In this process, the dust-containing gases are passed between two electrodes, between which a strong d.c., static electric field is maintained. This strong field ionizes the gas. The dust particles pick up an electrical charge and are attracted to one or the other of the electrodes. If one electrode is supplied with fins and the other is smooth, the particles will be attracted to the smooth electrode. This effect is also aided by having the ionizing electrode the negative pole and having a more intense field in its neighborhood. A recently developed unit of this type consists of two open-end aluminum cylinders, one being suspended concentrically within the other with a gap of about 4 in. between them. The outside of the inner cylinder has fins on it and is the ionizing or discharge electrode, while the inside of the outer cylinder is smooth and is the collecting electrode. A continuous flow of water over the collecting electrode washes away the dust as a sludge. The gas enters through vertical slots in the smaller cylinder and passes out through slots in the outer cylinder, the slots being staggered in the two cylinders with respect to each other to cause an abrupt change in direction of the gas, thus facilitating cleaning. The advantages of this type of gas-cleaning equipment are that the power consumption is low, the absence of any moving parts makes the apparatus silent and free from depreciation by wear, and the gas is free from large amounts of entrained moisture. Table 4-IX gives comparative data on the operation of different types of gas-cleaning equipment and emphasizes the lower power cost of the wet precipitating method.

The dust collected from all units in the cleaning plant can be reclaimed by drying and sintering in about the same manner as is used on ores. Usually, the amount of coke breeze in the dust is sufficient for sintering and none need be added. The sinter cake is broken up and again charged into the furnace.

Two types of machines are in use for compressing the air for the blast furnace and forcing it to and through the furnace: reciprocating blowers and turbocompressors. Plants that are rather old in point of service are generally equipped with reciprocating blowing engines. If blast-furnace gas is burned under boilers, these units are steam driven; otherwise the cleaned blast-furnace gas is burned directly in large gas engines which furnish the motive power. With the large increase in furnace capacity

within the last ten years, furnace operators have turned to steam-driven turbocompressors because of their many advantages. Steam is needed in the plant in any case and it is better economy to provide a central boiler plant that furnishes steam for the blowers and other uses than to run blowing engines with gas and have a separate steam plant for the auxiliary uses. Turbocompressors require the least expenditure of capital, permit the greatest flexibility of operation, are highly efficient, and take up only a fraction of the space occupied by the old reciprocating blowers. For these reasons, nearly all recently built plants and many modernized plants are equipped with these units.

TABLE 4-IX.—OPERATING DATA ON GAS-CLEANING EQUIPMENT*

Type	Cleanliness, grains per cu. ft.	Capacity per unit, cu. ft. per min.	Cost data			
			Complete per unit, dollars	Operating cost, dollars	Total cost per 1,000 cu. ft. gas, cents	Total cost per ton pig,† cents
Tower washer	0.30	75,000	50,000	14 32	0.0298	4 02
Two-stage McKee.	0 15	75,000	50,000	19 91	0.0349	4 714
Feld-McKee.....	0.10	75,000	70,000	31 84	0 0526	7 08
Disintegrator.....	0.008	30,000	30,000	46 36	0 132	17 80
Wet Cottrell.....	0 008	40,000	55,000	7.44	0.0469	6 33
Wet Cottrell plus tower.....	0.008	.....	.....	.....	0 0767	10.35
Disintegrator plus tower.....	0 008	.....	.....	...	0 1618	21 82

* HAVEN and THORNE, A.S.M.E., Iron and Steel Meeting, 1930.

† Based on 135,000 cu. ft. blast-furnace gas per ton of pig.

As stated previously, the air is heated in large stoves before entering the furnace. Four or five of these stoves are necessary to keep a single furnace supplied. They are cylindrical steel structures, brick-lined, about 100 ft. tall and 22 ft. in diameter, the interior being usually divided into two chambers. One of these chambers is open and serves as the combustion space in which cleaned blast-furnace gas, mixed with air, is burned. The flames and hot gases sweep through the other chamber which is filled with nested checker brick placed in staggered rows with spaces between for passage of the gases. The hot gases give up

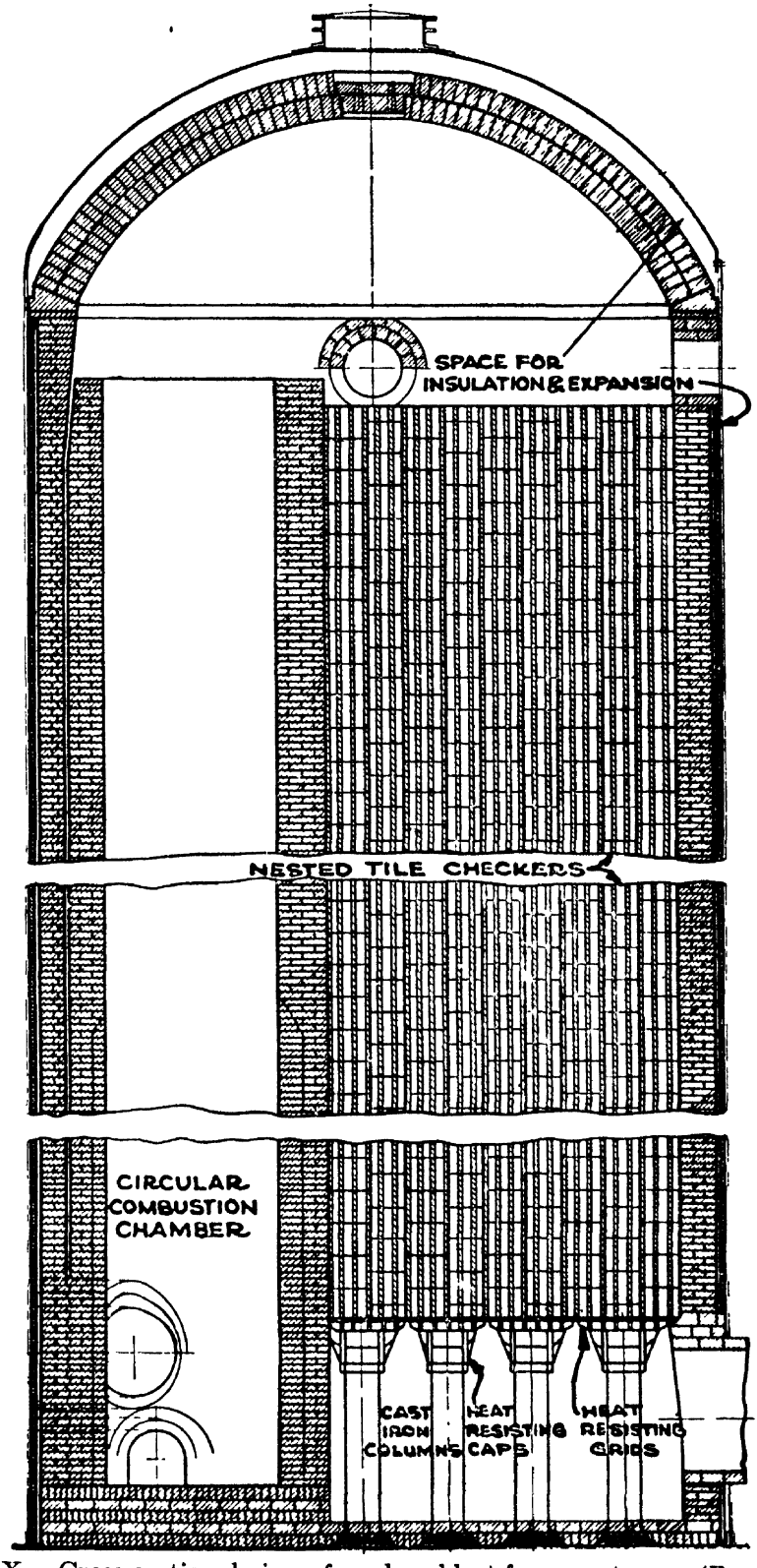


FIG. 14-IX.—Cross-sectional view of modern blast furnace stove. (*From Haven, W. A., Recent Developments in American Blast Furnace Design and Practice.*)

their heat to the checkerwork and pass out through a flue to the central stack which serves the whole battery of stoves. Recently designed stoves have been built with metal bottoms, grids, and cast-iron columns replacing the old masonry arches, thus increasing the sturdiness of construction. Figure 14-IX is a cross-sectional view of such a stove showing the circular combustion chamber, nested brick checkers, and metal columns and grids for supporting the checkerwork.

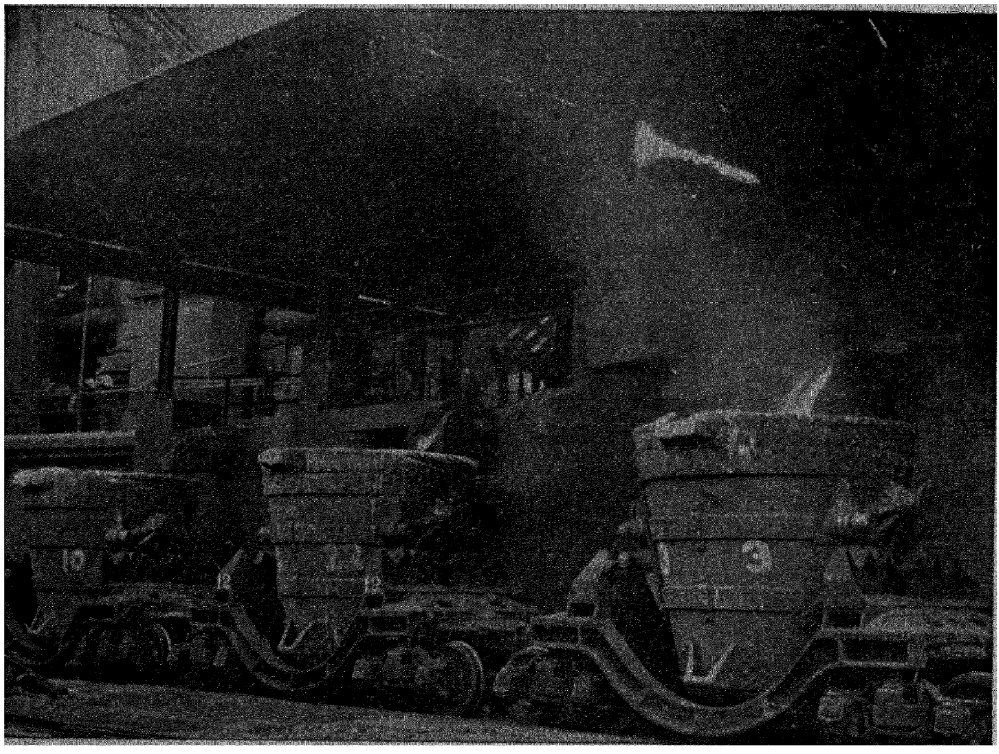


FIG. 15-IX.—Pig ladles in the process of being filled. (*Courtesy of the Youngstown Sheet and Tube Company.*)

When the stove "goes on blast," suitable valves are operated, which shut off the burning gas and introduce the blast in a reverse direction. Each stove serves to heat the total blast requirements of a furnace for about an hour, but it takes three hours to heat it up again, so that four stoves are in continuous operation—one hour on blast and three hours on heat. A fifth stove is sometimes supplied for emergencies. About 25 to 30 per cent of the blast-furnace gas is required to heat the stoves and 12 to 20 per cent to run the blowers, the rest being available for other uses. The heated blast travels to the furnace through the hot-blast main, the bustle pipe, the tuyère stock and the tuyère in succession, and finally into the furnace.

Distribution of the Products.—As the liquid iron runs from the furnace, it is sampled for analysis and run into ladles, as described above. These ladles (built on railroad car trucks, see Fig. 15-IX), are drawn away either to the mixer in the steel plant or to the cast house where it is cast into pigs. Mechanical pig-casting machines have replaced the sand-casting floor in front of the furnace. The modern casting machine, a sketch of which is shown in Fig. 16-IX, is usually composed of two rows of overlapping pig molds in the form of an endless chain. The iron flows from the ladle into a trough and from it into the molds, which are moving slowly past the lip of the trough. The molds are coated inside with lime to prevent sticking of the iron. As soon as the pigs are solid, they are sprayed with water and, as

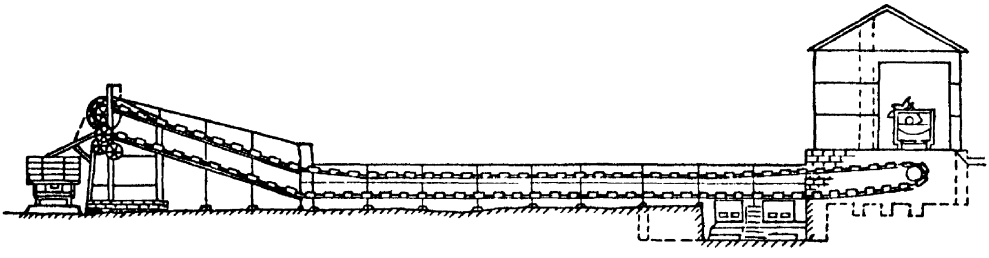


FIG. 16-IX.—A pig casting machine. (*After Stoughton.*)

the machine carries them over the end sprocket, they are dumped into cars.

Most of the blast-furnace slag is transported in the ladles, while molten, to the slag dump and dumped there. After weathering for a few months, it can be crushed and used as a filling material (aggregate) in concrete making. If the slag is to be used in the manufacture of Portland cement, it is granulated by pouring it, while molten, into a tank of water and spraying a stream of water on the molten slag as it pours from the lip of the ladle. Mineral wool, a material widely used for insulating purposes, is prepared from blast-furnace slag by blowing a high-pressure air blast into a stream of molten slag. This action blows the slag out into long, very fine threads. It solidifies in this condition almost instantaneously.

Operation of the Furnace.—The blast furnace is charged regularly and in a definite sequence. The stock-line recorder makes a continuous autographic record of the level of the stock in the furnace; autographic records are also made of the times of

hoisting each skip and of lowering each bell. The materials charged are coke, ore, limestone, and sometimes a small percentage of scrap iron. Table 5-IX gives two typical charging routines for a 1,000-ton furnace. The small bell is lowered after each item is dumped upon it and the large bell is lowered after all of the material or one "round" is deposited upon it.

TABLE 5-IX.—TYPICAL CHARGING SCHEDULES

Layer filling	Lb.	Mixed filling	Lb.
2 skips of ore	45,000	2 skips of ore	30,000
1 skip of stone	10,000	2 skips of coke	12,000
3 skips of coke	18,000	1 skip of stone	13,300
Total	73,000	2 skips of ore	30,000
		2 skips of coke	12,000
		Total	97,300

The materials entering the blast furnace pass through it in opposite directions. The solid materials coke, ore, and limestone pass downward through the furnace while the hot gases pass upward through the stock in a direction countercurrent to the stock. The hot blast burns the coke in front of the tuyères to CO_2, the latter being immediately reduced to CO. Carbon monoxide acts as the principal reducing agent in reducing the oxides of iron in the upper portion of the furnace stack, while solid carbon acts as the principal reducing agent at the higher temperatures in the lower portion of the stack. The gases at the tuyère level are at a temperature of about 2750°F. immediately after combustion and require about 20 sec. on the average to pass up through the stock, their final temperature at the stock line being in the neighborhood of 350°F. The heat in these gases is transferred to the descending stock, thus preheating it. The chemical reactions taking place in the shaft also absorb heat from the hot products of combustion.

With regard to the descending column of stock, it is gradually heated to higher and higher temperatures as it descends and the ore begins to be reduced by the CO in the gases, almost as soon as it is dropped into the furnace. About halfway down the shaft of the furnace, the $CaCO_3$ begins to be decomposed by the heat into CaO and CO_2 while by this time practically all the iron oxide has been reduced to a spongy mass of metallic iron. This

spongy iron has a large surface area per unit weight and is, therefore, able to absorb carbon quite readily, the carbon going into solid solution in the iron. This effect lowers the melting point of the iron so that by the time the iron enters the smelting zone (below the top of the bosh) it is molten and the droplets fall through the stock and collect in the crucible. At about the same time the slag becomes molten and begins to collect the impurities that are insoluble in the iron as it trickles down through the smelting zone. Oxides that have heats of formation higher than that of iron oxide cannot be reduced until the very high temperatures of the smelting zone are reached and are then probably reduced by solid carbon and not by carbon monoxide. The iron, containing carbon, manganese, silicon, phosphorus, and sulfur as impurities, collects in the molten state in the crucible and is covered with a layer of molten slag which, because of its much lower specific gravity, floats on top of the metal and, therefore, holds the oxidized impurities out of contact with the metal. From 8 to 14 hr. are required for the solid materials to descend from the throat to the hearth of the furnace.

The tap hole or iron notch is opened at regular intervals of 4, 5, or 6 hr. in order to drain the furnace of metal. The clay plug is dug out of the tap hole and the layer of frozen iron burned through with a jet of oxygen. A view of the furnace floor during tapping is shown in Fig. 17-IX. Since the tap hole is situated very near the bottom of the crucible, the iron is withdrawn from under the slag, but near the end of the tap the slag begins to flow with the iron and is diverted into a separate runner by the skimmer. After the furnace is drained, the tap hole is closed by a mechanical device called a *mud gun* which is swung around in front of the opening and shoots balls of specially prepared clay into the hole until it is entirely plugged up. Recent designs of mud guns are able to close the hole without shutting down the blast.

The modern blast furnace is capable of producing over 1,000 tons of pig iron per day with only a small operating crew, owing to the rapid strides in mechanization in recent years. The crew of a furnace per shift often consists of the following: 1 "blower" for each two or four furnaces, 1 keeper, 1 helper, 1 "cinder snapper," 1 "flue dust man," 1 hot-blast stove man, and perhaps 1 laborer. With oxygen for burning out the tap hole, mud gun,

short runners to slag and metal ladles, etc., one furnace is usually able to get along with 4 men and a fraction of a "blower" per shift. Back of the furnace a scale-car man is required, but, with mechanical handling to ore pockets and to the furnace top, about 5 or 6 men per shift per furnace can handle the stock to make 1,200 tons of pig iron per day.

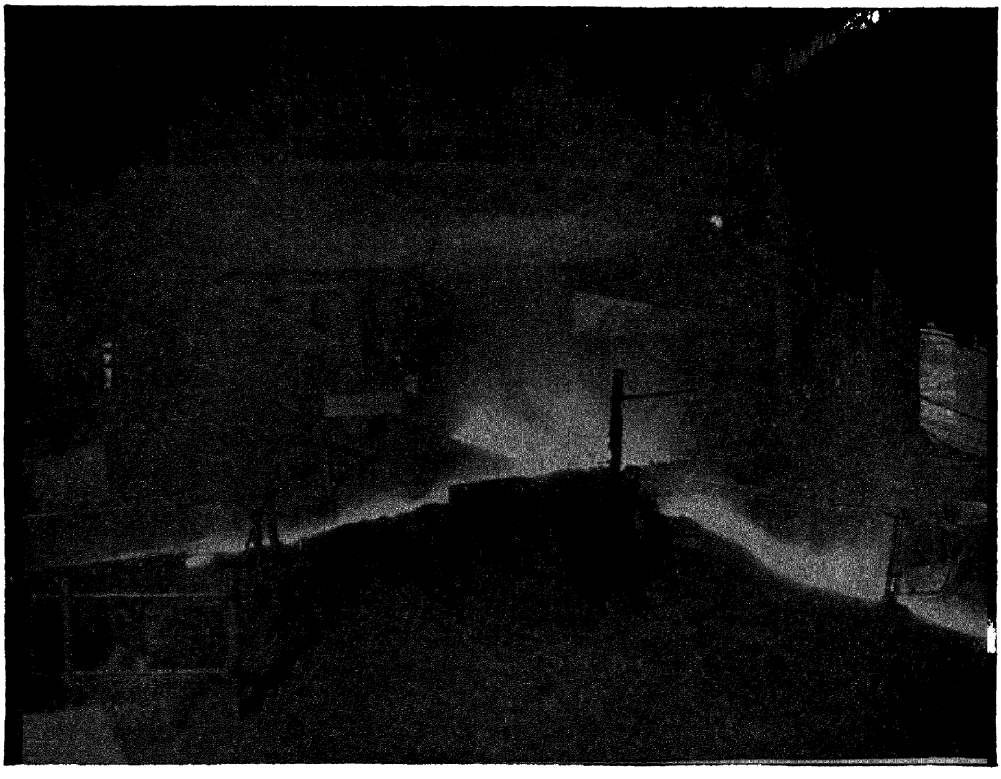


FIG. 17-IX.—Tapping a blast furnace. (*Courtesy of the Youngstown Sheet and Tube Company.*)

Chemical Theory.—As soon as the iron ore enters the top of the furnace, two reactions begin to take place between it and the gases:

$$2Fe_2O_3 + 8CO = 7CO_2 + 4Fe + C \quad (1)$$

$$3Fe_2O_3 + CO = 2Fe_3O_4 + CO_2 \quad (2)$$

This action increases in activity as the material becomes hotter. The carbon formed by reaction (1) deposits in a form similar to that of lampblack on the outside and in the pore spaces of the ore. This carbon also bakes on the furnace walls and helps to prevent deterioration of the brickwork by the scouring action of the stock and slag. Reaction (1) is, however, opposed by two reactions with carbon dioxide:

$$Fe + CO_2 = FeO + CO \quad (3)$$
$$C + CO_2 = 2CO \quad (4)$$

Reaction (3) begins at a temperature of 575°F. which normally corresponds to a point 6 or 7 ft. below the stock line while reaction (4) begins at about 1000°F. or about 20 ft. below the stock line. This latter reaction increases rapidly with increase

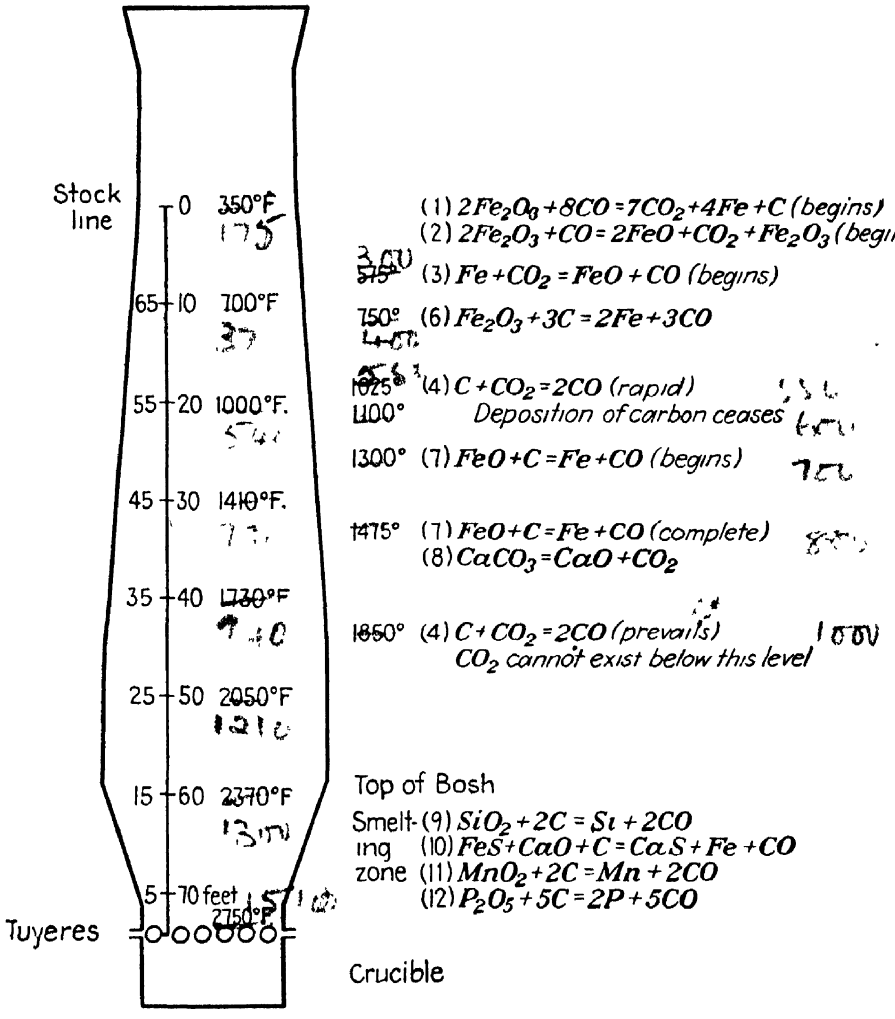


FIG. 18-IX.—Reactions in the blast-furnace stack. (*After Stoughton.*)

in temperature so that the deposition of carbon ceases at a temperature of about 1100°F. Figure 18-IX shows the relation between the principal reactions and the approximate positions and temperatures at which they occur in the column of stock. These values of temperature and distance vary from furnace to furnace, and from day to day in a single furnace, but they do

present a fairly accurate general picture of the way in which the reactions occur.

In its passage down the shaft, the ore has been constantly losing oxygen to the stack gases owing to the reducing effect of CO. FeO becomes stable at about 1100°F. so that Fe_2O_3 and Fe_3O_4 are practically nonexistent 25 ft. below the stock line. The Fe_3O_4 is reduced according to the equation

$$Fe_3O_4 + CO = 3FeO + CO_2 \qquad (5)$$

At about 750°F., solid carbon begins to act as a reducing agent on the higher oxides of iron according to the equation

$$Fe_2O_3 + 3C = 2Fe + 3CO \qquad (6)$$

As the temperature increases with descent of the stock in the shaft, the power of CO as a reducing agent decreases and that of solid carbon increases until, at a temperature of about 1300°F., it is able to reduce FeO to metallic iron

$$FeO + C = Fe + CO \qquad (7)$$

By the time the stock has descended about 35 ft. below the stock line, reaction (7) is practically complete and nearly all the ore has been reduced to metallic sponge iron. Experiments have shown that a small amount of FeO is present in the core of the furnace down to the top of the bosh but the amount is negligible. At about 1500°F. the decomposition of the limestone begins with the evolution of CO_2, according to the equation

$$CaCO_3 = CaO + CO_2 \qquad (8)$$

From the foregoing discussion it can be seen that in the upper 15 or 20 ft. of stock, the hematite and magnetite are reduced to FeO by carbon monoxide, thus forming large quantities of CO_2. If it were not for reactions (1), (3), and (4), the waste gases from the furnace would contain no CO and have no heating value, but these reactions forming carbon (which reduces CO_2) and carbon monoxide do take place and thereby waste a large amount of heat as far as the blast furnace itself is concerned because all three of these reactions absorb heat. From 20 to 35 ft. below the stock line is the zone of conversion of FeO into metallic iron by solid carbon and the region in which the limestone loses its CO_2 to the furnace gases. The sponge iron dis-

solves solid carbon by taking it up in solid solution, a procedure that lowers its melting point and causes it to melt at a lower temperature than would be the case if it were free from carbon. This action takes place in the zone extending from about 35 ft. below the stock line to the top of the bosh.

The smelting zone of the blast furnace lies in the bosh. Upon entering this region the iron melts and trickles down over the white-hot coke, thus becoming saturated with carbon. The solubility of carbon in liquid iron at a final tuyère temperature of 2750°F. is about 5 per cent. At a corresponding point the lime unites with the coke ash and impurities in the iron ore, thus forming a fusible slag which also trickles down and collects in the hearth. During this period in which the slag is in contact with the hot coke, oxides of manganese, silicon, etc. are reduced by the carbon. The amount of this reduction determines the composition of the pig iron because the reduced elements collect and are dissolved in the metal and the oxides collect in the slag. The only exceptions to this are that liquid iron dissolves its own sulfide (FeS) and also manganese sulfide (MnS), but to a less extent. The reactions by which the impurities are reduced and dissolved in the liquid iron follow.

Silicon.—The reduction of silicon usually takes place according to the following reactions:

$$\begin{aligned} SiO_2 + 2C &= Si + 2CO \\ SiO_2 + 2C + Fe &= FeSi + 2CO \end{aligned} \qquad (9)$$

Two factors affect the desired silicon in the iron: temperature and slag composition. The temperature for the reduction of silica (SiO_2) to silicon (Si) is higher than that for iron and it follows that the temperatures necessary to increase the silicon in the iron rise as the percentage of silicon rises. The increased temperature is obtained either by increasing the blast temperature or by increasing the percentage of coke in the charge. Since the blast temperature is kept near the upper limit at all times, the most dependable source of heat is in the coke percentage.

The slag composition also has a strong influence on the silicon in the iron. For any given temperature a slag high in lime will unite with a larger amount of SiO_2 and lower the amount of SiO_2 available for reduction to Si and thereby lower the amount of Si in the iron. For the same temperature a smaller amount

of lime will require a smaller amount of SiO_2 to satisfy its demand, thus resulting in more SiO_2 being available for reduction to Si and consequently more Si going into the pig iron. More heat in the form of blast heat or additional coke is therefore required to produce the same silicon content in a limey furnace than in a more acid ("sharper") furnace. Furnace operators attempt to carry as little lime as possible on a furnace and still produce satisfactory iron in order to keep the coke requirements at a minimum.

Sulfur.—Sulfur in the burden comes almost entirely from the coke in which it is present as dissolved sulfur and as FeS. FeS will dissolve in the iron unless converted to CaS by the following reaction:

$$FeS + CaO + C = CaS + Fe + CO \qquad (10)$$

A very small portion of the sulfur will be volatilized by the heat in the furnace and carried out in the gas; the remainder is removed in the slag and iron. Slags must be limey enough to extract almost all of the sulfur in the charge. Up to a certain limit the more lime in the charge the more sulfur is extracted. Beyond this limit, the slag may become so viscous that sulfur extraction is not efficient. Slags will hold slightly more than 2 per cent sulfur but sometimes it is not desirable to carry that high a percentage. To reduce the concentration, it may be necessary to increase the slag volume by charging amounts of slag-forming materials such as gravel.

A high temperature promotes the above reaction, causes most of the sulfur to dissolve in the slag, and explains the common rule that iron high in silicon is usually low in sulfur. In fact, when a blast-furnace operator speaks of "hot iron," he means iron high in silicon and low in sulfur.

Manganese dioxide is reduced by the following reaction:

$$MnO_2 + 2C = Mn + 2CO \qquad (11)$$

To a certain extent, the amount of manganese in the pig is dependent upon the character of the ores charged, but it may be controlled somewhat by the character of the slag made because a slag relatively high in SiO_2 will carry some of the manganese away in the form of manganese silicate, $MnO{\cdot}SiO_2$. A relatively

low or medium smelting temperature favors retention of manganese in the slag.

Phosphorus.—Almost all the phosphorus charged into the furnace continues on through into the iron. It is reduced according to the following reaction:

$$P_2O_5 + 5C = 2P + 5CO \qquad (12)$$

If the ores are high in phosphorus the pig iron will also be high in this element, and vice versa. After the materials once enter the furnace, there is no known method of controlling the amount of phosphorus in the pig iron.

Carbon.—Carbon is contained in pig iron in two forms: graphitic and combined. There is no control over the percentage of carbon in the iron as it comes from the furnace, although in general as the silicon content of the iron increases, the total carbon decreases. Carbon content will vary from about 4.5 per cent in ordinary 1.40 per cent silicon iron down to about 3.25 per cent in 4 per cent silicon iron. The combined carbon tends to decrease with the hotter or higher silicon irons, while the graphitic carbon increases. A considerable percentage of the graphitic carbon may separate from the iron in the iron runners or in the ladles. On a furnace having easily melted ores and pure materials giving a lower slag volume the combined carbon may be less.

Combustion Zone.—The U.S. Bureau of Mines has conducted a great deal of work on the mechanism of the smelting operation in the blast furnace by observations on both experimental and commercial furnaces in operation. The published results[1] of these investigations have done much to clarify the very complex mechanism of reduction and the travel of stock and gases in the furnace. An important piece of work was the exploration of the combustion zone in front of the tuyères in several furnaces. It

[1] The more important and general publications are

KINNEY, ROYSTER, and JOSEPH, Iron Blast Furnace Reactions, *U.S. Bur. Mines Tech. Paper* 391, 1927.

KINNEY, S. P., The Blast Furnace Stock Column, *U.S. Bur. Mines Tech. Paper* 442, 1929.

FURNAS and JOSEPH, Stock Distribution and Gas-solid Contact in the Blast Furnace, *U.S. Bur. Mines Tech. Paper* 476, 1930.

A digest of the above results is given in The Iron Blast Furnace, by T. L. Joseph, *U.S. Bur. Mines Information Circ.* 6779, May, 1934.

was found that all of the oxygen in the blast was consumed within a space 30 in. in a horizontal direction and 27 in. in a vertical direction from the center of the nose of the tuyère. The CO_2 produced was entirely reduced to CO within a horizontal distance of 40 in. and about the same vertical distance from the center of the nose of each tuyère. The combustion zone of the furnace, then, consists of a mushroom-shaped area in front of each tuyère, and in these areas all the combustion of coke by the air blast takes place. It was formerly thought that the combustion zone extended completely across the hearth of the furnace, and it was because of this misconception that hearth diameters were so slow to increase. These results showed that the combustion space did not extend across the hearth and that it was substantially independent of the diameter of the hearth. Consequently, new furnaces were built with much larger hearths and the production records climbed steadily from 700 to over 1,200 tons of pig iron per day.

This effect of unequal combustion at the tuyères causes considerable nonuniformity in the shaft. The stock directly above the combustion zones descends about one-third faster than the average for the column as a whole. With regard to combustion, the core of the furnace is comparatively unreactive in the smelting zone, the stock descending much slower than the average. In addition to this, the gas velocity, temperature, and pressure are decidedly nonuniform over the cross section of the shaft. The carbon dioxide content of the gas shows about a threefold variation, the temperature almost a fivefold variation, and the velocity of the gas about a sixfold variation across a plane near the stock line. High gas velocity is accompanied by high temperatures and comparatively low percentages of carbon dioxide. Table 6-IX gives the average values of gas compositions, temperatures, and velocities at various levels in a 700-ton blast furnace under normal operating conditions. From the average gas analyses at the different levels, the variations in values can be traced to the reactions taking place. The gradual increase in CO_2 content is at the expense of the CO, owing to the oxidation of CO to CO_2, while the sudden jump in CO_2 is due to the CO_2 released by calcination of the limestone. The reduction in CO_2 content as the gas nears the stock line is probably due to reactions (3) and (4). The increase in CO content between the

tuyère level and plane 4 is due to the reduction of the impurities by solid carbon, thus producing excess CO. The presence of hydrogen is mainly due to the decomposition of H_2O by hot carbon, according to the reaction

$$C + H_2O = CO + H_2$$

Control of the Operation.—For the best operation of the blast furnace it is very important that the greatest possible uniformity be maintained. The chemical reactions should take place at the same level in the furnace and the gases should pass uniformly through all parts of the descending stock column. We have seen above that absolute uniformity is not possible under present

TABLE 6-IX.—GAS COMPOSITIONS AT VARIOUS LEVELS IN BLAST FURNACE*

Plane	Distance below stock line		Diameter of plane		Gas composition, per cent by volume				Average temperature, °F.	Gas velocity, ft. per sec.
	Ft.	In.	Ft.	In.	CO_2	CO	H_2	N_2		
Top	0	0	17	0	14.7	24.8	4.1	56 4	400	8
1	3	0	17	0	14.9	25.2	3.4	56 5	725	121
2	11	0	17	6	15 2	25.3	3.2	56 3	1301	163
3	21	7	19	6	11.9	27 7	2.3	58 1	1575	132
4	44	1	23	4	5 5	34 7	0.9	58 9	1728	86 5
Tuyère	68	1¼	19	3	0 0	32 0	1 4	66 6	2372	115.7
Air	.	...	..	..	....	. ..	...	...	1138	

* Modified from KINNEY, S. P., The Blast Furnace Stock Column, *U.S. Bur. Mines Tech. Paper* 442, 1929.

operating conditions but the over-all conditions at any one furnace should be kept as constant as possible when producing a single grade of pig iron. The two most important factors in promoting uniformity in the furnace shaft are uniformity in sizing and distributing the raw materials at the stock line and uniformity in combustion at the tuyères. The ratio of carbon monoxide to carbon dioxide in the top gases is generally considered to be a good index of the efficiency of the furnace reduction; if the $CO:CO_2$ ratio is high, the efficiency of reduction is low while, if the ratio is low, the efficiency is high. The effect of sizing the ore to produce a uniform percentage of void spaces

throughout the cross section of the stock column is shown in Table 7-IX. From this it can be seen that careful sizing of the ore will increase the reduction efficiency of the furnace. The above result is furthered by sizing the coke and stone as well.

Fine, earthy ores offer more resistance to ascending gases and, therefore, require a larger proportion of the porous coke in the charge to keep the column permeable to the gases. The higher

TABLE 7-IX.—EFFECT OF ORE SIZING ON REDUCTION EFFICIENCY*

Ore sizing	No. of samples	Average top gas analysis, per cent by volume				Ratio $CO:CO_2$
		CO_2	CO	H_2	N_2	
No sizing	53	10 5	28 1	2 0	59 4	2 68
Two sizes	2	10 9	28 4	. .	60 7	2 60
Two sizes mixed	7	12 2	26 8	2 1	58 9	2 20
Three sizes	74	16 3	25 4	1 1	57 2	1.54

* KINNEY, S. P., Effect of Sized Ore on Blast Furnace Operation, *U.S. Bur. Mines Tech. Paper* 459, 1930.

the blast temperature, however, the less fuel is ordinarily required to produce a satisfactory smelting temperature and the entire charge is consequently less permeable. For these reasons, lower blast temperatures are used when smelting fine ores than when smelting lump ores. The speed of operation of the furnace is greater the larger the blast volume (cubic feet per minute), because the speed of operation depends directly upon the rate of combustion of the coke for the reason that the charge can descend only as fast as the coke can be converted to gas. There are two qualifications to this statement: (1) the hearth must be large enough to provide sufficient combustion space, and (2) the velocity of the blast must be great enough to drive the gas through the charge and distribute it uniformly through the furnace. Too large a gas volume causes the gas velocity at the furnace top to be so high that an excessive amount of flue dust is carried out of the furnace, thus making the cleaning of the gas too expensive. The blast pressure is dependent only upon the resistance the charge offers to the ascending gases. In fact, the column of stock in the furnace is almost, if not entirely, supported by the pressure of the ascending gases. If there

should be any jamming of the material in the stack, the blast pressure would rise and the volume would fall correspondingly. For this reason, modern furnaces are equipped with automatic devices that maintain the volume of blast delivered to the furnace at a constant value over a wide range of pressures. An autographic record is made of the gas volume by this device. The blast temperature is also automatically maintained at a constant value and recorded by a pyrometer in the following manner. The pyrometer located in the hot blast main leading to the furnace is connected to a recorder which is equipped to control the opening or closing of a valve which admits cold air to the hot blast main. Any rise in temperature of the blast in the main causes an increase in the pyrometer reading which, in turn, causes the valve admitting the cold air to open a little wider until the blast temperature is reduced to the desired value. Such an arrangement is necessary; otherwise, the blast temperature would vary widely as the stove heating the blast cooled and as a cool stove was replaced by a hot one.

The functions of the blast-furnace slag are to separate the gangue of the ore, the ash of the coke, and as much of the sulfur as possible from the iron. A typical analysis has already been given in Table 6-VIII but the analysis varies with different types of practice. The sum of the CaO and MgO contents is greater than the SiO_2 content and the ratio $(CaO + MgO):SiO_2$, called the basicity ratio, usually varies from about 1.2 to 1.6. The slag is usually basic; therefore, although Al_2O_3 is calculated as an acid, the ratio is often close to neutrality or even slightly on the acid side. For good operation, a slag volume of about 900 lb. per ton of pig iron is necessary. The upper limit is about 1,400 lb. per ton of pig owing to the excessive cost of high slag volumes.

One of the most important functions of the slag is to regulate and control the temperature of the smelting zone of the furnace. Although the total amount of heat generated in this zone depends upon the amount of coke used, the temperature in this zone depends primarily upon the melting point of the slag. Blast-furnace slags are on the limey side of the maximum fusibility, *i.e.*, if silica is added, the melting point is lowered while, if lime is added, the melting point rises. A slag actually melts over a wide range of temperature rather than at a single definite tem-

perature so that it is more useful to refer to the "free-flowing" temperature of the slag rather than the melting point. In general, the lower the free-flowing temperature of the slag, the lower the temperature of the smelting zone. For this reason more limestone is added to the charge in order to have a hotter furnace, by raising the free-flowing temperature of the slag. Of course, the more basic the slag the more coke must be used in the burden, but the actual control and regulation are by means of the slag composition rather than the fuel burden. The ratio of the amount of coke used to the amount of pig iron produced usually varies between 0.8 and 1.0. The hotter the furnace, the higher the silicon and the lower the sulfur in the pig, as has been already discussed. A hot furnace will produce an iron containing from 2 to 3 per cent of silicon.

One of the important contributions made to blast-furnace technique during and as a result of the depression is the art of slow blowing. The modern furnace with its large capacity could not be run at a normal rate without producing too much pig iron. It was formerly thought to be impossible to operate the furnace very far below its normal rate without causing serious irregularities in operation. Under necessity, however, it was tried and surprisingly good results obtained. By reducing the blast volume greatly, the efficiency of the furnace was increased,

TABLE 8-IX.—DATA ON EFFECT OF SLOW BLOWING*

	Normal operation	Slow blowing
Blast volume, cu. ft per min	48,000	25,000
Output, tons per day	762	372
Coke, lbs. per ton pig	1,638	1,707
Scrap used, per cent	12 6	None
Flue dust produced, lb. per pig	353	111
Metallic loss, per cent	6.50	0.33
Off-sulfur iron, per cent	0 36	None

* HAVEN, W. A., *Iron & Steel Inst.* (British) No. 1, 1933.

as shown in Table 8-IX, if allowance is made for the discontinuance of the use of scrap in the charge. In some cases, "fanning" the furnace has been used to advantage. By fanning is meant almost a complete shutdown, only enough blast being

admitted to keep the furnace hot. It has been used in conjunction with slow blowing by blowing for a period of from 4 to 12 hr. followed by a period of fanning for from 4 to 20 hr. in that sequence. It is probable that the best results are obtained when the period of blowing is not longer than that required to empty the furnace of stock "predigested" by fanning. The experience gained in slow blowing and fanning, in slack times, has been valuable particularly during the recent coal strikes, when production had to be curtailed.

Irregularities in Operation.—Even with the recent rapid advances in blast-furnace operation, irregularities in furnace operation occur and sometimes are corrected only after considerable difficulty. The blast furnace is a huge and very complex mechanism and, when something goes wrong, heroic measures are occasionally necessary to correct the fault. Several days sometimes elapse before some change in furnace operation, the cause of which is unknown in many cases, can be righted and the furnace returns to normal. A few of the more important troubles will be briefly described.

Slips are due to the wedging of stock in the upper part of the stack and are thought to be due to excessive carbon deposition which fills up the open spaces in the stock so that the ascending gases can penetrate it only with great difficulty. When this condition occurs, the stock beneath the wedged portion settles from that above, the blast pressure rises, and the wedged stock finally falls. The sudden release of pressure on the gases produces a result like that of an explosion. Large slips are apt to do serious damage to the furnace.

Hanging or scaffolding occurs near the top of the bosh and is probably caused by a sudden lowering of the fusion zone in the furnace. When the upper extremity of this zone lowers suddenly, owing to one cause or another, the pasty mass adheres to the walls with the result that an incrustation is formed which projects toward the center of the furnace. This mass offers obstruction to both the gases and to the descent of the stock. The gases may channel and the stock hang up on this material if it is not cleared away. It is sometimes necessary to use dynamite to break it loose.

Chimneying or pillaring is caused by a vertical area in the furnace in which coarse particles have segregated. Most of the

gases pass up through this area of least resistance, causing this portion to be badly overheated while the remainder of the column is relatively cold and inactive. When this condition occurs, the coarse particles are usually segregated around the walls of the furnace and the high temperatures produced gradually cut away the walls and a hot spot may appear on the shell after some time. By spraying this area with water, the furnace may be kept in operation for quite a while but it will eventually have to be shut down for repairs. The colder material in the center of the furnace almost invariably causes the iron to be cold and of poor quality.

Tuyère coolers extend into the furnace and are, therefore, subjected to high temperatures and sometimes burn through. The same is true of the bosh coolers but to a less degree. The result of a burned-out cooler is an excess of water vapor in the furnace, causing a cold hearth, high sulfur iron, and accompanying difficulties. "Off-iron," meaning pig iron of a different composition from that desired, may be caused by either too hot or too cold a furnace, depending upon conditions.

Grades of Pig Produced.—Typical analyses of the more common grades of pig iron produced in the blast furnace are given in Table 9-IX. Basic pig iron, for use in the basic open-hearth furnace, must be low in silicon in order to cut down the slag volume in the refining process and minimize cutting of the basic lining. The silicon content of Bessemer pig iron must be within certain limits because the oxidation of silicon furnishes most of the heat in the refining process and the bath of metal must be neither too cold nor have to be blown too long to remove the excess silicon. The phosphorus content of Bessemer pig must be low enough so that the steel will finish with not more than 0.100 per cent P. Bessemer pig is also used in the acid open-hearth process. Pig iron to be used for the manufacture of wrought iron in the puddling furnace is known as forge iron. That used to make malleable cast iron is known as malleable pig. Several grades of pig iron are used for making iron castings and are mixed to produce the desired final analysis on melting and casting.

Several high-carbon and low-alloy-content ferroalloys—pig irons containing large amounts of alloying elements—are made in the blast furnace by using special ores and varying the practice

somewhat. These materials are used as alloying elements in iron and steel, and some are used for deoxidizing steel at the end of the refining process. Ferroalloys containing higher percentages of alloying elements than those given in the table or those containing only small amounts of carbon, are made in electric furnaces or by the thermit process.

TABLE 9-IX.—TYPICAL ANALYSES OF BLAST-FURNACE PRODUCTS*

Trade name	Total C, %	Si, %	S, %	P, %	Mn, %
No. 1 soft	3 00±	2 75–3 25	0 05 and under	0 30–1 50	0.10–1.00
No. 1 foundry	3 25±	2 25–2 75	0 05 and under	0 30–1 50	0 10–1 00
No. 2 foundry	3 50±	1 75–2 25	0 06 and under	0 30–1 50	0 10–1 00
No. 3 foundry	3 75±	1 25–1 75	0 065 and under	0 30–1 50	0 10–1.00
Gray forge	3 50±	0 75–1 75	0 07 and under	Under 1 00	0.10–1.00
Standard acid Bessemer pig	3 50–4 00	1 00–1 50	Under 0 08	Under 0 09	0 20–1 00
Basic pig...	3 50–4 00	Under 1 25	Under 0 08	0 10–1 50	1 00–2 00
Malleable Bessemer	3 50±	0 75–2.00	Under 0 07	Under 0 20	0 50±
Ferrosilicon	0 50–2 00	10 00–50 00	Under 0 04	Under 0 10	0 20±
Silicospiegel	1 00±	5 00–15 00	Under 0 02	Under 0 10	15.00–25.00
Ferromanganese	6 00–7 00	0 50–1 00	Under 0 03	.	40.00–80.00
Ferrophosphorus	1 00±	1.50±	Under 0 05	10.00–25.00	
Spiegeleisen	4 50–6 00	1 00±	Under 0 04		15.00–35.00

* STOUGHTON, B., "The Metallurgy of Iron and Steel," McGraw-Hill Book Company, Inc., New York, 1934.

Charge Calculation.—There are several different methods of calculating the charge to the blast furnace. One of the simplest methods and at the same time one applicable to widely varying conditions has been chosen for explanation and illustration. The calculation of charges is not a regular or routine part of furnace operation. When a furnace is running regularly, minor adjustments of charge are often made simply on observation. For instance, if it is found that the slag is becoming a little too basic, the furnace operator merely increases the proportion of a siliceous ore slightly or decreases the amount of limestone. If a change in ore is necessary, the changes may be merely estimated and carried out. Even in starting a new furnace, the charge may be assumed to be the same as one previously used. In some of these cases, however, better results might be obtained by calculating the charge instead of using this practical trial-and-error method. In starting to smelt a new ore, a charge calculation may be

indispensable, while it is always useful in studying the furnace operation with improvement of the operation in view.

Some assumption must be made with regard to the composition of the iron. The usual procedure is to assume a pig iron composition that is desired and one that has been proved by experience to be feasible. The charge to the furnace is then calculated and the smelting conditions adjusted in such a way that the desired and assumed percentages of carbon, silicon, and manganese are present in the pig iron product. Another type of assumption that is sometimes made is to assume that a certain percentage of all the MnO_2 and SiO_2 present is reduced and enters the metal while the remainder is slagged. A good assumption by the first method might be carbon 4.5 per cent, silicon 1.5 per cent, manganese 0.8 per cent, and the balance iron. By the second method it might be assumed that 50 per cent of the MnO_2 (or MnO) and 10 per cent of the SiO_2 would be reduced and enter the metal, the remainder entering the slag. As far as the phosphorus is concerned, it is only necessary to see that, when all the phosphorus in the charge enters the pig iron, the amount present is not greater than the maximum amount allowable. The usual basis of blast-furnace charge calculations is 1,000 lb. of pig iron and the entire calculation is carried out from this basis.

The amount of coke to be used per 1,000 lb. of pig produced must also be assumed and is based upon the experience of the operator with regard to the heat requirements of the furnace and the amount of reducing action desired. Some figure in the neighborhood of 950 lb. of coke per 1,000 lb. of pig iron is usually chosen as the necessary amount to fill all smelting requirements.

At least two and sometimes three ores of different analyses are available for charging and the charge is made up by mixing these ores in such proportions that a desired slag and metal composition is obtained. If three ores are used, one of them is usually a high-grade ore, expensive and, therefore, used only in small amounts. It is customary to assume that a certain amount of the rich ore is used for every 100 lb. of one of the leaner ores. For example, it is often assumed that one part of the rich ore is used for every four or five parts of one of the other leaner ores. Often, scrap iron is used in place of the high-grade

ore. The analyses of all ores as well as the limestone must be known in order to calculate the charge.

The calculation of a blast-furnace charge ultimately resolves itself into finding a mixture of ores and limestone that will produce a desired slag composition after allowance is made for reduced impurities in the pig iron. The slag composition is gauged by a ratio between the principal slag-forming constituents, and the choice of this ratio is entirely a matter of the experience of the operator. It is dependent upon the smelting temperature desired, the combustion and reduction conditions required, the type of iron being made, and many other factors. It is best to dodge the issue of whether Al_2O_3 is to be considered as an acid or a base and calculate it as a separate constituent of the slag. Some such ratio as the following is often decided upon: SiO_2: Al_2O_3: $\Sigma CaO = 32:12:56$. This means that for every 32 parts of SiO_2 and 12 parts of Al_2O_3, there are 56 parts of ΣCaO in the slag. The term "ΣCaO" requires some explanation. This means "summated lime" and includes the other bases present, principally MgO and MnO. For example, if a limestone contains 47 per cent CaO and 3.6 per cent MgO, the ΣCaO term is calculated as follows: It is assumed that both form silicates in the slag, $CaO \cdot SiO_2$ and $MgO \cdot SiO_2$, respectively. Since the molecular weight of MgO is 40.3 and that of CaO is 56.1, 40.3 parts of MgO will flux as much silica as 56.1 parts of CaO. The 3.6 per cent of MgO in the stone is, therefore, equivalent to $56.1/40.3 \times 3.6 = 5.0$ per cent CaO. The ΣCaO in the limestone is, then, equal to $47.0 + 5.0 = 52$ per cent.

We can now set up the following problem for calculation: From the materials listed in Table 10-IX, it is desired to calculate a charge to yield 1,000 lb. of pig iron and a slag having the ratio $SiO_2:Al_2O_3:\Sigma CaO = 33:12:55$. Assume that the desired pig iron composition is 4.0 per cent C., 2.0 per cent Si, 1.0 per cent Mn, and 93 per cent Fe. The amount of coke used is 950 lb. per 1,000 lb. of pig iron. Assume that one part of ore *C* is used to 5 parts of ore *A*.

Of the materials given in the table, the amount of coke and proportion of ore *C* are set by the assumptions. Of the components listed, the Fe_2O_3 is reduced to iron and forms the base of the metal while the SiO_2 and MnO_2 remaining after the amount reduced and entering the metal is deducted, enter the slag.

The MnO_2 is changed to MnO and enters the slag in the latter form, necessitating a correction in this case. All of the CaO, MgO, and Al_2O_3 go to form the slag, the H_2O and the CO_2 from the limestone join the furnace gases, and a portion of the carbon enters the iron while the remainder goes to form CO and CO_2, The solution consists in finding the correct mixture of ores *A*. *B*, *C*, and limestone, and the correct amounts of each to produce 1,000 lb. of pig iron of the desired composition and a slag of the required $SiO_2 : Al_2O_3 : \Sigma CaO$ ratio.

TABLE 10-IX.—MATERIALS CHARGED

Component	Ore *A*	Ore *B*	Ore *C*	Limestone	Coke
Fe_2O_3	68 4	71 5	92 0	1 0	1.7
MnO_2	1 3	4 0	0 0	0 0	
SiO_2	11 5	14 0	5.1	4 5	5.4
CaO	4 0	2 3	0.2	48.0	0.8
MgO	3 0	1 5	0.1	3.8	0 6
Al_2O_3	6.3	1 5	1 5	1.3	3 8
H_2O	5 5	5 2	1 1	0.5	1.5
CO_2	..			40.9	
C	. .			...	86.2

The method of solution begins by assigning values of x, y, z, etc., to the weights of materials to be determined. The number of unknowns must not exceed the number of independent equations that can be set up to determine the unknowns. The slag ratio $SiO_2 : Al_2O_3 : \Sigma CaO = 33 : 12 : 55$ will provide two independent equations because the third possible equation is in reality only a combination of the other two. The two usable ones are

$$\frac{\text{Wt. of } SiO_2}{\text{Wt. of } Al_2O_3} = \frac{33}{12} \text{ and } \frac{\text{wt. of } SiO_2}{\text{wt. of } \Sigma CaO} = \frac{33}{55}$$

or

$$12 \times \text{wt. of } SiO_2 = 33 \times \text{wt. of } Al_2O_3 \quad (1)$$

$$55 \times \text{wt. of } SiO_2 = 33 \times \text{wt. of } \Sigma CaO \quad (2)$$

A third equation is obtained by running an iron balance on the furnace, *i.e.*, the total weight of iron charged must equal 93 per cent of the pig iron, or 930 lb., assuming no loss of iron in the process.

Of the four weights to be determined, only three need be counted as unknowns since the weight of ore C is known in terms of ore A. Therefore, let

$$x = \text{pounds of ore } A$$
$$y = \text{pounds of ore } B$$
$$z = \text{pounds of limestone}$$

all on the basis of 1,000 lb. of pig iron produced. Then

$$\tfrac{1}{5} \times (x) = 0.2x = \text{lb. of ore } C$$

The total SiO_2 in the slag must equal the amount in ore A, ore B, ore C, limestone, and coke minus the amount that entered the pig iron as silicon. For example, since ore A contains 11.5 per cent silica, the amount entering the slag from ore A is $0.115x$, because x is the weight of ore A in the charge, although undetermined as yet. The same procedure is used in determining the weight of SiO_2 from ore B, the limestone, and coke, the weight of the last-named being known (950 lb.). The amount of SiO_2 from ore C is $0.051 \times 0.2x$ lb. since $0.2x$ is the pounds of ore C in the charge. With regard to the silica reduced to silicon and present in the pig, the molecular weight of SiO_2 is 60.1 while that of Si is 28.1. There are 20 lb. of silicon present in 1,000 lb. of pig (2 per cent). Therefore, $(60.1/28.1) \times 20$ equals the pounds of silica reduced. The total SiO_2 (pounds) in the slag per 1,000 lb. of pig produced is, then,

$$\text{Total } SiO_2 \text{ in slag} = 0.115x + 0.14y + (0.051 \times 0.2x) + 0.045z + (0.054 \times 950) - \frac{60.1}{28.1} \times 20$$

All of the Al_2O_3 in the charge enters the slag. Therefore, by the above reasoning, the total Al_2O_3 in the slag is

$$\text{Total } Al_2O_3 \text{ in slag} = 0.063x + 0.015y + (0.015 \times 0.2x) + 0.013z + (0.038 \times 950)$$

Condensing the above two equations, we get

$$SiO_2 \text{ in slag} = 0.1252x + 0.14y + 0.045z + 8.6 \qquad (3)$$
$$Al_2O_3 \text{ in slag} = 0.066x + 0.015y + 0.013z + 36.1 \qquad (4)$$

From equation (1) above, we know that by multiplying equation (3) by 12 and equation (4) by 33, the two are made equal.

$$1.503x + 1.68y + 0.54z + 103 = 2.18x + 0.495y + 0.429z$$
$$+ 1192 - 0.677x + 1.185y + 0.111z = 1089 \quad (5)$$

The next step in the solution is to find the ΣCaO in the slag. This term is made up of the CaO, MnO_2, and MgO present in the three ores, the limestone, and the coke. In addition, part of the manganese dioxide is reduced and enters the metal, an amount that must be subtracted from the total MnO_2 entering with the charge. The MnO_2 is converted to MnO by multiplying by the molecular weight ratio (MnO/MnO_2) because it is present in the slag as MnO.

$$\text{MnO in slag} = \frac{70.9}{86.9} \times (0.013x + 0.04y) - \frac{79.0}{54.9} \times 0.01 \times 1000$$
$$= 0.0106x + 0.0326y - 12.9$$

The CaO equivalent of this MnO is

$$\frac{56.1}{70.9} \times (0.0106x + 0.0326y - 12.9)$$

$$\text{Equivalent CaO} = 0.0084x + 0.0258y - 10.2$$

$$\text{MgO in slag} = 0.03x + 0.015y + (0.001 \times 0.2x) + 0.038z$$
$$+ 0.006 \times 950$$
$$= 0.0302x + 0.015y + 0.038z + 5.7$$

The CaO equivalent of this MgO is

$$\frac{56.1}{40.3} \times (0.0302x + 0.015y + 0.038z + 5.7)$$

$$\text{Equivalent CaO} = 0.0421x + 0.0209y + 0.0529z + 7.95$$

$$\text{CaO in slag} = 0.04x + 0.023y + (0.002 \times 0.2x) + 0.48z$$
$$+ 0.008 \times 950$$
$$= 0.0404x + 0.023y + 0.48z + 7.6$$

The ΣCaO in the slag, then, is the sum of the CaO equivalents of the MnO and MgO plus the CaO itself.

$$\Sigma CaO = 0.0909x + 0.0697y + 0.533z + 5.35 \quad (6)$$

From equation (2) we know that by multiplying equation (3) by 55 and equation (6) by 33, equations (3) and (6) are made equal.

$$6.9x + 7.7y + 2.48z + 473 = 3.0x + 2.3y + 17.6z + 177$$
$$3.9x + 5.4y - 15.12z = -296 \quad (7)$$

By the same procedure as that used above, the total weight of iron charged can be determined as follows: A correction must be made from Fe_2O_3 to Fe by multiplying by the ratio of their molecular weights.

$$\text{Total Fe} = \frac{111.7}{159.7} \times [0.684x + 0.715y + (0.92 \times 0.2x) + 0.01z + 0.017 \times 950]$$
$$= 0.607x + 0.500y + 0.007z + 11.3 \qquad (8)$$

But we know that this must equal $0.93 \times 1{,}000 = 930$ lb. of iron per 1,000 lb. of pig produced, assuming no iron loss in the process.

$$0.607x + 0.500y + 0.007z = 918.7 \qquad (9)$$

Equations (5), (7), and (9) are three equations in the three unknowns x, y, and z, and can be solved simultaneously to provide absolute values of ores A, B, C and limestone, as follows:

$$-0.677x + 1.185y + 0.111z = 1089 \qquad (5)$$
$$3.9x + 5.4y - 15.12z = -296 \qquad (7)$$
$$0.607x + 0.500y + 0.007z = 918.7 \qquad (9)$$

Multiplying equation (5) by 0.607 and (9) by 0.677 and adding the two equations, we can eliminate x.

$$-0.411x + 0.719y + 0.0674z = 661$$
$$0.411x + 0.338y + 0.0047z = 621$$
$$1.057y + 0.0721z = 1282 \qquad (10)$$

By using the same method we can eliminate x between equations (7) and (9) by multiplying (7) by 0.607 and (9) by 3.9 and subtracting them.

$$2.365x + 3.28y - 9.19z = -179.8$$
$$2.365x + 1.95y + 0.0273z = 3582$$
$$1.33y - 9.2173z = -3761.8 \qquad (11)$$

Equations (10) and (11) can now be solved simultaneously for y and z by multiplying (10) by 1.33 and (11) by 1.057 and subtracting.

$$1.403y + 0.0959z = 1707$$
$$1.403y - 9.74z = -3978$$
$$9.836z = 5685$$
$$z = 578 \text{ lb. of limestone}$$

Substituting this value of z in equation (11) we obtain

$$1.33y = -3761.8 + 5330$$
$$y = \frac{1568}{1.33} = 1{,}178 \text{ lb. of ore } B$$

Finally, by substituting these values of y and z in equation (7), we can obtain the value of ore A.

$$3.9x + 6360 - 8740 = -296$$
$$x = \frac{2084}{3.9} = 535 \text{ lb. of ore } A$$

The amount of ore C charged $= 0.2 \times 535 = 107$ lb.

The final charge per 1,000 lb. of pig iron produced is, then,

Ore A	=	535 lb.
Ore B	=	1,178 lb.
Ore C	=	107 lb.
Limestone	=	578 lb.
Coke	=	950 lb.
Total	=	3,348 lb.

We can check the foregoing figures by substituting these values in equations (3), (4), and (6), calculating the total slag volume, and finding the percentages of SiO_2, Al_2O_3, and ΣCaO.

$$\text{Total } SiO_2 = 67 + 165 + 26 + 8.6 = 266.6$$
$$\text{Total } Al_2O_3 = 35.3 + 17.7 + 7.5 + 36.1 = 96.6$$
$$\text{Total } \Sigma CaO = 48.6 + 82.2 + 308 + 5.35 = 444.2$$

The total slag volume is 807.4 lb. and the percentages of SiO_2, Al_2O_3, and ΣCaO in the slag are

$$SiO_2 = \frac{266.6}{807.4} \times 100 = 33.0 \text{ per cent}$$
$$Al_2O_3 = \frac{96.6}{807.4} \times 100 = 12.0 \text{ per cent}$$
$$\Sigma CaO = \frac{444.2}{807.4} \times 100 = 55.0 \text{ per cent}$$

A check on the desired slag ratio of $SiO_2 : Al_2O_3 : \Sigma CaO = 33 : 12 : 55$ is, therefore, obtained.

This solution is approximate in that no account is taken of the phosphorus or sulfur and no allowance for iron loss in the slag is made. These corrections can easily be made by inserting appropriate members in the original equations and solving as above. It was thought best to omit these small factors because they affect the final values of the charge to only a slight extent but they serve to complicate the solution to a considerable degree.

The Burden Calculation.—The calculation of the blast-furnace burden is made to check the furnace operation rather than as a means of operating the furnace. An accurate record is kept of all changes that may be made from time to time, and of the weights and analyses of all the materials charged. These data are all assembled at certain times, placed on a burden sheet, Table 11-IX, and the theoretical amounts of the various ingredients of the raw materials and the products are calculated. In studying the burden sheet and the calculations, attention should be made to the fact that the weights of the ores, scale, scrap, cinder, coke, and stone, together with their analyses, are usually given and all other figures are supplied by calculation.

The ores are charged so that the percentage of ores consisting of 28 per cent No. 1, 28 per cent No. 2, 22 per cent No. 3, 11 per cent No. 4, and 11 per cent No. 5 are distributed over, say, a five-round cycle. One round might consist of 7 skips including 3 skips of ore and limestone and 4 skips of coke. A typical order of charging would be ore, coke, ore, coke, ore, coke, and coke.

The total ore according to the burden sheet is 28,800 lb. The amount of ore charged per skip would then be 28,800/3 or 9,600 lb. This weight of one ore would then be charged in the skip and the different percentages of ore charged would be discernible only over a five-round cycle, although on the burden sheet the actual percentage of the different ores charged is shown for a round.

Coke will be charged at the rate of 3,750 lb. per skip.

All other materials charged, except the limestone and coke, are considered as total ore. For instance, such materials as open-hearth cinder, scale of all kinds, converter cinder, converter shot, gravel, turnings (swarf), and steel scrap, if charged, are to be considered as total ore in the calculations.

TABLE 11-IX.—TYPICAL BLAST-FURNACE BURDEN SHEET

Materials	Charge		Fe		SiO_2		$CaO + MgO$		Al_2O_3		P		Mn		S	
	%	Weight, lb.	%	Weight, lb.	%	Weight, lb.	%	Weight, lb.	%	Weight, lb.	%	Weight, lb.	%	Weight, lb.	%	Weight, lb.
No. 1 ore	28	8,064	52 75	4,250	3 88	313	0 37	30	2 36	190	0 084	6 8	0 59	48	0 011	0 88
No. 2 ore	28	8,064	48 23	3,882	6 58	530	0 33	27	2 62	211	0 070	5 6	1 13	91	0 010	0 81
No. 3 ore	22	6,336	54 50	3,460	6 86	435	1 66	105	0 72	46	0 050	3 2	0 44	28	0 004	0 25
No. 4 ore	11	3,168	45 84	1,452	6 19	196	0 38	13	3 63	115	0 065	2 1	1 48	47	0 011	0 35
No. 5 ore	11	3,168	54 12	1,715	8 12	257	3 70	117	1 53	48	0 061	1 9	0 17	5	0 009	0 28
Total ore		28,800		14,759		1,731		292		610		19 6		219		3 0
Open-hearth cinder		2,000	20 26	405	19 38	388	41 10	822	2 50	50	1 10	22 0	6 00	120	0 20	4 0
Coke		15,000	1 19	179	4 76	714	0 67	100	2 85	427	0 016	2 4			1 10	165
Subtotal				15,343		2,833		1,214		1,087		44 0				172
Limestone		5,000			2 20	110	53 34	2,667	0 80	40	0 008	0 4			0 08	4
Total charge				15,343		2,943		3,881		1,127		44 4		339		176

Theoretical Slag

	Lb.	%
SiO_2	2,590*	32 9
Al_2O_3	1,127	14 3
$CaO + MgO$	3,881	49 4
MnO	88†	1 1
S	176‡	2 2
	7,862	99 9

Theoretical Pig-iron Analysis

Si	1 00
Mn	1 75
P	0 29

Ratio, ore to coke	2 35·1
Ratio, $SiO_2 + Al_2O_3$ to $CaO + MgO$	1 1 04
Yield of pig iron per charge	7 36 tons
Coke per ton of metal	2,038 lb.
Stone per ton of metal	679 lb.
Slag volume per ton of metal	1,068 lb.

* SiO_2 in slag = total SiO_2—SiO_2 to pig iron
= 2,943 − 353
= 2,590 lb.

† It is assumed in this calculation that 80 per cent of the Mn goes to the iron. This figure varies considerably with the various practices. For purpose of calculation the Mn will be considered as MnO.

$$339 \times 0\ 80 = 271 \text{ lb. Mn to the iron}$$
$$339 - 271 = 68 \text{ lb. Mn to the slag}$$
$$\frac{\text{MnO}(55 + 16)}{\text{Mn}(55)} \times 68 = 88 \text{ lb. MnO to the slag}$$

‡ For purposes of calculation it is assumed that all the sulfur enters the slag. When proper slag in quality and quantity is carried, it generally absorbs around 95 per cent of the sulfur present.

For general purposes, the burden given would be calculated from the charge entering the furnace in order that the base to acid ratio may be determined. However, on starting a furnace, let us first consider the limestone calculation for an acid to base ratio of 1:1.04 which is the ratio given on the burden sheet.

Let x = lb. of limestone in charge.

Total iron in charge = 15,343 lb.

Pig iron is considered 93 per cent Fe.

$$\text{Total pig iron} = \frac{15{,}343}{.93} = 16{,}500 \text{ lb.}$$

Si for basic iron in burden calculations is considered 1.00 per cent. A certain proportion of the SiO_2 in the charge is reduced to silicon, Si, and goes into pig iron. This proportion of silica is independent of any flux and the amount must be determined before the calculation of flux can be made.

$$\text{The chemical ratio to reduce } SiO_2 \text{ to Si} = \frac{SiO_2}{Si} = \frac{60}{28} = 2.14.$$

SiO_2 to be deducted = 16 500 × 1.00 per cent × 2.14 = 353 lb. of SiO_2 to pig iron.

$$\begin{aligned}
SiO_2 \text{ in limestone} &= 0.022x \\
Al_2O_3 \text{ in limestone} &= 0.008x \\
\text{Total } SiO_2 \text{ in slag} &= (2{,}833 - 353) + 0.022x \\
\text{Total } Al_2O_3 \text{ in slag} &= \underline{(1{,}087) + 0.008x} \\
\text{Total acid} &= 3{,}567 + 0.03x \\
CaO + MgO \text{ in limestone} &= 0.5334x \\
\text{Total base} &= 1{,}214 + 0.5334x \\
\frac{\text{Total acid}}{\text{Total base}} &= \frac{1}{1.04} = \frac{3{,}567 + 0.03X}{1{,}214 + 0.5334X}
\end{aligned}$$

x = 4,972 lb. of theoretical limestone required (approximates 5,000 lb. charged)

$$\text{Ratio of ore to coke} = \frac{30{,}800}{15{,}000} = 2.05:1$$

This ratio represents a measure of the furnace efficiency. If the ratio is low, the cost will increase; if it is high in proportion, the cost will decrease. However, for proper working of the furnace, a balance between the two must be reached.

Ratio of $SiO_2 + Al_2O_3$ to $CaO + MgO$:

$$\begin{aligned}
\text{Total } SiO_2 &= 2{,}943 \text{ lb.} \\
SiO_2 \text{ to Si} &= \underline{\ 353 \text{ lb.}} \\
&\quad 2{,}590 \text{ lb. available } SiO_2 \\
\text{Total } Al_2O_3 &= \underline{1{,}127 \text{ lb.}} \\
\text{Total acid} &= 3{,}717 \text{ lb.} \\
\text{Total base } (CaO + MgO)\ &3{,}881 \text{ lb.} \\
\text{Ratio} &= 3{,}717 : 3{,}881 :: 1 : x \qquad x = 1.04 \\
&= 1 : 1.04
\end{aligned}$$

This ratio represents the criterion for good operating conditions. It is through the control of this ratio that the operator controls the basicity, the viscosity, and the desulfurizing characteristics of the slag.

$$\text{Yield of pig iron per cnarge} = \frac{16{,}500}{2{,}240} = 7.36 \text{ tons}$$

$$\text{Coke per ton of metal} = \frac{15{,}000}{7.36} = 2{,}038 \text{ lb.}$$

$$\text{Stone per ton of metal} = \frac{5{,}000}{7.36} = 679 \text{ lb.}$$

Slag volume:

$$\text{Total slag} = SiO_2 + Al_2O_3 + CaO + MgO + MnO + S = 7{,}862 \text{ lb.}$$

$$\text{Slag per ton of metal} = \frac{7{,}862}{7.36} = 1{,}068 \text{ lb.}$$

$$\text{Mn in iron} = \frac{271}{15{,}343} \times 100 = 1.77 \text{ per cent}$$

$$\text{P in iron} = \frac{44.4}{15{,}343} \times 100 = 0.289 \text{ per cent}$$

Suggested Questions and Problems for Study and Class Discussion

1. List the commercial ores of iron in descending order with regard to (*a*) iron content when pure, (*b*) specific gravity, and (*c*) tonnage mined annually. Give a principal location of each type of ore.

2. Why are the blast furnaces not built near the Lake Superior mines?

3. Tell how iron ores are mined. Which is the cheaper method and why?

4. Why is the practice of grading iron ores necessary at the present time? How is it done?

5. List the principal impurities present in Lake Superior hematites and indicate which are desirable and undesirable, giving reasons for your statements.

6. What is meant by beneficiation of iron ores? Why is it necessary to beneficiate some ores at the present time?

7. How are iron ores sintered? What are the advantages of sintering?

8. Indicate in detail the process of transporting iron ore from the Mesabi range to Pittsburgh.

9. Give a short résumé of the history of iron manufacture from earliest times to the present day.

10. What materials are charged into the blast furnace? What are the principal functions of the furnace?

11. Give a brief description of the principal construction features of the furnace.

12. What methods are used for preventing segregation of coarse particles in the charge? Describe the operation of one such device.

13. List the principal items of auxiliary equipment necessary to operate the furnace and give a brief description of each.

14. To what uses may blast-furnace gas be put? Describe briefly how a gas-cleaning plant operates.

15. Describe the methods used in disposing of the liquid products of the blast furnace.

16. Describe in detail the operation of the blast furnace.

17. Discuss the chemical theory of the blast furnace, giving all necessary equations.

18. Describe the conditions occurring in the combustion zone of the furnace. What effect do these conditions have on the column of stock above the combustion zone?

19. Discuss in detail the reasons for the changes in gas composition at different levels in the furnace as given in Table 6-IX. Give equations where necessary.

20. Why is the $CO:CO_2$ ratio a good indication of blast-furnace reduction efficiency? How may this ratio be kept at a minimum?

21. What advantages may be derived from controlling the blast temperature and volume?

22. Discuss in detail the functions of the slag in blast-furnace operation and control.

23. List and describe briefly the principal irregularities in blast-furnace operation that may occur, giving a remedy for each.

24. The analyses of the materials charged into a blast furnace are as follows:

Component	Ore *A*	Ore *B*	Limestone	Coke
Fe_2O_3	67 2	71 0	1 0	1.5
MnO_2	2.1	4 2	0 2	
SiO_2	10 4	15 1	3 7	5 6
CaO	4 2	2 6	48 0	0 6
MgO	3.5	1 1	4 6	0 8
Al_2O_3	7 1	1.5	1 2	3 5
H_2O	5.5	4.5	0 4	1 8
CO_2	....	....	40 9	
C	....	....	....	86.2

In addition, 20 lb. of scrap iron of the following composition is charged with every 100 lb. of ore *A*: 4.5 per cent C, 2.5 per cent Si, 1.0 per cent Mn, 92 per cent Fe. Calculate a charge to produce 1,000 lb. of pig iron containing 3.5 per cent C, 2.0 per cent Si, 1.3 per cent Mn, 93.2 per cent Fe. The desired slag ratio is $SiO_2 : Al_2O_3 : \Sigma CaO = 31 : 11 : 58$. Assume that 980 lb. of coke are charged per 1,000 lb. of pig iron produced.

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CHAPTER X

IRON FOUNDING

The art of iron founding consists, in the general case, in melting a mixture of pig iron and iron and/or steel scrap to obtain a melt of the desired chemical composition and pouring this molten metal into a mold of any desired size and shape, which the metal assumes and retains when solidified and cooled. The mold is usually made of some kind of sand, although permanent metal molds are used for some types of work and will be mentioned later. Iron founding is a complex art as each different type of casting is a separate problem in itself and it is manifestly impossible to cover more than the bare essentials in the space of a single chapter. The topics of melting equipment and their operation, molding practice, and the types and uses of the iron castings produced will be briefly covered in the present chapter.

Cast iron is one of the oldest ferrous materials known to man and is, at the same time, one of the least understood. It is the cheapest of the ferrous materials and must be cast into shape as it does not possess the necessary plasticity to form it into the desired shapes by mechanical methods when in the solid state. Until just the last few years, cast iron was almost universally considered by designing engineers as a cheap, brittle material possessing little strength in tension or shear and practically no ductility, but having comparatively good crushing strength and resistance to wear and abrasion. Cast iron was further considered by them as being rather undependable because its properties varied so widely from casting to casting and its properties were incapable of modification by any kind of treatment after solidification. Within recent years, however, changing economic conditions have caused a widespread search for cheaper engineering materials of good physical properties and consequently the internal structure and constitution of cast iron, as well as the methods of producing it, have been intensively studied by metallurgists all over the world with surprisingly good results. It can be truthfully said that at the present time cast

iron as a material of engineering construction is just beginning to assume the position it deserves, and a rapid increase in its use is expected by nearly everyone who is in a position to realize the factors causing this change. Even the large amount of experimental work already done on cast iron has only scratched the surface but what has been accomplished has pointed the way to a better understanding and control of the factors governing the properties of the casting. In addition, the use of alloying elements, the development of methods of heat-treatment, and the advent of electric melting have all played an important part in the increasing use of cast iron. In the foundry itself, science is rapidly taking the place of the old rule-of-thumb methods and rapid improvement is to be looked for in this direction.

MELTING THE METAL

Three types of furnaces are used for melting iron for castings: the cupola, the air furnace, and the electric arc furnace. Of these, the cupola is the most widely used for melting iron for ordinary castings of all kinds. The air furnace is used predominantly in melting iron for malleable castings and hence will be considered in detail in Chap. XI. The electric arc furnace is used mainly for melting alloy cast irons and the so-called "high-test" cast irons. In addition, molten metal from the blast furnace is sometimes stored in a refractory lined vessel called a *mixer*, its composition adjusted (if necessary) by adding molten metal melted in cupolas, and the resulting mixture poured into castings. This method saves the expense of remelting the pig iron and, if the iron foundry is an integral part of a blast furnace and steel plant, is often used, particularly in casting ingot molds. The disadvantages of this method are many and prohibit its use in most cases: Molds cannot be prepared fast enough to take care of the large tonnage of metal produced by the blast furnace; blast-furnace taps come at inconvenient times for pouring castings; the composition of blast-furnace pig iron varies too widely from tap to tap, necessitating the employment of either a highly trained man who can judge the metal composition by eye alone, or expensive rapid methods of chemical analysis; it is too difficult to adjust the pouring temperature of the molten pig, either by itself or mixed with cupola metal; and, finally, it is seldom economically feasible to locate the foundry at a blast-furnace plant.

For these reasons, the pig iron from the blast furnace is usually cast into pigs and remelted under such conditions that the composition and pouring temperature of the iron are capable of close control.

Cupola Construction.—The cupola, shown in partial section in Fig. 1-X, is a straight shaft furnace, open at the top and constructed of riveted boiler plate lined with special fire-clay brick known as cupola blocks. The cupola is charged through doors about halfway up the shell with alternate layers of coke and iron and with perhaps a little limestone added near the end of the heat to flux the coke ash. Air is blown in through tuyères near the bottom to burn the coke, the heat of combustion being sufficient to melt the iron.

The bottom of the cupola is composed of a pair of hinged cast-iron doors which are supported by a heavy rod during the operation of the furnace and are dropped at the end of the day's run in order to permit the unconsumed fuel and the residue of iron in the cupola to fall out and be removed. The taphole is located at one side of the bottom of the cupola. The sand bottom, which is tamped in on top of the bottom doors, is sloped so that the entire contents of the furnace can be drained through the taphole. The slag hole is located on the opposite side of the shell and several inches higher up in order to provide a reservoir for the molten metal. The cupola is encircled near its base by a chamber, known as the *wind box*. The air blast is forced into the wind box through the blast pipe by means of a blower. The wind box is connected to the interior of the cupola by the tuyères, which are of cast iron and flare inward slightly.

The height of the tuyères above the bedplate varies with the type of work being done in the foundry. If only a small amount of molten metal is needed at one time, as in pouring small castings, or if the iron is allowed to run from the cupola continuously, only a small amount of space is needed in the *basin* or *crucible* and the tuyères are set near the hearth bottom. On the other hand, if a large amount of iron is needed at one time, as in pouring large castings, the tuyères must be set correspondingly higher above the hearth, as it is obviously necessary to keep molten metal and slag from entering them. In addition, from one to three rows of tuyères are provided, depending upon the operating conditions. Two rows are the usual practice, the lower row

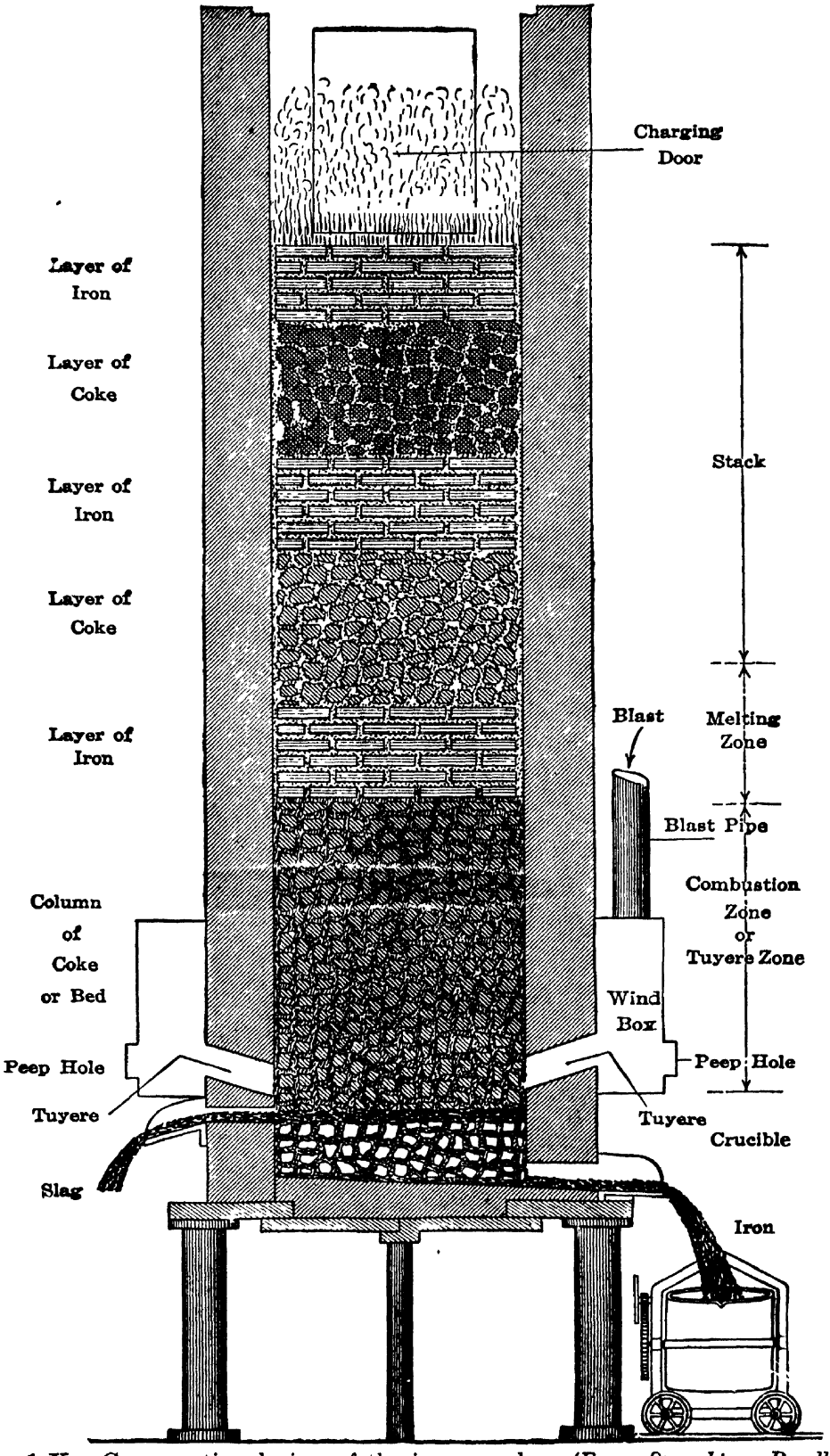


FIG. 1-X.—Cross-sectional view of the iron cupola. (*From Stoughton, Bradley, "Metallurgy of Iron and Steel."*)

forming nearly a continuous slot around the circumference of the cupola and the upper row, a few inches above, being staggered with respect to the lower row and fewer in number. Two rows of tuyères provide better fuel economy and quicker melting conditions than a single row. Also, the melting rate is always under control as the upper row of tuyères can be partly or completely blocked off if slower melting is desired. The wind box obviously acts as a manifold to distribute the wind to the tuyères.

A charging platform is built at the level of the charging doors to facilitate charging the solid materials into the cupola. One of several different types of mechanical charging devices is almost always used, as hand-charging methods are too inefficient

TABLE 1-X.—CAPACITIES OF CUPOLAS*

Cupola diameter inside lining, in.	Tons iron melted per hr.	Cubic feet blast per min.	Relative velocity blast, ft. per sec. (cupola empty)
30	3	1,500	5 09
36	4 5	2,250	5 30
42	6	3,000	5 20
48	8	4,000	5 30
54	10	5,000	5 24
60	13	6,500	5 52
66	16	8,000	5 61
72	19	9,500	5 60
78	22	11,000	5 52
84	26	13,000	5 63
90	30	15,000	5 66

* MOLDENKE, R., "Principles of Iron Founding," McGraw-Hill Book Company, Inc., New York, 1930

under present conditions. The two-impeller type of pressure blower, the popular type at present, is usually equipped with a device to measure the volume of air delivered to the cupola. The older and cheaper fan blower is being used less and less because, if the material in the cupola packs together, the pressure rises to a point where the fan will not deliver any air. Cupolas are built in various sizes, as shown in Table 1-X, and the choice of a size for a certain set of conditions depends upon many factors. A few cupolas are built with diameters of 120 in. or more. For a new foundry that has an uncertain market, it is

best to install a cupola considerably larger than the known needs and decrease the diameter to the desired size by increasing the thickness of the lining. Then, as the market expands, the cupola diameter can be increased by decreasing the lining thickness. The blast data given in Table 1-X are calculated on a requirement of 30,000 cu. ft. of air per minute to melt a ton of iron. It is to be noticed that the relative velocity of the blast increases but slightly as the size is increased. The blast pressure usually used is under 1 p.s.i.

Charging the Cupola.—As noted before, the solid materials charged are metal, coke, and a little limestone if a long run is to be made. The metals charged are pigs, iron scrap (defective castings, gates, risers, etc.), and steel scrap, the relative proportions of each depending upon the desired composition of the castings to be poured, the type of casting being made, and the prevailing market price of the various ingredients—an important consideration as a good metallurgist always tries to use the most of the cheapest raw material and still obtain the desired composition. Cast-iron pipe is usually made without scrap. This industry accounts for better than half a million tons of cast iron per year in the United States. Jobbing foundries, on the other hand, use from 30 to 40 per cent of bought cast-iron scrap besides their own return scrap. The total production of gray-iron castings in this country probably represents about 75 per cent pig iron plus return scrap and 25 per cent bought scrap. Steel scrap is ordinarily used in the cupola only when a low carbon content is desired in the castings—below the amount present in the pig and scrap available for charging.

Ordinary crude limestone, oyster shells, and marble chippings (all high in $CaCO_3$) are used, the amount being from about 20 to 50 lb. per ton of iron melted and this amount is added beginning with about the fifth iron charge.

The amount of coke used will be from one-fourth to one-twelfth of the weight of iron melted, depending upon the amount of steel scrap used (high melting temperature) and the pouring temperature desired. The chief requisites of foundry coke are purity, large size, good strength, and a minimum of reactivity with carbon dioxide gas. Since the coke merely furnishes heat by combustion, incomplete combustion—the presence of CO in the stack gases—represents wasted energy and a distinct

loss, hence the minimum reactivity requirement. The specifications of the American Society for Testing Materials with regard to analysis are given in Table 2-X. A high sulfur content is quite objectionable and many private specifications limit it to less than 1 per cent. The phosphorus content is not usually important. The coke can be made by either the beehive or the by-product method. If by-product coke is used, the coal mixture

TABLE 2-X.—FOUNDRY COKE SPECIFICATIONS

Constituent	Per Cent on Dry Basis
Volatile matter	Not over 2.0
Fixed carbon	Not under 86 0
Ash	Not over 12 0
Sulfur	Not over 1.0

to be coked should contain from 25 to 28 per cent of volatile matter, thoroughly coked, and the resulting coke screened over a 3-in. screen. Beehive coke is still specified by the majority of iron foundries.

In preparing the cupola for charging, the first step is to patch the lining where it has become worn by the previous day's operation. From a point about 2 ft. above the tuyères to the bottom of them, the acid lining is in contact with basic FeO and slag, resulting in considerable cutting away of the lining in places. The most severe cutting action is restricted to a zone above the tuyères, called the melting zone, where the oxide scale on the iron becomes molten. This patching must be carefully done every day or the worn spots will burn through and cause hot spots on the shell, scaffolding, and other troubles. The worn spots are patched by filling them with a mixture of sand and clay wet with water and smoothing them with a trowel so that these spots will conform to the interior shape of the cupola. A good practical daubing mixture consists of ¼ blue clay (or fire clay), ¼ ground firebrick, and ½ fire sand (or heavy molding sand). The slag hole is formed at the same time by putting a bar in the opening in the shell, packing the lining material around it, withdrawing the bar, and filling the resulting hole with a clay ball. The top of the slag hole should be at least 2 in. below the bottom of the lower tuyères. The bottom is next made up by wedging the bottom doors in place and ramming in sand moistened with

water, or "tempered" as it is called, being sure to shape the bottom so that all of the iron will drain out of the tap hole.

The cupola may be lighted by means of either a wood fire or a specially designed oil burner, the latter method being fairly recent and coming into considerable prominence at the present time. In the former case, shavings and kindlings are laid on the hearth in sufficient amount to ignite the coke. A bed charge of coke is placed in the cupola before any iron is charged and this is of considerably greater weight than the subsequent charges of coke, which are charged alternately with charges of iron. A portion of the bed charge is laid on the wood and, after it is thoroughly ignited, the remainder is introduced, only enough being reserved to level off the top of the bed charge before introducing iron. If oil is used, the burner is introduced through the taphole and the coke ignited. When the coke charge is burning well, the breast (the portion of the lining around the tap hole) is built up and the blast turned on gently to ignite thoroughly the entire charge of coke on the bed, all but a small portion of the bed charge of coke being added at this time.

When the fire is visible through the coke as viewed from the charging doors, the breast, taphole, and slag hole closed and the blast on, the bed charge is leveled and charging of the iron should begin as the coke should not be permitted to burn red hot all the way through. The amount of the bed charge of coke depends upon the cupola itself and the type of operation used. It is assumed in the present discussion that ordinary gray iron is being melted and that no steel scrap is used in the charge. Every cupola has a zone at and above the tuyères where it is the hottest, this zone being known as the melting zone. In a cupola that has been running for some time, this melting zone is easily ascertained by the condition of the lining because the melting zone is characterized by the presence of liquid FeO which fluxes the lining to some extent. The upper limit of the melting zone is usually from 15 to 30 in. above the upper tuyères, and the bed charge should be leveled off at the top of the melting zone. A small amount of coke in the bed charge will lower the upper level of the melting zone, and a large amount will raise it. The type of charge will also influence the height of the bed charge because scrap iron will melt earlier than heavy pigs. If a large proportion of scrap iron is used in the charge, the melting zone should be

somewhat lower than if the bulk of the charge is pig iron. Also, the quality of the iron melted is usually better with a high bed charge than a low one but, of course, the cost is greater. The melting zone of the cupola should always be at the same level in order to procure the best results.

With the bed charge of coke at the right height, the iron is introduced upon it. The amount of the first iron charge varies with different melters but usually varies from 2½ lb. of iron per pound of coke in the bed charge to 4 lb. of iron per pound of coke. The amount of the first iron charge also depends upon the total amount of iron to be melted and governs the subsequent coke and iron charges. Assuming that the bed charge of coke is 1,500 lb., the following charging schedule is fairly typical: On top of the leveled bed charge is placed 4,500 lb. of iron and this iron is carefully leveled. A layer of 250 lb. of coke is placed on the iron and 2,500 lb. of iron then placed upon the coke. The charge is thus built up of alternate leveled layers of iron and coke in the ratio of 250 lb. of coke to 2,500 lb. of iron until either the amount of iron to be melted is charged or the cupola is filled to the level of the charging doors. In any one iron layer, the pig iron is charged first and the scrap iron on top of it because, being free from scale, the scrap usually melts more rapidly than the pig iron. Thus, if the pig iron is charged first, it reaches the melting zone first and both pig and scrap iron are melted at about the same time.

A certain amount of slag is necessary to cover the molten iron in the crucible in order to prevent its oxidation by the air blast. If the coke is not too pure, the coke ash will form a sufficient volume of slag, but with high-purity charging materials limestone is necessary in order to form a sufficient slag volume. If used, it is placed on top of the iron charge, beginning with about the fifth iron charge, in amounts not exceeding 50 lb. per ton of iron. If more limestone is used than is necessary, the basic CaO will cut the acid lining rapidly in the melting zone. If the cupola will not hold the entire charge, the additional layers of coke and iron are added after melting has started and the charge has begun to sink. After the cupola is charged it is well to allow it to stand for about an hour before the cold blast is put on for melting. The peepholes in the wind box are left open so that the coke will burn by natural draft. This preheats

the lower charges to such an extent that when the blast is put on, melting begins rapidly and evenly and continues at a uniform rate throughout the heat.

Operation of the Cupola.—As melting begins, a layer of iron is resting on top of white-hot solid coke. As the air from the tuyères meets this coke, the carbon is gasified and the hot gases produced melt the iron as they pass upward. The relatively thin layer of iron melts in from 5 to 10 min. and during this time the coke beneath it is consumed as well. The charge sinks progressively and a new layer of fuel rests on the bed to replace the layer previously burned and a new layer of iron rests on top of that. The alternate charges of coke and iron are so proportioned that the new layer of iron will occupy exactly the position of its predecessor. In other words, the cupola is operated so that certain zones of action are maintained in definite positions in the cupola, with the result that rapid, hot, and economical melting is obtained.

The *crucible zone* extends from the bottom of the cupola to the tuyère level. The object of this zone is to form a place in which the iron and slag may collect after they have melted and trickled down from the melting zone. If the cupola is designed for continuous tapping, the crucible zone is relatively shallow and the metal flows from the tap hole into a ladle in a continuous stream. If, on the other hand, intermittent tapping is used, the crucible zone is deeper and the tap hole is opened only at intervals. When the cupola is first started, the first hundred pounds or so of metal melted is too cold to pour into castings and is allowed to run from the tap hole. The taphole is then closed and the metal allowed to accumulate in the crucible until the slag reaches the tuyère level, when the tap hole is opened and the cupola is drained until slag begins to appear on top of the iron flowing from the spout. The taphole is then closed, as the metal should be free from slag. This condition is an indication, however, that by the time the crucible is again full, a sufficient volume of slag will have accumulated to drain off through the slag hole. Shortly before the next tap, therefore, the slag hole is opened and the slag permitted to escape. After the slag has once begun to run freely, the slag hole will take care of itself, the slag rising on top of the iron as it collects and flowing out through the slag hole whenever it rises to that level. The top

of the metal must be kept between these two openings so that metal will not flow from the slag hole and slag will not flow from the taphole. If continuous tapping is used, the size of the taphole should be regulated to maintain the top level of the metal between these two openings. Hotter metal may be obtained by using continuous tapping because the metal is not blown upon by the cold blast. Also, the metal is subjected to more oxidation when held in the crucible and its composition is more difficult to control. It is not considered good practice to use the crucible as a reservoir except for short periods.

The *combustion zone* is that portion of the shaft in which the blast comes in contact with and burns the red-hot coke and all the heat of the operation is produced in this zone. As there is always a column of coke extending to the bottom of the cupola, combustion of the coke begins immediately above the surface of the slag collected in the crucible. The upper limit of this zone depends upon the pressure of the air blast—the greater the pressure the higher it extends above the upper tuyères. For the best results, the top of the combustion zone should usually be within 24 in. of the upper line of tuyères. Combustion should be as complete as possible, as the presence of CO in the top gases represents a loss of heat. On the other hand, excess oxygen oxidizes the metal too much and results in an even greater loss. It is impossible to operate the cupola without some CO being present in the escaping gases but the amount should be as low as possible.

The *melting zone*, the region in which all of the melting of the iron takes place, is situated immediately above the combustion zone. During melting, the iron is supported on a column of coke which is the only solid material below the melting zone. When each layer of iron enters the melting zone, it should be 15 to 24 in. above the upper tuyères and, as fast as it melts, the iron trickles down over the coke to the crucible. It requires from about 5 to 10 min. for each layer of iron to melt and during this interval the column of coke beneath it is burning and sinking. Consequently, the last of the iron in the layer will melt at a point 7 to 10 in. below the first and, if the charge and blast pressure are properly proportioned, each iron charge will enter the melting zone before the preceding charge is completely melted at the bottom of the zone, causing a continuous stream

of iron to be delivered. Furthermore, the coke burned will be exactly replaced by the next layer of coke coming down and the position of the melting zone will remain constant—a very important factor in successful cupola operation. The melting zone, as indicated by the cutting of the lining, should not be more than 12 in. deep and necessarily overlaps the combustion zone to some extent.

The *preheating zone* extends above the melting zone to the top of the charge. The function of this zone is to contain material that can be preheated by the gases as they ascend. Also, the material helps to keep the heat concentrated in the melting zone where it should be in order to produce hot metal.

The campaign of the ordinary foundry cupola lasts only for 3 or 4 hr. As a general rule, the morning is spent in patching the lining, laying out the charging materials for charging, and making the molds. The bed charge is lighted about noon and burned in for an hour or more and metal charged until four or five in the afternoon. The supports are then pulled out from underneath the bottom doors and the sand bottom, coke, slag, etc., left in the cupola are allowed to drop and are quenched with water.

When the heat is charged, the soaking period ended and the blast turned on for melting, the first metal should begin to run sluggishly from the tap hole within 15 min. of the time the blast was put on. In another 10 min. the first layer of iron should be entirely melted and with proper proportioning of the charge, melting should proceed continuously. If the coke layers are too thick, there will be a delay when each iron charge enters the melting zone and the extra coke will have been practically wasted. If the iron layers are too thick, the last of the layer will melt too near the tuyères, come in contact with oxygen in the blast, and be badly oxidized. In addition, the blast will cool it and, under these conditions, the iron will first run hot and then cold when continuous tapping is used. The blast volume should be so regulated that the escaping gases are nearly neutral in character but on the reducing side (presence of CO). If very hot iron is needed, more coke should be used and slower melting is to be expected. The last few hundred pounds of metal coming from the cupola at the end of the daily campaign is

never poured into castings because it is usually more oxidized than the rest of the heat and contains more sulfur. The total iron loss in the process averages about 7 to 8 per cent.

Chemical Changes in the Cupola.—As the iron trickles down over the hot coke to the crucible, it absorbs sulfur in amounts depending upon the amount of coke present and the sulfur content of the coke. The sulfur pickup will vary from about 0.02 to 0.05 per cent of the iron—*i.e.*, if the pig charged contained 0.08 per cent sulfur, the castings will contain from 0.10 to 0.13 per cent S. The sulfur content of the middle of the run will be less than in that produced at the beginning and end of the heat because, at the beginning, the coke ratio is higher and, at the end, the oxidizing conditions are usually more severe. The more fluid the slag, the more sulfur it will probably absorb. For this reason a little fluorspar, CaF_2, is often added with the limestone. The other functions of the slag are to flux the dirt on the metal and the ash of the coke and to carry off the FeO unavoidably formed in the melting process.

As the metal trickles past the air blast coming from the tuyères, silicon is oxidized. The castings usually contain 0.10 to 0.25 per cent less silicon than the metal charged. Thus, if the charge contains 2.5 per cent silicon, the castings will contain 2.25 to 2.40 per cent Si. There is also an accompanying loss of about 10 to 20 per cent of the manganese due to oxidation. The carbon content of the melted metal depends chiefly upon the temperature in the cupola and the length of time the molten metal is in contact with the hot coke. The carbon content of the heat can best be controlled by controlling the time the metal is held in the reservoir of the cupola. A lower and more uniform carbon content can usually be obtained by using continuous tapping than by employing intermittent tapping. The phosphorus goes through unchanged and is always higher in the castings than in the charge because of the iron oxidized and lost in the process.

Cupola Melting High-test Cast Iron.—High-test cast irons are cast irons with physical properties superior to those of ordinary gray cast iron, containing a comparatively low carbon content and oftentimes varying amounts of special alloying elements. These irons can be and often are melted in the cupola with some changes in practice but the electric arc furnace is

coming into greater prominence for the purpose of melting these cast irons.

The melting of these irons in the cupola requires special operating conditions because more than 40 per cent of steel scrap is necessary in order to obtain the range of carbon content of from 2.75 to 3.10 per cent usually required. If intermittent tapping is used, the following order of charging the metal layer is usually recommended:

1. Pig iron on coke.
2. Foundry scrap.
3. Ferroalloys (containing the alloying elements).
4. Steel scrap.

Of course, the ferroalloys are omitted if alloy cast iron is not being made. This order of charging is to be preferred because the pig iron melts first and it contains sufficient silicon and manganese to ensure deoxidation of the remainder of the charge as it melts. The steel melts last and, therefore, remains in contact with the coke for only a short time and less carbon is absorbed by it. It is desirable to tap out each metal charge as it is melted. If continuous tapping is employed, the following order of charging the metal is probably best:

1. One-half of the pig iron and coke.
2. Steep scrap, remainder of pig iron, foundry scrap, and ferroalloys (if any), well mixed.

This charging method ensures sufficient silicon and manganese at all times to prevent oxidation in the continuously melting charge.

The bed charge of coke required usually varies between 42 and 48 in. above the tuyères regardless of the cupola size. This is a larger bed charge than is usually used in ordinary gray iron practice because the steel scrap has a higher melting point than pig iron. A little limestone is sprinkled on top of the bed charge after it is ignited and burned in and the cupola charged by either of the above methods, depending upon the type of tapping used. In order to obtain good hot metal, the ratio of subsequent metal charges to coke charges should be 7.5 or 8 to 1. With this ratio, a metal temperature of 2700°F. or above can be obtained. About 20 lb. of limestone per ton of metal is added on top of each metal charge. The area of the tuyères should be 25 per cent of the cross-sectional area

TABLE 3-X.—COMMERCIAL MATERIALS FOR ALLOYING CAST IRON*

	Pure nickel	"F" nickel	N C C [1] pig	Ferro-chromium	Spiegeleisen	Silico-spiegel		Silvery pig	Ferro-silicon	Ferro-manganese	Ferro-molybdenum [5]
						A	*B*				
Carbon	Trace	0 20–0 30	1 0–1 5	6 0–7 0	4 0–6 0	1 0–1 5	2 0–3 0	0 9–1 75		6 0–7 0	0 10 max.
Silicon	Trace	5 0–6 0	1 0–1 5		Under 1 0	5 0–15 0	6 0–8 0	7 0–14 0 [2]	79 0–89 0	Under 1 0	5 0–7 0
Manganese			0 30–0 60		10 0–35 0	15 0–25 0	20 0–25 0	1 3–2 2		78 0–82 0	Nil
Nickel	99 95	Avg. 92 0	56 0–59 0								Nil
Copper	0 01–0 03	0 20	23 0–25 0								Nil
Chromium			7 5–8 5	66 0–70 0							Nil
Phosphorus					Under 0 15	Under 0 15		Under 0 10		Under 0 25	0 05 max.
Sulfur	Trace	0 025			Under 0 05	Under 0 025		Under 0 04			0 05 max.
Iron	0 01–0 04	1 0–2 0	Balance	Balance	Balance	Balance	Balance	Balance	10 0–20 0	Balance	Balance
Form	Squares	Pig (*a*)—Shot (*b*)	Pigs	Powder	Pigs	Pigs	Pigs	Pigs	[3]	[4]	Granular
Size	13–125 lb	(*a*) 5 lb (*b*) ¼" dia	5 lb	20 mesh	50 lb +	50 lb +	50 lb +	50 lb +	[3]	[4]	¼ in. to 20 mesh
Method of adding	In furnace	Ladle or furnace	In furnace	In ladle	In furnace	In furnace	In furnace	In furnace	Ladle or furnace	Ladle or furnace	Ladle or furnace
Melting point	2650°F	2275–2350°F.	2300°F	2200–2370°F	1950–2265°F			2335°F.	2425–2580°F.	2280–2325°F.	2950–3000°F.

* From "Recommended Practice for Melting 40% or more of Steel Scrap in the Cupola," International Nickel Company.

[1] For production of Ni-resist cast iron.

[2] Usually averages 8 per cent silicon.

[3] Obtainable in sizes ranging from 50-lb lumps to crushed to desired screen, also in briquets containing 1 and 2 lb of silicon

[4] Obtainable in sizes ranging from 50-lb lumps to crushed to desired screen, also in briquets containing 2 lb of manganese and ½ lb. of silicon.

[5] Ready solubility of molybdenum in iron is considered to overcome high melting point

of the cupola at the tuyère level and only one row of tuyères should be used, as otherwise the coke bed may have to be so high that carbon absorption by the metal becomes excessive. The charge should be soaked for an hour under natural draft and, after the blast is turned on for melting, iron should be trickling down in from 3 to 5 min. The initial metal charge should melt in from 17 to 22 min. and subsequent charges in from 12 to 15 min. The slower rate of melting is due to the higher melting point of the steel scrap.

The alloying elements and ferroalloys commonly added to cast iron are listed in Table 3-X, together with their composition and important properties. Those which may be charged into the furnace will not oxidize appreciably under good cupola operating conditions while those which must be added in the ladle oxidize too rapidly for cupola charging. In adding small-sized alloys to the ladle, it is best to pour them down a trough directly into the stream of metal as it enters the ladle. In this way, the impact of the stream mixes the alloys thoroughly and dissolves them rapidly.

Electric Furnace Melting.—The majority of the electric melting of cast iron is done in rocking electric arc furnaces, an installation of which is shown in Fig. 2-X, although some is made with probably equal success in a three-phase direct-arc furnace known as the Moore 'Lectromelt furnace. These furnaces are used to melt both plain and alloy cast iron of all descriptions, although they show to the best advantage in comparison with the cupola when melting cast iron which requires a close control of analysis and of which high physical properties are desired. They are also used for the production of high-test plain and alloy cast irons by the process known as *duplexing* in which pig iron and scrap are melted in the cupola, transferred while molten to the arc furnace, the composition of the heat adjusted by the addition of proper amounts of steel scrap and ferroalloys (if necessary), the heat superheated to the desired degree, cooled slowly to the desired pouring temperature, and poured into castings.

The indirect-arc rocking furnace consists essentially of a steel cylinder closed at both ends, lined with a refractory, and mounted horizontally on a base that rocks the furnace back and forth during operation. The furnaces are made in sizes

ranging from 50-lb. capacity experimental installations to 7,000-lb. capacity (molten metal). In the smaller sizes the furnace shell rests on motor-driven rollers and is friction driven

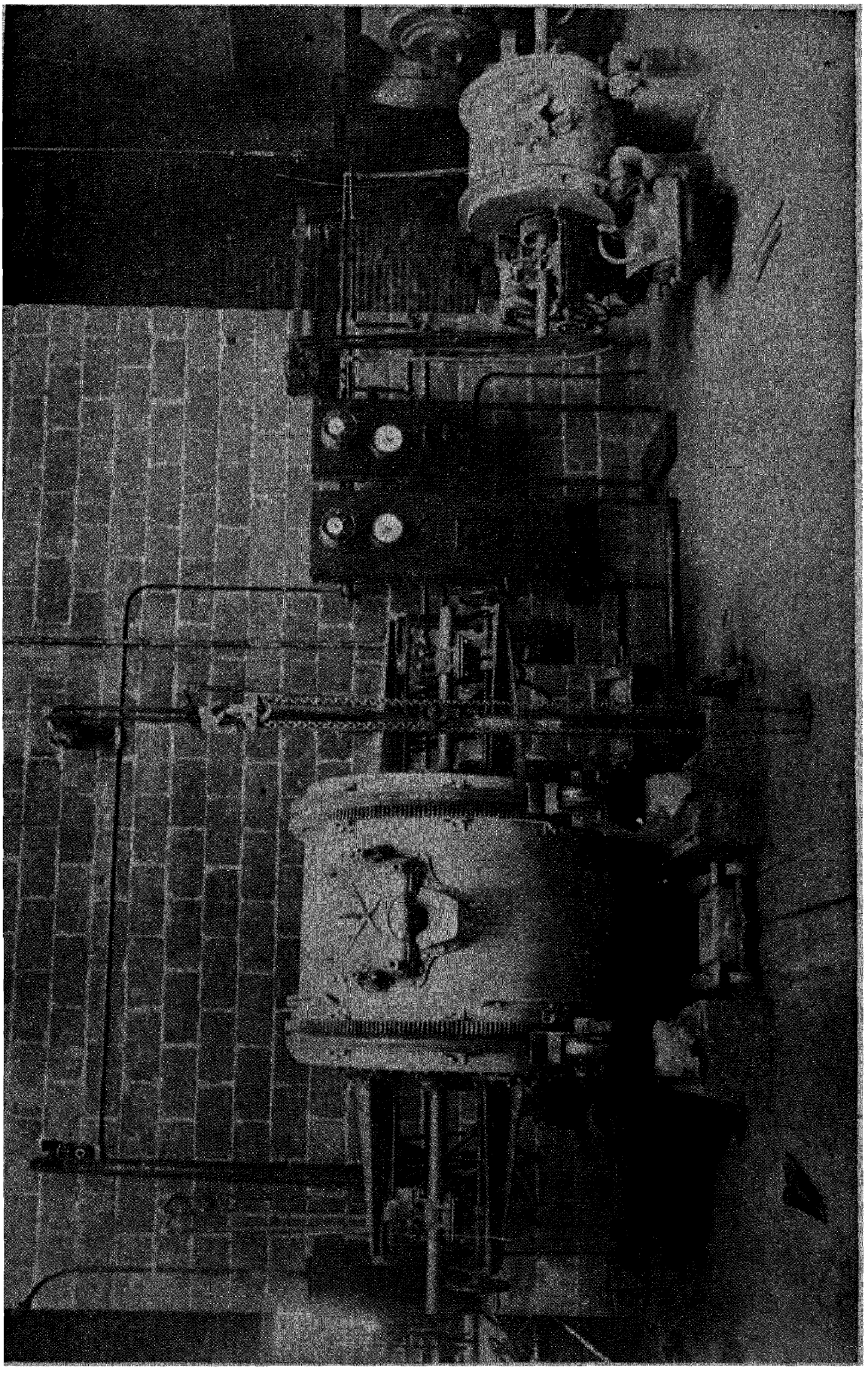


FIG. 2-X.—Indirect-arc, rocking electric furnace. (*Courtesy of the Detroit Electric Furnace Company.*)

while the large sizes are driven by gears. The metal in the furnace is not in the electric arc circuit but is heated entirely by radiation from the arc which is struck and maintained between

two horizontal graphite electrodes that enter at the center of the ends of the furnace shell. The charging door is located at the center of the side of the shell. As the shell rocks, the metal washes up almost to this door and, as the direction of rotation is reversed, the shell rotates until the metal almost reaches the door on the other side.

The rocking arc furnace has several important advantages for melting cast iron. A high degree of superheat, necessary in producing some irons satisfactorily, can be easily attained and accurately maintained. It has the further advantage of accurate control of composition and ease of producing and reproducing any desired analysis. This is due to the nonoxidizing atmosphere of the closed melting chamber, the fact that the arc does not make contact with the metal and hence does not burn out carbon and other elements, and the absence of a slag which prevents variable silicon pickup. The automatic mechanical stirring of the charge ensures complete uniformity of the bath composition, causes thorough mixing of the ingredients of the charge, and protects the lining from overheating. This melting method possesses the further advantage of being able efficiently to melt charges consisting partly or wholly of borings and similar finely divided materials—an important economic consideration as much scrap of this size is available. Finally, the composition of consecutive heats may be easily varied through wide ranges of composition without affecting the operating conditions. This method of melting is more costly than cupola melting in the general case, but the advantages gained often outweigh the increase in cost when making high-test and alloy irons within close composition limits.

Cupola Charge Calculation.—Cupola charge calculations are of considerable importance because, knowing the changes in composition that take place in a particular cupola, the foundryman can calculate the amounts of the various ingredients in the charge which, when melted and mixed, will produce the desired composition for pouring into castings. The foundry must have on hand pig and scrap of different analyses in order to produce the desired composition by mixing them and the correct chemical analyses of these materials must be known. In addition, the attempt is always made to use the most of the least expensive charging material and still obtain the desired

analysis of the casting. Incidentally, the fact that blast furnaces produce pig irons of different compositions is of advantage to the foundry because, otherwise, expensive ferroalloys would have to be used in order to meet the silicon and manganese specifications on many castings.

Suppose that it is desired to make castings of the following composition:

	Per Cent
Carbon	3 0
Manganese	0 65
Silicon	1 10
Phosphorus	0 18 (0 20 max.)
Sulfur	0 11 (0 12 max.)

and that it has been found by experience that 50 per cent of steel scrap is necessary in the charge in order to produce the low carbon content desired under the operating conditions. The analyses of the materials available for charging are given in Table 4-X. The carbon analysis is not given because the percentage of carbon in the final castings is a function of the cupola operation rather than the carbon content of the charging materials although it is known that the steel scrap is low in carbon,

TABLE 4-X.—MATERIALS AVAILABLE FOR CHARGING

Material	Si, %	Mn, %	P, %	S, %
Steel scrap	0 20	0 85	0 100	0 070
Pig *A*	2 20	0 63	0 738	0 020
Pig *B*	2 35	0 78	0 044	0 020
Iron scrap	2 10	0 85	0 300	0 100

the pig irons are high in carbon, and the iron scrap is moderately high in carbon. By comparing these figures with the desired composition of the casting, it can be seen that the desired silicon content is about halfway between that of the steel scrap and the pig irons and iron scrap; the desired manganese content lies near the lower limit of that of the charging materials; no trouble should occur from too high a phosphorus content if too much of pig *A* is not used; and the sulfur specification should cause no trouble if the metal does not absorb too much from the coke.

Let us assume further that, owing to the changes in composition during melting in the particular cupola used, 20 per cent of the

manganese and 10 per cent of the silicon in the total charge is lost through oxidation, and the sulfur content is increased by 0.02 per cent owing to absorption from the coke. The phosphorus goes through unchanged but, since there is an iron loss, the phosphorus content of the final castings is assumed to be 0.01 per cent greater than that of the mix charged. These figures may be judged only with experience in the operation of the particular cupola used and the type of operation employed.

If these changes occur, we can calculate the desired composition of the mixture from the desired final analysis, as follows: If the desired silicon is 1.10 per cent and the loss is 10 per cent of this, the silicon content of the charging mixture should be $1.10 \times 100/0.90 = 1.22$ per cent. Likewise, the manganese content of the mix should be $0.65 \times 100/0.80 = 0.81$ per cent. The phosphorus and sulfur are, then, $0.18 - 0.01 = 0.17$ per cent and $0.11 - 0.02 = 0.09$ per cent, respectively. The composition of the charge to take care of these changes during melting should be, then,

	Per Cent
Silicon	1 22
Manganese	0 81
Phosphorus	0 17
Sulfur	0 09

The amount of steel scrap of known analysis is set at 50 per cent. The problem therefore resolves itself into finding the proper mixture of the pig iron scrap to make up the remaining 50 per cent. Considering silicon first, the amount of silicon in 100 lb. of the total charge is 1.22 lb., but half of this 100 lb. is made up of steel scrap containing 0.20 per cent silicon while the remaining 50 lb. is the mixture containing pig iron and iron scrap. If we let w equal the weight (pounds per pound of metal) of silicon desired in the pig and scrap iron mixture in order to produce 1.22 per cent Si in the total mix, we may find the value of w by running a silicon balance, as follows:

$$\underset{\text{Lb. Si in total charge}}{100 \times 0.0122} = \underset{\text{Lb. Si in steel scrap}}{50 \times 0.002} + \underset{\text{Lb. Si in pig and iron scrap}}{50 \times w}$$

$$1.22 = 0.1 + 50w$$

$$w = \frac{1.12}{50} = 0.0224, \text{ or } 2.24 \text{ per cent Si in pig and iron scrap}$$

By letting u equal the pounds of manganese per pound of metal in the pig and iron scrap mixture and running a manganese balance:

$$\underset{\text{Lb. Mn in total charge}}{100 \times 0.0081} = \underset{\text{Lb. Mn in steel scrap}}{50 \times 0.0085} + \underset{\text{Lb. Mn in pig and iron scrap}}{50 \times u}$$

$$0.81 = 0.425 + 50u$$

$$u = \frac{0.385}{50} = 0.0077, \text{ or } 0.77 \text{ per cent Mn in pig and iron scrap}$$

We can now adjust the mixture of pig A, pig B, and iron scrap to fit these values of manganese and silicon and find out later if the phosphorus and sulfur values fall within the desired limits. On the basis of one ton (2,000 lb.) of total charge, we have 1,000 lb. of steel scrap (already accounted for) and 1,000 lb. of the pig and scrap iron mixture. Therefore, let

$$x = \text{pounds of pig } A$$
$$y = \text{pounds of pig } B$$

Then,

$$1{,}000 - x - y = \text{pounds of iron scrap}$$

A silicon balance on these three charging materials gives us the following equation:[1]

$$\underset{\text{Si in pig and scrap}}{1{,}000 \times 2.24} = \underset{\text{Si in pig } A}{2.20x} + \underset{\text{Si in pig } B}{2.35y} + \underset{\text{Si in scrap iron}}{(1{,}000 - x - y) \times 2.10}$$

This reduces to

$$0.10x + 0.25y = 140 \qquad (1)$$

Likewise, a manganese balance produces the following equation:

$$1{,}000 \times 0.77 = 0.63x + 0.78y + (1{,}000 - x - y) \times 0.85$$

This reduces to

$$0.22x + 0.07y = 80 \qquad (2)$$

Equations (1) and (2) may be solved simultaneously by eliminating x between them. This can be done by multiplying (1) by 0.22 and (2) by 0.10 and subtracting as follows:

[1] In reality, the percentages should be divided by 100 in order to obtain pounds of element per pound of metal but the same result is obtained by multiplying every member of the equation by 100 as done here, thus simplifying the calculation somewhat.

$$\begin{aligned} 0.022x + 0.0055y &= 30.8 \\ 0.022x + 0.007y &= 8 \\ \hline 0.048y &= 22.8 \\ y &= \frac{22.8}{0.048} = 475 \text{ lb. of pig } B \end{aligned}$$

This value of y may be substituted in equation (1) to obtain the value of x, as follows:

$$0.10x + 119 = 140$$

$$x = \frac{21}{0.10} = 210 \text{ lb. of pig } A$$

The amount of iron scrap charged is, then,

$$1{,}000 - 210 - 475 = 315 \text{ lb.}$$

of iron scrap. The amounts of the various ingredients to be charged per 2,000 lb. of total charge are

	Pounds
Steel scrap	1,000
Pig *A*	210
Pig *B*	475
Iron scrap	315
Total	2,000

This calculation can be readily checked by determining the amounts of Si, Mn, P, and S entering the charge from each of the ingredients. This can be done by multiplying the amount of each ingredient by the percentage of each element present, divided by 100. These data are collected in Table 5-X. The totals represent the total amounts of silicon, manganese, phosphorus, and sulfur entering the cupola per ton of metal charged. Their individual percentage of the charge can then be determined

TABLE 5-X.—DATA FOR CHECKING CALCULATION

Material	Lb.	Si, lb.	Mn, lb.	P, lb.	S, lb.
Steel scrap	1,000	2 00	8 5	1 00	0 7
Pig *A*	210	4 62	1 322	1 47	0 042
Pig *B*	475	11.18	3 705	0 209	0 095
Iron scrap	315	6.62	2 68	0 945	0 315
Total	2,000	24.42	16 207	3 624	1 152
Per cent of elements	.....	1 221	0 81	0.191	0.058

by multiplying each of these totals by 100/2,000. The calculation can be seen to check very closely with the composition of the charge which was calculated from the desired final composition of the castings and the known changes in composition produced by melting. Both the phosphorus and sulfur are found to be on the low side of the specifications.

MOLDING AND POURING PRACTICE

The most important part of iron founding is the making of the mold because if it is incorrectly made a defective casting results. It is also true, of course, that, if the casting does not have the desired composition or the metal is badly oxidized during melting, a defective casting will be obtained but much more trouble usually occurs in the molding department than in incorrect melting operations.

Most molds are made of sand and are known as loam molds, green sand molds, and dry sand molds, depending upon the way in which they are made. In nearly all cases, new sand molds must be made for each pouring operation as there are only a few insignificant cases where castings can be removed from a sand mold without ruining the mold. This is an expensive procedure and a considerable amount of work has been done on developing permanent molds without complete success being attained. Permanent molds machined from graphite and preheated to a high temperature before pouring have been used with some success and are said to last for a large number of castings. Molds for chilled castings are permanent to some extent because metal sections form part of the mold in order to chill those portions of the castings in contact with them and effect rapid solidification. Finally, centrifugal cast-iron pipe is cast in permanent metal molds. The metal is poured into a rapidly rotating mold which throws the metal around the sides and produces a hollow pipe under the pressure of centrifugal force. The pipes are cast with the flanges on them and are taken out of the mold while still red hot and put into annealing ovens.

Molding Materials.—*Molding sand* possesses the qualities that enable it to be tempered (moistened with water) and formed to definite shapes which it will retain when molten metal is poured in it. It has the requisite chemical composition to enable it to resist fusion from the heat of the molten metal in contact

with it. The sand should also be capable of being retempered and used for successive molds without the addition of more than a small amount of new sand to provide bond. Sands suitable for molding are found in several states, but the characteristics of the sands from these localities vary quite widely and all of them are not suited to every class of work. Mixtures of sands from different beds will often give a desired grade and quality of molding sand, although none of the component sands are suitable for that particular work.

The principal requirements of a good molding sand are resistance to fusion, bond, permeability, and porosity. Molding sands are composed mainly of silica, SiO_2, with small and varying amounts of Al_2O_3, Fe_2O_3, CaO, MgO, K_2O, Na_2O, and combined water. The refractoriness of a molding sand increases with increase in silica content but the bond decreases as the silica increases because the content of clay in the sand decreases. A lime content of above 1 per cent lowers the resistance of the sand to fusion. If the sand fuses, it vitrifies and forms a scale on the casting. Permeability, or the ability of the tamped sand to permit the passage of gases through it, is a very important property. The gases formed in the mold by liberation from the metal, the air present in the mold when the metal is poured into it, and the water present in the sand (green sand molds) which is converted to steam, must all escape principally through the sand of the mold. The difference between permeability and porosity lies in the fact that porosity is the ratio of voids or pore spaces in the sand to the total volume of the sand, while the permeability depends on the area of the passageways through the sand formed by these voids. As air fills these pore spaces of the sand and it expands when heated, the sand must have sufficient bond to resist this expansion as well as the pressure of the metal itself. The finer grained sands composed of sharp, angular-shaped particles are probably best for general molding work as they have good porosity, a good bond, and a more open structure than sands composed of rounded grains.

Chemical analysis will determine the amounts of bonding material in the sand and give an index of its refractoriness but will not determine whether or not a good casting can be produced with the sand. Microscopic tests are also necessary, because they reveal the shape and size of the grains and determine how

closely the mold can be rammed. Many different tests have been devised for determining the properties and suitability of sands for molding work but the details of these tests are beyond the scope of this book. The interested reader is referred to the *Transactions of the American Foundrymen's Association* for descriptions of the tests.

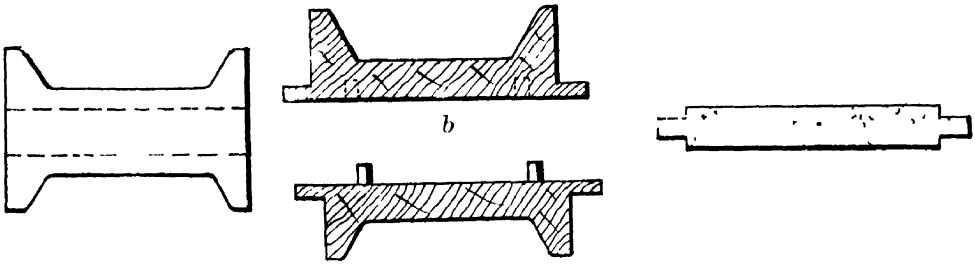
Core sand exhibits many differences from molding sand. Cores made of sand are used to form cavities in the castings by anchoring the cores in the molds and pouring the metal around them. Because cores are usually almost surrounded by metal and, therefore, subjected to very high temperatures, core sands are very high in silica and possess no bonding material. Fine sand with angular grains is used for most small cores while coarser sand is used for cores in large castings. *Core binders* are mixed with the sand for the purpose of bonding the grains of sand. These may be obtained in both the liquid or dry form and are composed chiefly of wheat flour, rye meal, powdered rosin, and linseed oil. The cores are made by mixing the sand and binder, moistening with water, molding the cores to the desired shape, and usually baking them in an oven at a low temperature (about 400°F.) to harden them and dry them out. These are called dry-sand cores and are stronger and more resistant to the stresses imposed upon them by the molten metal than unbaked cores which are known as green-sand cores. Cores are often made by machine, particularly in production foundries where large numbers of the same casting are made daily.

Facing materials or washes are used on the surface of the sand mold in order to make a very smooth surface on the casting and to produce a mold surface that will resist the melting and chemical action of the hot metal so that the castings may be easily cleaned of sand. The common wash for dry sand molds (baked) is graphite dust which is made into a paint with water and applied with a brush to the mold surface before it is baked in the oven. In the case of green-sand molds (unbaked), pulverized soapstone is dusted on the surface through a piece of cloth and then spread uniformly with a special tool.

Making the Mold.—*Loam molds* are built into the required shape with sand by hand, aided by machines. Loam molding is used principally on very large castings, particularly machine frames, large gears, etc. This type of molding is obviously

quite limited in application and nearly all sand molds are made by ramming sand around a pattern (usually of wood) of the desired shape and size, which is subsequently removed, leaving the desired cavity. The pattern should be made enough larger than the desired final size of the casting to allow for shrinkage. Cast iron shrinks about $\frac{1}{8}$ in. per ft. in cooling from the molten state to room temperature.

Pattern molding is as varied as there are different types of castings. A little thought will convince one that there are very few patterns that can be almost completely buried in sand and then be removed without destroying the impression left in the sand. For the most part, therefore, the pattern must be



a c d

FIG. 3-X.—(*a*) Casting. (*b* and *c*) Split pattern. (*d*) Core. (*After Rosenholtz.*)

made in two or more parts and the wooden frame that contains the pattern and sand, called the *flask*, must be split into a like number of parts. In many cases a pattern split into two parts can be removed without difficulty, in which case the flask is divided into two parts, and one-half of the pattern is imbedded in each. The lower half of the flask is known as the *drag* and the upper half the *cope*, the latter being an old English word for "cap." If the pattern must be split into three or more parts in order to withdraw it successfully, the sections of flask inserted between the drag and the cope are known as *cheeks*. Since the types of castings vary so widely, it is best, for the purposes of explanation, to describe the making of a mold for a particular casting rather than attempt a general discussion. The methods of making other castings can then be inferred from the description of the particular case.

Suppose it is desired to cast the spool, a drawing of which is shown in *a* of Fig. 3-X. It is composed of a cylindrical section with tapered flanges on both ends and a circular hole extending

longitudinally through its center. It is obvious that a pattern split into two parts can be withdrawn from the sand successfully because each half of the pattern will be half-round in cross section and there are no reentrant angles to cause difficulty. The split pattern shown in *b* and *c* is then made of wood and is equipped with pins and holes so that the two parts may be fitted together with exactly the same relative positions of the parts. The projections on the ends of the pattern form recesses in the sand of the mold into which the projections on the ends of the dry-sand core *d* will fit, thus anchoring the core in the mold so that it will not float out under the buoyant force of the metal. The position of the core in the completed mold is shown in Fig. 4-X.

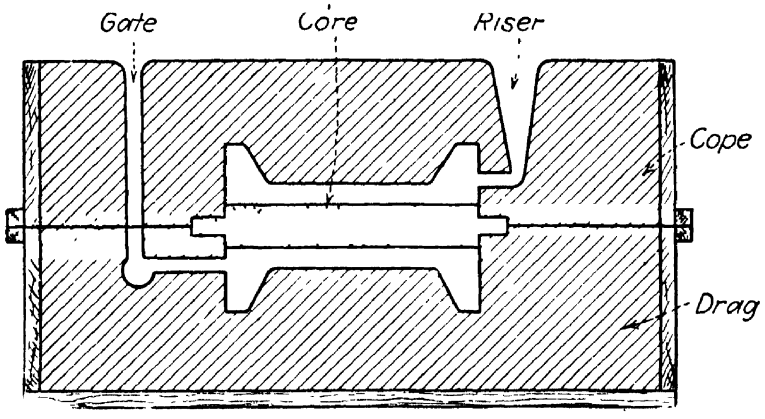


FIG. 4-X.—Cross section of mold ready to pour. (*After Rosenholtz.*)

The drag is placed on a bench with its upper edges down flat on the bench, and the *b* portion of the pattern is laid inside the drag with its flat surface down and also flat on the bench. This ensures that the flat surface of *b* and the edges of the drag will be flush with each other. The remaining space in the drag is now filled in with sand which is rammed in by the molder. The sand has been previously tempered with water and thoroughly mixed so that when a handful is squeezed between the fingers, it contains just sufficient moisture to stick together. The degree of tempering or moistening the sand is a matter of experience. It is almost impossible to set directions down in writing because the molder gauges the tempering by feel alone. The degree of ramming is also a matter of experience. If rammed too loosely, the sand will fall from the walls of the mold when the pattern is removed and, if rammed too hard, the gases will

have difficulty in escaping and a defective casting will result. The sand must be rammed in to just the right degree and pneumatic portable rammers are in use to aid the molder in this rather difficult and exacting job.

When the drag is finished it is turned over, exposing the flat surface of *B* flush with the sand at the top of the drag. A fine silica sand with no bond, called a *parting sand*, is now sprinkled over the surface to facilitate the separation of the cope from the drag that follows later. The *C* portion of the pattern is next fitted into the *B* portion by means of the pins and the cope placed on the drag. Sand is next placed in the cope, and a rod is then driven down into it at one side of the pattern through the sand into the drag. This rod, called the *gate stick*, is inserted to form the gate through which the metal is poured into the mold. At the same time, a tapered plug is placed in the sand to form the riser at the other end of the casting. The sand is now rammed in around the pattern until it is flush with the upper edges of the cope. The cope is next *vented* by driving a stiff wire into the sand almost down to the pattern and repeating this process many times. This procedure is necessary in order that the escaping gases will be rapidly carried out through the sand. The gate stick and the plug forming the riser are then removed and the tops of these openings beveled so that sand will not break from the sharp edges and fall in.

The cope is carefully lifted from the drag and turned over beside the drag so that one-half of the pattern is retained, flat face upward, in each half of the flask. The pattern is removed from the cope by inserting a screw in a small hole in the flat face of the pattern, carefully tapping this screw in four directions to jar the sand loose from the pattern and lifting the pattern out of the sand with a quick upward motion. This is a ticklish operation and requires a good sense of balance and long experience on the part of the molder, because any side motion of the pattern will break the edges of the mold and make patching operations necessary. Indeed, a large part of the molder's time is taken up in patching imperfections on the mold surface after the pattern is removed. Portions of the mold surface that are apt to break loose and fall can be held in place by inserting large-headed nails in the mold surface until the heads are flush with the wall. The pattern is removed from the drag in the above manner, the

imperfections patched, and the channel, called the *sprue*, from the well at the bottom of the gate to the mold cut with a special tool. The core, already prepared, is placed in position in the drag after the mold surface has been faced and the cope placed back on the drag, forming the completed mold.

The foregoing description applies to a green-sand mold but exactly the same method is used in making dry-sand molds except that a liquid facing material is used, and the completed mold is baked in an oven at about 400°F. for a sufficient time to drive out all the moisture and harden the mold. In some few cases, skin-dried molds are used and are prepared by spraying the green-sand mold surface with a flammable liquid such as gasoline and igniting it. This treatment dries out the mold surface and produces a slightly better surface on the casting than a green-sand mold provides.

No set rules can be given for the choice of green-sand or dry-sand molds for a certain casting because both are used. In fact, different foundries making the same casting often differ widely in their molding technique because this is principally a matter of experience. The advantages and disadvantages of dry-sand molds as compared to green-sand molds are aptly set forth by Professor Bradley Stoughton[1] and his analysis of the subject follows:

> Dry-sand molds are often cheaper to make and require less molding skill for the following reasons: (1) The sand does not have to be tempered so carefully, that is, brought to the proper conditions of dampness, since the moisture is eventually to be driven off by the drying. In green-sand molds, if the sand is too wet, it is liable to "cut" (be eroded by the stream of metal) and get dirt into the casting, and also to be impervious to the gases. (2) The sand requires less care in ramming, because, whether too hard or too soft, the expansion and contraction in drying will adjust its firmness and porosity. (3) Furthermore, the dry sand is stronger, which is an advantage, when the sand is liable to be under pressure from the metal, or to have the metal fall upon it from a height. (4) Dry-sand castings are also more liable to be sound, because there is less gas in the pores of the sand.
>
> The disadvantages of dry-sand castings are: (1) The mold is liable to shrink during drying and therefore be less true to the pattern; (2) the castings are more liable to "check" (*i.e.*, crack in cooling), because the

[1] STOUGHTON, BRADLEY, "The Metallurgy of Iron and Steel," McGraw-Hill Book Company, Inc., New York, 1934.

mold is firmer and so does not give way so easily to the crushing action when the casting contracts; (3) molds exposed to the direct action of the flame during drying, or heated too hot, are liable to be burnt and therefore rendered useless, causing a loss; (4) in handling, the molds are liable to be damaged; and, furthermore, it is more costly to repair a dry mold than a damp one, because the adjacent sand must first be damped, the damage repaired, and then a flame applied to dry the wound; (5) it takes longer to complete an order. The actual cost of heat is not very great and usually is less of an item than the extra labor of handling for drying.

Cores.—The function of cores, already referred to, is to assist in forming the metal. The core in the mold of Fig. 4-X is subjected to a great crushing strain when the metal shrinks, and the binder that holds the core sand together must be of such a nature that it will burn away when the heat of the metal reaches it and will allow the sand to disintegrate. This prevents the resistance of the core from breaking the hot and tender casting and also permits the sand to be cleaned out easily after the casting cools. It is obvious that this disintegration of the core should not take place until enough solid metal has formed around the core to prevent the casting from sagging when the core crumbles. Cores are sometimes built around an iron pipe riddled with holes so that the gases may more readily escape through this vent.

On the other hand, cores should have sufficient strength to resist the buoyant stresses imposed by the metal in the mold and the surging action of the metal in flowing around them. Cores may be set in the drag or hung from the cope but should be anchored at several places if possible. Metal chaplets, which are absorbed by the molten metal, are often used to brace cores in the mold during pouring.

Gates and Risers.—The gate is the opening into which the metal is poured from the ladle and connects with the mold by means of the sprue. The riser is designed to carry off most of the air in the mold which is displaced by the molten metal and, when filled with metal, to maintain the metal in the mold under the pressure due to the column of liquid metal in the riser and to help feed the casting as it solidifies and shrinks. The placing of gates, sprues, and risers is governed principally by experience although there are certain principles involved which must be followed. For small castings, a single gate and riser are usually

sufficient, but, in the case of large castings, the metal must be fed in from several places in order to fill the mold satisfactorily. The mold is generally filled from the bottom by means of a gate and sprue instead of from the riser at the top for the following reasons: (1) The stream of metal would probably come in contact with cores and knock them to pieces. (2) The metal, falling from a considerable height, would strike the bottom of the mold with enough impact to scour out the sand and destroy the shape of the casting. (3) This sand would be carried into the casting and produce imperfections in the casting owing to its presence. (4) Finally, the metal, on striking the bottom of the mold, would spatter up on the sides of the mold and freeze there, forming imperfections on the surface of the casting, known as cold shuts.

The general principles of gating may be summarized as follows:[1]

1. The metal must be forced into the mold fast enough to prevent its chilling at any point, so that sprue and gates must be amply large; in the case of a thin casting, for example, this may necessitate having the metal enter at a number of different points at the side of the mold.

2. On the other hand, unnecessary size is to be avoided since the sprues have only the value of scrap.

3. The stream of metal must not wash against the sand in such a way as to cut it.

4. The metal must not have too far to run. In large or long castings this may necessitate gating at several different points.

5. As far as possible we must arrange to pour into a reservoir and to have the rate of pouring such that this reservoir shall be kept as nearly full as possible in order that any slag or dirt accidentally getting in at this point may tend to float to the top of the metal and not be carried into the casting proper.

6. The point at which the metal enters is the hottest part of the casting, and this must be borne in mind when considering the question of feeding, to avoid shrinkage cavities. Sometimes it is desirable to chill this location in order to artificially oppose these conditions.

7. In placing a gate we must remember that, as the metal shrinks, it will draw the sprue toward the casting. Since the sprue is the hottest part, there may be a tendency for this contraction to tear the metal in two and especially to tear the sprue off at the point where it joins the casting proper, thus making an unsightly defect.

[1] *Ibid.*

Design of Castings.—The purchaser of castings can save himself considerable expense and the foundryman much trouble if he designs castings that can be easily molded. The trouble is that most designers of castings do not understand the foundryman's problems. There is a great need for better mutual understanding between the designer and the manufacturer.

The commonest error in designing castings is to make the corners too sharp, which makes them liable to crack or *check* at the corners because of the crystalline character of the solid metal. The crystals of which solid metals are made up start to form at the surface and grow inward perpendicularly to the surface. This results in a line extending inward from all corners, this line marking the junction of the crystals. As these junction lines are not so strong as the crystals themselves, they are sources of weakness. A gently rounded corner minimizes this effect if it does not entirely eliminate it and a stronger casting is obtained if all corners are generously filleted, even if the fillets must be machined out afterwards.

Castings check from the strain produced by the contraction of the metal tending to crush the sand. It is wise to avoid long lengths of metal connecting two parts that project into the sand. Unequal cooling strains often cause checks, as well. If a casting is poured consisting of a thick and thin section in contact with each other, the thin section solidifies first, shrinks away from the thick section, and yields very little to the subsequent shrinkage of the thick section. Also, the thick section is stronger and is apt to break away from the thinner section. Generous fillets should be provided where sections of different thicknesses meet in order to minimize this condition.

Pouring the Casting.—With the mold prepared for pouring, the cope is weighted down so that the buoyant force of the metal will not lift it and allow a fin of metal to flow between the cope and the drag and solidify there. The molder obtains a hand ladle full of metal at the proper temperature (assuming a small casting) and pours it down the gate of the mold in a steady stream, taking care not to break the stream at any time. It is best to keep the gate full of metal at all times in order to minimize the washing of sand into the mold. Pouring is continued until the level of the metal rises to the top of the riser.

The casting is allowed to solidify and cool and then is dug out of the sand. The nails, sprues, gates, and risers are cut off

and the surface of the casting cleaned. It may, or may not, be subjected to heat-treatment to relieve internal strains, soften it to increase its machinability, or modify its physical properties in other ways. These heat-treatments are beyond the scope of this chapter but are covered in Vol. III of this series.

TYPES OF CASTINGS PRODUCED

There are many different analyses of cast iron in use for different types of castings. Typical analyses are given for different types of castings in Table 6-X. The analysis is different for the same type of work in light, medium, and heavy sections for

TABLE 6-X.—TYPICAL ANALYSES OF SOME COMMERCIAL GRAY IRON CASTINGS*

Casting	Total C, %	Si, %	Mn, %	P, %	S, %	Ni, %	Cr, %	Mo, %
Auto cylinder, plain iron	3 25	2 25	0 65	0 15	0 10			
Auto cylinder, Ni-Cr iron	3 25	2 25	0 65	0 15	0 10	0 75	0 30	
Auto cylinder, Ni-Cr iron, heavy duty	3 25	1 90	0 65	0 15	0 10	1 75	0.45	
Auto cylinder, Ni iron	3 25	1 80	0 65	0 15	0 10	1 25		
Auto pistons, plain iron	3 35	2 25	0 65	0 15	0 10			
Auto pistons, Mo iron	3 35	2 25	0 65	0 15	0 10			0.50
General castings (auto), soft iron	3 40	2 60	0 65	0.30	0 10			
Piston rings (auto), individually cast	3 50	2 90	0 65	0 50	0 06			
Brake drums (auto)	3 30	1 90	0 65	0 15	0 08	1 25	0 50	
Brake drums (auto)	2 75	2 25	0 70	0 15	0 08			0.50
Cams	3 10	1 50	0 65	0 15	0 10	2.00	0 60	
Machinery iron								
Light service or thin section	3 25	2 25	0.50	0 35	0 10			
Medium service or heavy section	3 25	1 75	0 50	0 35	0 10			
Heavy service with heavy section	3 25	1 25	0 50	0 35	0 10			
Water pipe, sand-cast								
Light and medium	3 60	1 75	0 50	0 80	0 08			
Heavy	3 40	1 40	0 50	0 80	0 08			
Chilled plow shares	3 60	1 25	0.55	0.40	0 10			
High-strength iron, plain	2.75	2 25	0 80	0 10	0.09			
High-strength iron, nickel	2 75	2 25	0 80	0 10	0 09	1 00		
High-strength iron, Mo	2 75	2 25	0 80	0 10	0.09			0 35
Heat-resistant iron, fire pots, kettles, etc	3 50	1 15	0 80	0 10	0.07			
Caustic pots, Ni-Cr	3 30	0 70	0 50	0.10	0 08	1 50	0.60	
Caustic pots, plain	3 60	1 00	0 75	0 20	0 07			
Ingot molds	3.50	1 00	0 90	0.20	0.07			
Car wheels	3 35	0 65	0 60	0 35	0 12			
Air cylinders, ammonia cylinders, plain iron	3.25	1 25	0 65	0 20	0 10			
Heavy compressor cylinders, nickel iron.	3 00	1 10	0 80	0.20	0 10	2.00		
Light compressor cylinders, Ni-Cr.	3 30	2.10	0 55	0.25	0 10	1.25	0.45	
Light forming and stamping or forging dies, Ni-Cr iron	3.30	1.50	0.60	0 20	0.10	2.00	0.60	
Heavy forming and stamping or forging dies, Ni-Cr iron	3.00	1.25	0.60	0.20	0 10	2.75	0.80	
Light forging dies, Mo iron	3.30	2.00	0.60	0.20	0.10			1 00
Heavy forging dies, Mo iron	3.10	1.50	0.60	0.20	0.08			1.00
Valves and fittings (medium)	3.30	2 00	0.50	0 35	0.10			

* AMERICAN SOCIETY FOR METALS, "National Metals Handbook," 1939.

reasons to be brought out later. By using variations in melting and molding practice, equally good castings can be made from metals of quite different analysis. It is not to be inferred that the analyses given in the table are the only ones that can be used for a given type of casting.

Constitution of Cast Iron.—Since the subject of the constitution of cast iron is really beyond the scope of this book, a detailed discussion of the subject is given in Vol. III of this series. However, in order to understand the reasons for choosing the foregoing analyses and the effect of size of section on the analysis for a given type of work, the following brief survey of the subject is given at this time.

The carbon in liquid cast iron is entirely in solution in the iron but, when solidified, a large proportion of this carbon combines with iron to form iron carbide, called *cementite,* the formula of which is Fe_3C. This cementite is unstable because of the high temperature and the presence of the impurities, notably silicon, and tends to decompose into iron and graphite (carbon) according to the equation

$$Fe_3C = 3Fe + C$$

The amount of decomposition occurring in any specified case is dependent upon many factors, among them being the method of melting, the pouring temperature, the rate of cooling, and the composition of the iron. The graphite formed by this decomposition collects in the iron in the form of curved flakes as shown in Fig. 5-X, which is a photomicrograph of a polished but unetched piece of gray cast iron. The undecomposed cementite is present in the cast iron at room temperature in either the form of fine plates intermingled with plates of iron (called ferrite), or in massive form (large areas) at the juncture of the crystalline grains of the metal. This is not shown in Fig. 5-X because the polished surface of the metal is not etched. If the amount of carbon retained in the combined form as cementite is greater than 0.87 per cent, massive cementite is present in the crystal boundaries; if the combined carbon is 0.87 per cent, all of the combined carbon is in the form of fine plates alternating with plates of iron (ferrite), this arrangement of ferrite and cementite being known as *pearlite;* while, if the combined carbon content is less than 0.87 per cent, the combined carbon is still present

in plates mingled with plates of ferrite as pearlite, but ferrite is present in massive areas in the crystal boundaries.

The control of the physical and mechanical properties of cast iron depends upon the control of the amounts and distribution of the various constituents (massive ferrite, pearlite, massive cementite, and graphite) that go to make up its internal structure



FIG. 5-X.—Unetched structure of gray cast iron showing large graphite flakes. 100 diameters magnification.

because each of these has different properties. Massive ferrite is soft, ductile, possesses fairly good strength (40,000 p.s.i.), and high ductility. Pearlite is the strongest constituent present in cast iron, has a tensile strength of about 115,000 p.s.i., medium hardness, and fairly low ductility. Cementite, in common with other intermetallic compounds, is extremely hard, brittle, and wear-resistant with practically no strength in tension.

Graphite is soft, has no strength in itself, and weakens the matrix in which it is imbedded by breaking up the continuity of the mass by the interlocking nature of the flake formation. The widely varying properties of these constituents make it possible to vary the properties of cast iron through wide limits by varying the relative amounts and the distribution of these constituents. In fact, cast irons can be produced with tensile strengths ranging from under 15,000 to over 70,000 p.s.i. and varying from a very soft and easily machinable material to one so hard and brittle that it may be powdered by blows of a hammer. The control of the properties consists in controlling the amounts of combined and graphitic carbon and the distribution of the latter—in other words, controlling the decomposition of cementite. It is obvious that, in an iron of constant total carbon content, as the amount of combined carbon decreases, the amount of graphite increases in proportion and vice versa, since the sum of both is equal to the total carbon. The means for controlling this decomposition will now be taken up.

The *faster* the *rate of cooling*, the less the decomposition of cementite because, since most of the decomposition takes place during solidification, the less time the cementite has to decompose the less will be decomposed. Also, with faster rates of cooling the graphite flakes are smaller and less angular and hence cut down the strength of the matrix less than if they were larger and more curved as when slow rates of cooling are used. Figure 6-X shows the appearance of a gray iron containing small flakes, the sample being prepared in the same way as that of Fig. 5-X. This effect of rate of cooling causes the variation in the analysis with size of section because large castings obviously cool much slower than small ones.

The lower the *silicon content* of the cast iron, the less the decomposition of cementite because silicon promotes graphitization and high silicon irons are high in graphite and low in combined carbon, other factors being equal. *Sulfur*, on the other hand, retards graphitization. A small amount of sulfur has more effect in retarding graphitization than a large amount of silicon has in promoting it. If a small amount of combined carbon is desired, then, the iron should be high in silicon and low in sulfur. *Manganese* acts in two ways with regard to its effect on graphitization. It combines with sulfur to form

MnS and, if manganese is added up to the amount necessary to combine with the sulfur, it progressively promotes graphitization because it tends to reduce the influence of sulfur and give the effect of silicon full sway. On the other hand, if manganese is added in excess of that necessary to combine with sulfur, it tends to retard graphitization because it forms a double carbide



FIG. 6-X.—Unetched structure of gray cast iron showing small graphite flakes. 100 diameters magnification.

of iron, $(FeMn)_3C$, which is more stable than Fe_3C alone. If other conditions promote graphitization and the amount of phosphorus is normal, *phosphorus* tends to promote graphitization because it lengthens the time of solidification during which time the decomposition of cementite takes place. But, if the phosphorus is high and other factors are not particularly favorable to graphitization (low Si, high S, rapid cooling), phosphorus

retards cementite decomposition. Finally, the greater the amount of *total carbon*, the greater the ratio of graphitic to combined carbon, other factors being equal, because Fe_3C is naturally unstable in cast iron and an increase in its amount increases the driving force of the decomposition.

The *pouring temperature* probably exerts a small influence on the graphitization of cast iron because a high pouring temperature promotes slower cooling by putting more heat into the mold before solidification is complete and thereby promoting cementite decomposition. The *degree of superheat* and *method of melting* seemingly have more effect on the size of the graphite flakes than on the amount of graphite formed as highly superheated electric furnace irons tend to have very small flakes, considerably smaller than cupola irons of the same composition. A review of the foregoing brief discussion will convince one of the difficulty of controlling the structure and properties of cast iron. This is why cast irons of approximately the same analysis often vary so widely in properties.

Properties of Cast Iron.—The graphitization of the cementite in cast iron during solidification and cooling has led to the common classification of iron castings into white and gray cast iron. In *white cast iron*, the decomposition of cementite has been entirely prevented, no graphite is formed, and the material exhibits a white crystalline fracture and partakes of the properties of cementite of which it is largely composed. It is extremely hard, brittle, and wear-resistant but is very weak and does not have many uses in itself. The factors that promote the formation of white cast iron are

1. Extremely rapid rate of solidification (thin section).
2. Moderate pouring temperature.
3. Low total carbon (2.25 to 3.00 per cent).
4. Low silicon (0.75 per cent and ~~over~~ below).
5. Low manganese (0.20 per cent and ~~over~~ below).
6. High sulfur (0.25 per cent and ~~below~~ above).
7. Normal to high phorphorus (0.75 per cent and ~~below~~ above).

Gray cast iron has a dark gray fracture due to the graphite flakes that it contains and possesses a matrix composed of pearlite or pearlite and massive ferrite, as the case may be. In the general case, it is fairly soft and has moderate strength, practically no ductility, good to moderate machinability, and

moderate to low wear resistance. The factors that promote the formation of gray cast iron are

1. Slow rate of solidification and cooling.
2. Moderate to high pouring temperature.
3. Medium to high carbon (3.00 to 3.75 per cent).
4. High silicon (1.00 per cent and over).
5. Medium manganese, depending on sulfur content.
6. Low sulfur (0.10 per cent and under).
7. Normal to low phosphorus (0.30 per cent and under).

Chilled cast iron is produced by regulating the conditions and analysis in such a way that, by inserting metal chills in the mold so that the surface of the casting is rapidly solidified, white cast iron can be produced to a maximum depth of about 1 in. while the core of the casting will be composed of gray cast iron. In this way, the surface hardness and wear resistance of white cast iron are combined with the greater strength and lower brittleness of gray iron. Among the more common chilled iron castings are plow shares, chilled rolls, chilled car wheels, and wearing plates of various kinds. *Mottled cast iron* is intermediate between white and gray cast iron. It contains graphite flakes, but the matrix is composed of pearlite and massive cementite, making it quite hard and brittle.

The tensile strength of gray cast iron varies from below 15,000 to about 50,000 p.s.i. in the unalloyed condition. The compressive strength is greater than the tensile strength, the ratio of compressive to tensile strength ranging from 4.5 to 1 for the weaker irons to 2.5 to 1 for the stronger irons. The transverse strength is usually low. Cast irons possess practically no ductility. The wear resistance and hardness of cast iron increase with the combined carbon content. The shrinkage on casting decreases with increase in graphite content because the decomposition of cementite results in an increase in volume. The reason why intricate castings usually contain high phosphorus and moderate to high silicon contents is that phosphorus prolongs solidification and the expansion on graphitization forces the mushy metal into all parts of the mold. The closest that ordinary cast iron comes to having a shrinkage cavity is in white iron castings which sometimes show spongy spots in the center.

The best combination of strength, hardness, wear resistance, toughness, machinability, and soundness is obtained when the

analysis, pouring, and mold conditions are so regulated that very fine and uniformly distributed graphite flakes are formed in a fine-grained matrix consisting entirely of pearlite, without either massive ferrite or massive cementite being present (combined carbon = 0.87 per cent). An analysis that has found wide use for medium and heavy sections is

	Per Cent
Total carbon	2 90
Silicon	2.10
Manganese	1 00
Phosphorus, under	0 10
Sulfur, under	0 10

Cast irons exhibiting this structure and properties are known as "high-test cast irons" and are defined as those which develop tensile strengths in excess of 40,000 p.s.i. In the unalloyed state, the strength rarely exceeds 50,000 p.s.i., but if alloying elements are used the strength may be further increased to 70,000 p.s.i., a value that can be obtained by proper pouring and casting treatment of the following analysis:

	Per Cent
Total carbon	2 60
Silicon	2 15
Sulfur	0.08
Phosphorus	0 08
Manganese	0 70
Nickel	1 10

The principal alloying elements used in cast iron are nickel, chromium, molybdenum, vanadium, titanium, aluminum, and zirconium. The general effects of these alloying elements are to better the mechanical properties out of proportion to the increase in cost caused by their use, but the specific benefits derived by the use of each element are beyond the scope of this text but will be considered in detail in Vol. III.

Advantages of Cast Iron.—The choice of whether to use cast iron or cast steel for a given casting, when both develop properties suitable for the work in hand, usually depends upon the following. The advantages of cast iron as an engineering material, and the reasons why it is used as much as it is, are (1) its cheapness, (2) its fluidity which renders it easily cast into more intricate shapes than cast steel, (3) its lesser shrinkage when cooling from

the molten state, (4) its relative freedom from pipes and blowholes when properly molded, and (5) its relative freedom from cracking on cooling. Its principal disadvantages are (1) poorer physical properties than cast steel, (2) lack of ductility, and (3) lack of malleability. Probably the two most important advantages of cast iron are its cheapness and high fluidity.

Suggested Questions and Problems for Study and Class Discussion

1. What are the reasons for the recent rise of cast iron as an engineering material?

2. Describe the construction of the cupola.

3. List the materials charged into the cupola and give the requirements of each.

4. Describe the charging of the cupola.

5. What zones are present in the cupola during operation? What takes place in each?

6. What chemical changes take place in the cupola?

7. What changes in cupola practice are necessary when melting part steel scrap in the cupola? What types of iron are produced by this practice?

8. What are the advantages and disadvantages of electric furnace melting?

9. Describe in detail how a cupola charge calculation is made.

10. List the requirements of molding sands. Do the same for core sands.

11. Give a definition for the following:

a. loam mold	*f.* sprue	*k.* parting sand
b. pattern mold	*g.* riser	*l.* mold wash
c. cope	*h.* chills	*m.* gate
d. drag	*i.* dry-sand mold	*n.* gate stick
e. core	*j.* green-sand mold	

12. Describe in detail the making of a mold requiring a split pattern.

13. What are the advantages and disadvantages of dry-sand molds compared to green-sand molds?

14. Give the general requirements of cores and the general precautions necessary in using them.

15. What are the general rules regarding the placement of gates?

16. Describe the general precautions necessary in designing castings.

17. Describe in detail the constitution of cast iron.

18. What are the physical properties of the constituents of cast iron? Show how these characteristics affect the properties of the metal as a whole.

19. What factors must be controlled in order to control the decomposition of cementite in cast iron? How does each factor affect the decomposition?

20. What factors promote the formation of white cast iron? Of gray cast iron?

21. What are the general mechanical properties of white and gray cast iron?

22. Under what conditions is the best combination of properties attained in unalloyed gray cast iron?

23. What is "high-test cast iron"? How is it produced? Give a typical analysis.

24. What are the advantages and disadvantages of cast iron as an engineering material?

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CHAPTER XI

MALLEABLE CAST IRON

We have already seen that, from a standpoint of strength, the graphite in cast iron weakens the matrix because of its presence and the particular formation in which it occurs. The weakening effect of the graphite is greater the larger the number of flakes, the larger they are in size, and the more they interlock with each other in breaking up the continuity of the matrix. It was early realized that if the mode of formation of the graphite could be changed from interlocking flakes to small round nodules or balls, the effect of its presence on the continuity of the matrix would be much less and the iron would have better strength and, of equal importance, much greater ductility. The process by which this can be accomplished was invented by Réaumur in 1722 but the method has been in use for only about a century and of importance for less than fifty years. Also, the process has been modified considerably in American practice but the principles are the same. The process consists essentially of making *white cast iron* and giving it a suitable annealing treatment in order to decompose all of the cementite present in the casting. The graphite produced by the reaction precipitates in the form of round nodules called *temper carbon* instead of in the form of elongated flakes.

PRODUCING THE WHITE IRON

White iron for making malleable cast iron is melted in the cupola, the air furnace, the open-hearth furnace, and the electric arc furnace, depending upon conditions. Of these the air furnace is the predominant type and will be described in some detail.

The Air Furnace.—The air furnace is a long and comparatively narrow reverberatory furnace built of fireclay brick and fired with coal, powdered coal, or gas. Figure 1-XI is a cutaway view of a powdered-coal-fired malleable iron furnace of a typical design, although there are many other types differing in details of construction. The reducing flame from the burner is directed just

over the surface of the bath without coming in contact with it so that the metal is heated entirely by radiation from the flame and the roof. The heat is said to strike the low roof and "reverberate" down on the metal, hence the name reverberatory. Silica brick is usually used in building the furnace lining while the roof is made in sections by setting the bricks in a metal frame so that the roof may be removed in sections by a crane and the furnace charged from the top. The furnaces are built in sizes ranging from a little under 10 tons to 45 tons capacity.

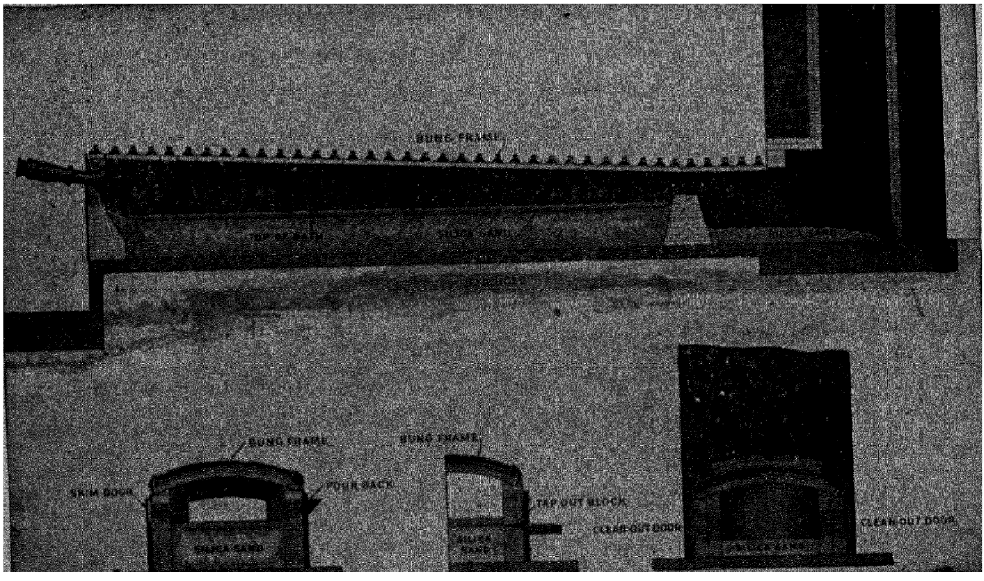


FIG. 1-XI.—Cutaway view of a powdered-coal-fired malleable air furnace. (*Courtesy of the Harbison-Walker Refractories Company.*)

The side walls are constructed of two rows of firebrick laid against heavy cast-iron plates which are held in place by vertical supports mounted in the foundation. On one side of the furnace two or more openings are provided for stirring, skimming, or sampling the metal in the bath. Additional air is introduced through a door or open brickwork at the bottom of the stack to lower the temperature of the gases.

With the brickwork in place, the final step in preparing the furnace for operation consists in making the sand bottom. A sand containing over 95 per cent SiO_2 is fritted uniformly over the bottom. In duplex malleable plants the bottom is made of superduty fire brick or high-alumina brick. Sometimes, crushed firebrick is mixed with the sand to increase the durability and refractoriness of the material. A layer of this mixture (1 to 2 in. thick)

is spread uniformly over the hearth, the furnace brought up to a high temperature and maintained until the sand glazes over (frits), forming a hard, dense lining which will resist the penetration of the molten metal. Another layer of sand mixture is spread over the hearth and the process repeated until from five to six layers have been fritted in place in this way. Care is taken to see that the entire hearth is sloped toward the tap holes. The average bottom lasts from six to twelve heats before it has to be replaced by a new one. A longer life is obtained if the furnace is charged with care in order to prevent the charge from gouging the bottom and if a strongly reducing flame is used during melting in order to minimize the formation of FeO which fluxes the acid bottom.

Air Furnace Operation.—Not more than 20 per cent of bought scrap is used in the charge and a good deal of this is steel scrap because of its lower carbon content and because iron scrap is too impure, too variable in composition, and too uncertain in sampling and chemical analysis to be used to a great extent. A large amount of return scrap is used, however, consisting of gates, sprues, and defective castings. This return scrap is low in total carbon and silicon and high in sulfur because it has already undergone the changes in melting. This return scrap must be carefully cleaned of sand to avoid difficulty in melting. The pig iron used to make up the remainder of the charge is known as "malleable Bessemer" and is of special grade (see Table 9-IX). The charge is calculated in the same manner as for the cupola except that the changes in composition on melting are different and depend upon the air furnace used and how it is operated.

The furnace is now ready for charging. The sand bottom is covered with wooden boards so that the materials, when placed in the furnace, will not damage it. The metal charge is distributed over the full length of the hearth and is piled up nearly to the roof. The sprue is charged first, the steel and malleable scrap are charged on top of the sprue, while the pig iron is charged last. After the charging is completed the bungs are replaced, the fire is started, and the heat melted as rapidly as possible.

When the metal is partly melted, the melter stirs or rabbles the heat thoroughly by pushing it around in the furnace with a long bar. This treatment equalizes both the composition and temperature of the metal.

The purpose of the air furnace is to melt the iron and bring it to the proper temperature for casting. Some oxidation is unavoidable, however, but it is not intentional. It is best to get the desired analysis by a proper mixture of charging materials and not by oxidation of silicon and carbon. The oxidation of iron, silicon, and manganese causes the formation of a slag which collects on top of the metal and is skimmed off. The amount of oxidation is dependent upon the condition of the furnace atmosphere and the length of time it takes to melt the heat. The time for melting a 5-ton heat is about 3 hr. while 8 to 9 hr. is required for a 35-ton heat. The metal loss by oxidation averages from 2 to 5 per cent of the charge.

With the heat at the desired temperature and thoroughly rabbled, it is ready for testing. One of the advantages of air furnace melting is that the foundryman can hold the heat in the furnace for a sufficient length of time to adjust small errors in composition. A small amount of the metal is removed from the furnace with a spoon and poured into a sand mold, forming a small test bar which is broken in two and the fracture observed. As the cross section of the test bar is approximately the same as that of the castings to be poured and as the mold conditions used are the same, a good idea of the structure of the castings may be obtained. When the fracture of the test plug shows large, clear white crystals without any pinholes on the rim and only traces of graphite flakes (mottling) in the core, the bath is ready to tap. In heavy sections ($\frac{3}{4}$ to 1 in. in cross section), a larger amount of mottling is usually allowed in the core. If the fracture shows pinholes in the rim, it means that the metal has been oxidized or "burned" and is useless. It must be cast into pigs and remelted. If the test piece is mottled throughout, usually indicating too high a silicon content, the heat can be held in the furnace to allow for silicon oxidation or low silicon pig can be rabbled into the bath. If the test piece is white all the way through, it is probably too low in silicon to anneal easily and high-silicon pig is rabbled into the bath, the temperature readjusted, and tested again until faint traces of mottling are observed at the core of the test piece.

The conditions of temperature and composition being adjusted, the heat is ready to pour. It is necessary to pour the heat very rapidly to preserve uniformity of composition because the metal

left in the furnace is losing silicon and carbon, and the longer the time of tapping the furnace, the greater the difference in composition between the beginning and the end of the tap. Two tapholes are opened and the heat poured as rapidly as possible. Since the castings are usually small and the metal must be poured into the mold as rapidly as possible, the bulk of the work is done with hand ladles holding 40 to 50 lb. each. As malleable iron castings are made in large quantities from the same pattern, molding machines are popular for this work. Also, since large numbers of small cores of the same size are required, core-making machines are widely used. Large gates and sprues are used because the metal chills rapidly in pouring.

The advantages of the air furnace over the cupola for producing white iron castings for malleablizing may be summarized as follows:

1. Since the metal is not in direct contact with the fuel, the absorption of sulfur is less. Of course, a low sulfur fuel is required in the air furnace as well, because the metal can pick up sulfur from the furnace gases but the amount derived is less in the general case.

2. For the same reason, the carbon content can be definitely lowered and controlled by the addition of steel scrap to the charge. In the cupola there is always a carbon pickup but in the air furnace the total carbon in the charge can be maintained at a low and definite value.

3. With a good melter in charge, the air furnace heat can be made to closer specifications for analysis than a cupola heat.

4. The air furnace can utilize larger sizes of scrap than the cupola. In the final analysis, the choice between the air furnace and the cupola rests on the question of quality because, while air furnace metal makes higher quality castings, it is more expensive to melt and the air furnace is used when quality castings are desired.

Other Melting Methods.—*Cupolas* are used for melting iron for malleable castings to some extent and are similar to those used for melting metal for ordinary gray iron castings. The amount of coke used per ton of metal melted is greater, however, than in gray iron practice because the metal has a higher melting point and must be fluid because of the small sizes of the castings

into which it is poured. The average fuel ratio is one part of coke to four parts of iron.

The advantages of the cupola for malleable cast iron work are

1. The composition of the heat is probably more uniform from beginning to end with proper operation than the product of the air furnace, as there is only a slight change in sulfur content during the heat, being slightly higher at the end.

2. The temperature is more uniform throughout the heat. In the air furnace, the metal at the top of the bath is always hotter than that at the bottom.

3. The cupola is cheaper to install and operate and requires less skilled labor to operate than the air furnace. The first cost of the air furnace is high, the cost of making bottoms is greater, and the fuel cost is higher because maximum fuel economy is always obtained when the metal and fuel are in direct contact as in the cupola. The air furnace probably requires more expert supervision than the cupola and for that reason higher priced labor is required. For these reasons the cost of cupola melting is considerably less.

4. The cupola can be started and stopped more readily. Also, it is not possible to make several mixtures during the same heat in the air furnace, as can be done in the cupola. The former is advantageous because small amounts of metal are withdrawn for pouring in making castings for malleablizing, and flexibility is desired of a melting method. The cupola operates equally well with small and large heats while the size of the charge in the air furnace can be varied only between definite limits. Different mixtures are often desired because castings of different thicknesses are wanted.

The principal drawbacks to the use of the cupola are greater uncertainty with regard to carbon content, the poorer quality of the product, and the greater difficulty of malleablizing it. For these reasons, most white iron for malleablizing is made in the air furnace, and what is melted in the cupola is usually refined and superheated in either the air furnace or the electric arc furnace.

Open-hearth furnaces are used to some extent in large malleable foundries where the output is sufficient to keep the furnaces running day and night. The furnaces are the same as those used for steel melting except that they are smaller than the

average steel-melting furnace. The details of the construction and operation of the open-hearth furnace are omitted here because the furnace is discussed at great length in Vol. II of this series. It consists essentially of a long, narrow, shallow hearth in which the metal bath is contained. The hearth lining is made of sand and slag sintered in place by the heat of the furnace. Producer gas, oil, or natural gas is used as fuel and is admitted alternately at both ends of the furnace, thus keeping the hearth temperature uniform. The waste gases are used to preheat the air for combustion and the producer gas as well, if it is used as a fuel. This permits much higher temperatures to be attained than the air furnace is capable of.

The advantages to be gained by the use of the open hearth for malleable work are

1. As a consequence of the high-temperature situation, the heat can be melted much faster than by either the cupola or air furnace melting methods, resulting in a large daily tonnage. In fact, only about one-half the time is required. The maximum temperature obtainable in the air furnace is about 2800°F. while that of the open hearth is 3100°F. Furthermore, hotter metal can be obtained from the open hearth when desired.

2. Better control of temperature is obtained and the temperature of the bath is more uniform, owing to reversing the direction of the flame at intervals.

3. Owing to the shorter time required to produce heats, the fuel economy is better than with the air furnace and sometimes equal to the cupola.

4. It is possible to effect a reduction in the phosphorus and sulfur content of the charge by proper manipulation, allowing cheaper raw materials to be charged. Since a dolomite lining is used, a basic slag can be worked up which will oxidize phosphorus and, to a certain extent, sulfur and retain them in the slag as $3CaO \cdot P_2O_5$ and CaS. Further, the basic lining is not attacked by FeO and the slag used and has a long life if not cooled down frequently. A dolomite lining cannot be used in the air furnace because it cracks too badly when cooled and heated to be used in furnaces that operate intermittently.

The disadvantages of the open hearth in the malleable foundry are

1. High cost of installation.

2. More skilled labor required.
3. Expensive repairs and upkeep.
4. Necessity of continuous operation to maintain fuel economy and the dolomite bottom.
5. The necessity for a large floor space on which to place molds.

The last two disadvantages are the most serious because the furnace can be installed only in large production foundries which have a sufficient volume of business to keep the furnace running continuously. Molds cannot be made at night since artificial light causes shadows that make the work of finishing molds confusing and difficult. Hence a large amount of space is required in which to set molds for the large tonnage produced in 24 hr. For foundries that can handle the output of such a furnace, however, it is an excellent melting tool.

Electric furnaces are also used in melting iron for malleable castings, particularly in duplexing and in making synthetic mixtures for "short-cycle malleable" which will be discussed later. Owing to the difficulty of malleablizing cupola white iron, much of this iron is transferred to the electric furnace and superheated in it, as it has been found that this treatment shortens the time necessary for malleablizing. The direct-arc, indirect-arc rocking, Lectomelt, and Hydro-arc-type furnaces are all in use in malleable-iron foundries today, in proportion to the job to be done and the experience of management.

The direct-arc furnace possesses the advantages of being able to control the sulfur content of the heat if a basic lining is used, besides the general advantages of electric melting considered in Chap. VII. The rocking arc furnace possesses the same advantages for malleable work as it does for gray iron melting. The principal advantages of electric melting in the malleable foundry are the high degree of superheat possible, their ability to convert cupola melted metal into high-grade castings for malleablizing, and their ability to melt synthetic mixtures high in steel scrap. For example, one foundry is producing a white iron for short-cycle annealing that contains 1.9 per cent carbon and 1.9 per cent silicon, an analysis very difficult to produce by other melting methods. The important disadvantages are their high cost (particularly the electrical equipment), small tonnages per heat, and the high cost of electrical power in most places. Hence, they are generally used only when other melting methods

are not applicable for the production of the high-quality work desired.

Composition of the Iron.—The precautions necessary in producing white cast iron, such as rate of cooling, pouring temperature, and composition, have already been discussed in Chap. VII and hold equally well in producing white iron for malleablizing with the following important qualification. In making ordinary white cast iron there is no particular drawback to operating under extreme conditions in order to be absolutely sure that white iron will be produced. In the case of malleable cast iron, however, the cementite in the white iron must be subsequently decomposed, and the factors that prevent the decomposition of cementite on casting also retard its decomposition during the annealing treatment. Since the annealing treatment is costly—the annealing cost in the United States in a normal year is over $18,000,000[1]—every attempt is made to reduce the annealing time to a minimum. This makes it necessary to control the conditions so closely that, on casting, no graphite flakes are produced yet the composition is such that the iron will malleablize quickly. This is done by solidifying the iron as rapidly as is commercially possible in sand molds and adjusting the composition so that graphite flakes just fail to appear on casting. The sulfur content is reduced as low as possible and the silicon content raised as high as the foundryman dares to go. This effect is further aided by thin sections—a malleable casting greater than ¾ in. in thickness is rarely made—and by low total carbon, as well as a high degree of superheat previous to pouring. The foregoing accounts for the care that is taken in inspecting the test pieces in air furnace practice and why the composition is so carefully adjusted to produce just a trace of graphite in the core of the test piece. When the castings are poured, the rate of solidification is always a little more rapid than when making the tests.

The approximate limits of composition within which most cupola and air furnace white iron castings for malleablizing fall, are given in Table 1-XI. The silicon content will depend upon the size of the casting (the principal factor affecting the rate of cooling) and the amount of total carbon. Metal melted in the cupola requires a higher silicon content by about 0.25 per cent

[1] WHITE and SCHNEIDEWIND, *Metal Progress*, **25**, 6, June, 1934.

than the air furnace product, other factors being equal, because of the greater difficulty in decomposing the cementite in cupola iron. For air furnace castings, the silicon content is commonly 0.50 to 0.60 per cent where the castings are ¾ in. thick (about the maximum size) and is increased to 1.00 per cent and over as the size of the casting is decreased to a very thin section, because the effect of rate of solidification and cooling becomes greater. In calculating the charge, the percentage of silicon that will be burned out in melting must be added. The silicon loss in the cupola is from 0.15 to 0.25 per cent, while in the air furnace it varies from about 0.2 to 0.5 per cent, depending upon the length of time the heat is held in the furnace after melting and the temperature.

TABLE 1-XI.—ANALYSES OF WHITE IRON CASTINGS FOR MALLEABLIZING

Element, per cent	Air furnace melted	Cupola melted
Total carbon	2 40–2 85	2 75–3 00
Silicon	0 50–1 10	0 75–1 30
Manganese*	0 20–0 25	0 20–0 50
Phosphorus	Under 0 20	Under 0 20
Sulfur	0 04–0.07	0 04–0 25

* The manganese must always be at least twice the sulfur.

Sulfur increases the tendency of castings to check and retards the cementite decomposition on annealing, as well as lowering the strength. The tendency to check or crack is particularly important in white cast iron because the shrinkage of white iron is about double that of gray cast iron. High-grade malleable castings rarely carry over 0.06 per cent sulfur but the inferior grades often contain much larger amounts than this. As the size of the casting decreases, the allowable sulfur content may be increased slightly because high strength is not usually such a necessity in small castings and, being small, they have less length for contraction.

A low manganese content is usually desired because high manganese retards cementite decomposition on annealing, hardens the iron, and makes it difficult to machine. On the other hand, the manganese content must be at least twice, and preferably three times, the sulfur content in order to protect the

casting from the injurious effects of sulfur. Manganese also decreases the dangers of checking on cooling and tends to protect silicon from oxidation during the melting process in the air furnace.

Phosphorus increases the ability of the metal to run freely and fill the mold completely—a very desirable effect because of the small thickness of most castings and the low total carbon. On the other hand, phosphorus makes the malleable casting hard, difficult to machine, and liable to crack on cooling, and reduces the malleability of the material and its resistance to shock or impact. Hence a maximum phosphorus limit of 0.20 per cent is usually specified.

A low total carbon content is desired in malleable castings, because the silicon may be made higher for easier annealing and because low total carbon makes for increased strength. Low carbon, however, makes the metal more sluggish in pouring and produces greater shrinkage in the castings. It is difficult to produce iron for malleablizing in the cupola with a carbon content very much below 3.0 per cent because of the carbon absorption. The carbon may be reduced as low as desired in the air furnace but the large amount of steel scrap required materially increases the time of producing the heat. Irons with the lowest total carbon are made entirely or duplexed in the electric furnace.

THE MALLEABLIZING TREATMENT

After the white iron castings are cooled, they are carefully cleaned of the sand that sticks to their surfaces. They should be handled with care as they are quite brittle and are liable to crack if subjected to a sharp blow. They are then ready for the annealing treatment. In many foundries the castings are shaken out of the sand while hot, thus subjecting them to an air quench. This has the advantage of increasing the rate of cementite decomposition on annealing.

Several types of malleable castings are made by varying the annealing treatment. They are known as all-black, black-heart, and white-heart malleable castings. In making *all-black* malleable castings, the white iron castings are annealed without a packing or in a nonoxidizing packing such as lime or fire clay. The cementite is completely broken down by the treatment

into round globules of graphite, known as *temper carbon*, but almost none is oxidized, resulting in a material whose fracture is black all the way through; hence the name "all-black" malleable castings. This material is several thousand pounds per square inch lower in tensile strength than black-heart castings because it does not possess a decarburized rim and the relatively small tonnage that is made goes into pipe fittings and other castings of which high strength is not required.

Black-heart malleable castings are made by annealing the white iron castings in an oxidizing packing, such as Fe_2O_3. The cementite is entirely decomposed into temper carbon and iron, but the temper carbon formed at and near the surface of the casting is burned out by the packing, producing a rim of from $\frac{1}{64}$ to $\frac{1}{16}$ in. in thickness composed entirely of iron. The fracture of such a casting is black in the center where the temper carbon is present, with a white rim where the carbon is burned out, hence the name "black-heart" malleable. In the manufacture of *white-heart* malleable castings, the same packing material is used but the annealing treatment is prolonged until the temper carbon is entirely burned out of the castings, and they are composed only of iron and the voids where the temper carbon formerly was located. This treatment requires over twice the annealing time necessary for black-heart malleable and cannot be accomplished commercially on sections greater than $\frac{1}{2}$ in. in thickness. White-heart castings are not so strong as black-heart castings and, whereas the process is used in Europe to a great extent, it is used very little in the United States. Incidentally, the process by which white-heart malleable castings are produced is the original process developed by Réaumur.

Constitution of Malleable Iron.—We know from Chap. X that white cast iron at room temperature consists of pearlite (alternate thin plates of ferrite and cementite) and a large amount of massive cementite at the boundaries of the crystals. Between the point at which melting begins and a temperature of about 1310°F., however, white cast iron consists of a mixture of massive cementite and a solid solution of carbon in iron known as *austenite*. On cooling through this temperature (1310°F.), the iron in which the carbon is in solid solution undergoes an allotropic transformation, and the new crystal form of iron produced has only a very limited solubility

for carbon (under 0.05 per cent). The remaining carbon that was in solution above the transformation point is precipitated as cementite in the form of thin plates alternating with plates of iron (ferrite) in which the carbide is not soluble—*pearlite*, in other words. When the white cast iron is reheated, the reverse change from pearlite to the solid solution of carbon in iron (austenite) takes place at a temperature of about 1350°F., a higher temperature than that at which the transformation takes place on cooling. The presence of varying amounts of silicon, manganese, phosphorus, and sulfur, as well as the rate of heating and cooling, affects the values of temperature at which these changes take place. Actually, there is a narrow range of temperature in which the transformation occurs although, theoretically speaking, it should take place at a constant temperature with very slow heating or cooling and in the absence of any impurities except carbon.

When graphite flakes are formed during the solidification of gray cast iron, the iron is in a mushy stage. This accounts for the size and characteristic form of the graphite in this material. On the other hand, when temper carbon is produced by the decomposition of cementite during the annealing treatment, it is liberated in solid iron. This accounts for the vast difference in the form in which the graphite occurs in malleable iron compared to gray cast iron. The temper carbon assumes the characteristic form of approximately spherical nodules composed of extremely fine individual particles of carbon which have migrated together from their points of formation in the matrix to form the nodules. A photomicrograph of a polished but unetched specimen of malleable cast iron is shown in Fig. 2-XI and illustrates the form and distribution of the temper carbon in the ferrite matrix.

Owing to the two forms in which the cementite occurs (massive cementite and part of the pearlite), the fact that both must be completely decomposed, and also the fact that the higher the annealing temperature the shorter the time, the castings are not annealed at a single temperature, but in two stages. The temperature is raised to well above the transformation temperature, called the critical temperature, and the iron exists at this temperature in the form of a mixture of massive cementite and the austenite. A small portion of the massive cementite dis-

solves in the solid solution on heating above the critical temperature because the dissolving power of iron for carbon increases with temperature above the critical temperature. If the iron is maintained at this elevated temperature (between 1600 and 1700°F., in commercial practice) long enough, all of the massive cementite will be decomposed into temper carbon and iron. The temperature is then slowly reduced until the transformation temperature is passed. During cooling between the top anneal-

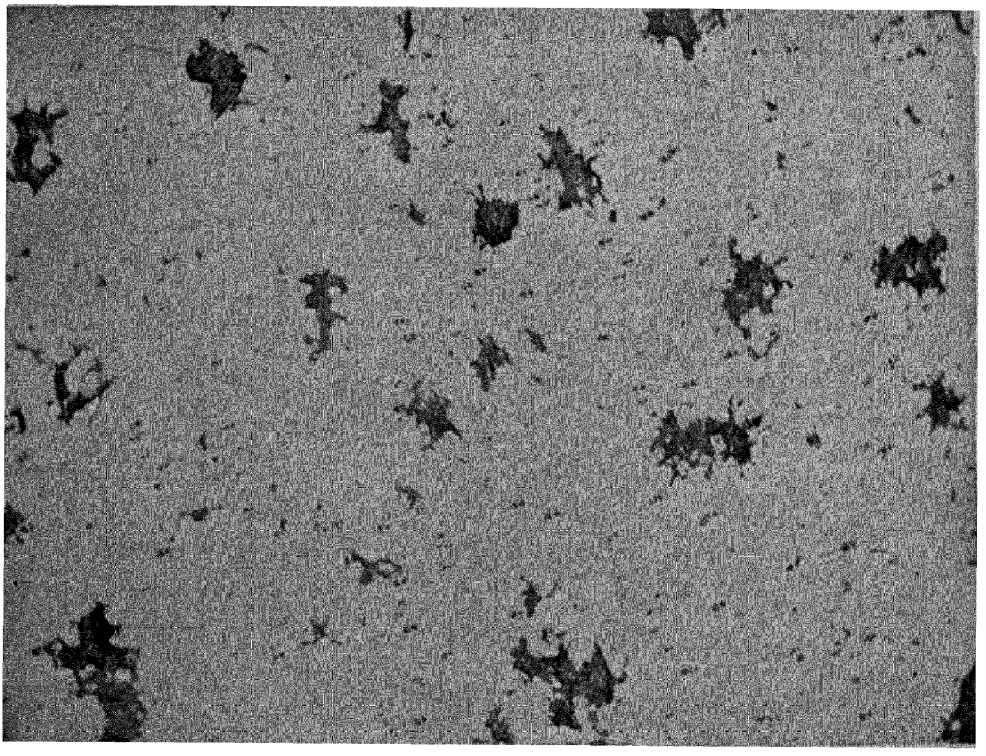


FIG. 2-XI.—Unetched photomicrograph of a specimen of malleable cast iron showing the temper carbon. 100 diameters magnification. (*Courtesy of the National Malleable and Steel Castings Company.*)

ing temperature and the transformation range, the decreasing solubility of carbon in the austenite causes the precipitation of the massive cementite dissolved on heating and it decomposes as it is formed. In passing through the transformation temperature the austenite transforms into pearlite, and the cementite, which is a part of the latter, decomposes soon after it is formed. This is the second stage of the malleablizing treatment and must last sufficiently long to decompose the remainder of the cementite. The temperature used is from 1250 to 1300°F. In most commercial malleable practice, however, the two stages of annealing

merge into one another so closely that a distinction between them is not obvious. The halt at the lower temperature is omitted but the rate of cooling is so slow that, when the critical temperature is reached, the cementite decomposes almost as rapidly as it is precipitated by the decomposition of the austenite into pearlite. When 1250°F. is reached, malleablization is complete and the iron consists only of ferrite and temper carbon.

Annealing Equipment and Operation.—The cleaned castings are placed in large cast-iron or steel annealing boxes called *saggers* and either an iron cover placed over the top of the box or a thick layer of packing used for a covering material. The annealing boxes are rapidly oxidized and last only for from 10 to 20 heats before they must be scrapped and new ones substituted. Iron ore, mill scale, or other iron oxide material is used as a packing. The packing must surround the castings at every place, both inside and out, and no two castings must touch.

Both batch-type annealing ovens and continuous tunnel kilns are used for the annealing treatment. The older batch-type oven is a rectangular heating chamber with a much smaller combustion chamber attached at one end and separated from the heating chamber by a high bridge wall. Only a relatively narrow opening near the roof but extending nearly across the width of the heating chamber is left for the passage of the hot products of combustion. The flues for conducting the gases out of the heating chamber are set in the floor at various points so that the gases must pass completely around the saggers in order to escape and thus heat them evenly from all sides. They are heated with coke, coal, powdered coal, oil, or gas as local conditions dictate although gas is the best from the standpoint of rigid temperature control. Powdered coal gives the best fuel economy.

The continuous tunnel kiln is a long, low, narrow chamber equipped with tracks and cars on which the saggers are loaded for their slow travel through the kiln. The kiln is heated by gas burners and the required temperature zones are maintained relative to the speed of travel of the material in order to produce the desired annealing cycle. The temperature at the discharge end of the kiln is maintained at the lowest temperature of the annealing cycle used and, as the car emerges from the kiln, a car loaded with white castings is introduced at the charging end. The castings are not usually packed when annealed in the con-

tinuous kiln. This type of annealing equipment is not much used because of its very high first cost, but its use does shorten the annealing cycle and lowers the heating costs because of shorter time and better application of heat. In the batch-type oven a large amount of heat is lost through cooling during each cycle, while in the continuous kiln a section is maintained with the desired temperature gradient.

The rigid temperature control in this kiln makes it possible to reproduce the theoretical annealing cycle in practice. A high temperature zone is maintained of sufficient length to give the desired annealing time during the first stage of the anneal, as the cars are pushed slowly through the kiln. A zone with a steep temperature gradient comes next in which the castings are rather rapidly cooled to the critical temperature or just below it. Finally, a constant temperature zone is maintained for the second stage of the anneal.

For an iron of the following typical composition, annealed with oxidizing packing (black-heart malleable) in batch type annealing ovens:

	Per Cent
Carbon	2 40
Silicon	1 10
Manganese	0 25
Phosphorus	0 15
Sulfur	0 05

the following typical annealing cycle is used:

	Time, Hr.
(1) Heat to 1650°F	20
(2) Hold at 1650°F	50
(3) Cool to 1250°F	70
(4) Cool for handling	5

It can be seen that the total time required is a trifle over six days and accounts for the high cost of the malleablizing treatment because of the cost of the fuel and the expense of having material tied up for this length of time.

The saggers are charged into the oven by means of a mechanically operated charging bar and heated as rapidly as is consistent with uniformity of temperature to the top annealing temperature employed. They are held at this temperature until all of the massive cementite existing at this temperature is decomposed

and then slowly and uniformly cooled to decompose the rest of the cementite precipitated as a result of cooling. By the time the critical temperature is reached, the rate of cooling has become very slow and the cementite in the pearlite formed is readily decomposed. Throughout the process, the decarburization of the rim is taking place but the majority of this action occurs at the higher temperatures. When the end of the annealing cycle is reached, the oven doors are opened and the saggers cooled as rapidly as possible to a temperature at which they can be handled. If the castings have warped out of shape slightly, they possess sufficiently high ductility to be hammered back into shape by a steam-operated hammer. The hammer has dies that conform to the correct shape of the casting. The castings are straightened in this way without injury if they are not warped to any great extent.

Control of the Process.—In practically no other metallurgical process must the conditions of chemical composition, furnace operation, heating temperatures, and times of operation be more closely controlled than in the manufacture of high-grade malleable castings. An error in judgment during any step in the entire procedure, including making and casting the white iron, will spoil the finished castings and render useless the best of care and supervision used in the other stages of the operation.

The time of annealing must be sufficient to break down the cementite but a longer time than is necessary should be avoided for the following reasons: (1) the added heating costs, (2) the temper carbon tends to draw together in larger nodules, thus decreasing the strength of the matrix, and (3) the metal may become "overannealed" or else "burned" by being oxidized. By "overannealed" is meant that, if annealing is continued too long, the temper carbon tends to recombine to form cementite, resulting in a so-called *steely* fracture of the iron and lowered strength and ductility. The annealing time is less the higher the upper annealing temperature, but too high a temperature (above 1750°F.) should be avoided because the resulting castings are usually low in strength and ductility. The castings become "burned" when the annealing is conducted for too long a time at too high a temperature and because of the oxidation of the boundaries between the grains of the ferrite due to penetration of oxidizing gases. Finally, if the castings are cooled too rapidly,

a steely fracture is apt to be obtained unless the composition of the metal is adjusted within very narrow limits.

The decarburization of the rim in black-heart malleable and of the entire casting in white-heart malleable castings is probably due to the following cause. The carbon actually present at the surface is removed by the iron oxide packing, according to the following reaction:

$$3C + Fe_2O_3 = 3CO + 2Fe$$

which forms CO gas. This produces a region of low carbon concentration at the surface, and carbon in solution in the iron of the interior of the casting begins to migrate (in solution) to the region of low carbon concentration at the surface and is in turn oxidized. The decarburized rim, therefore, gradually widens as the annealing treatment progresses. In producing white-heart malleable castings, well over 100 hr. at the upper annealing temperature is required to produce the desired decarburization in castings ½ in. thick. Recombination of temper carbon with iron to form cementite does occur to some extent in making white-heart castings but this combined carbon is burned out as well and does not affect the over-all result.

Properties and Uses of Malleable Castings.—The average physical and mechanical properties of blackheart malleable

TABLE 2-XI.—PHYSICAL AND MECHANICAL PROPERTIES OF MALLEABLE CASTINGS*

Property	Average Value
Specific gravity	7.15–7.45
Shrinkage allowance	Average, 1.5 per cent
Tensile strength	54,000 p s.i.
Yield point in tension	36,000 p s.i.
Elongation in 2 in	18 per cent
Reduction of area	18–23 per cent
Hardness	100–140 Brinell
Impact strength	7.75 ft.-lb (Charpy)
Endurance limit	25,000 p.s.i.

* AMERICAN SOCIETY FOR METALS, "National Metals Handbook."

iron castings of approximately the chemical composition given on page 422 and annealed in batch-type ovens are given in Table 2-XI. In making the white iron castings the shrinkage is almost as great as that of steel but, on annealing, the castings

expand, owing to the decomposition of temper carbon, the result being an over-all contraction about equal to that of soft gray cast iron.

The elongation is a measure of the ductility of the metal which is fairly good, as is the toughness which is measured by both the reduction of area and the impact strength. Malleable iron has as high a strength as the average unalloyed gray cast iron, is much more ductile, and usually is softer. Its toughness and endurance values are much higher than for gray cast iron. By endurance limit is meant the stress that the material will stand when the stress is rapidly alternated between tension and compression for several million times. The term "malleable" iron is a misnomer in that the material is not malleable in the sense that gold is malleable, but its ductility and toughness are so much greater than for cast iron that it was called malleable iron when it was first introduced into general use.

Malleable castings have a multitude of applications. A condensed list of products in which malleable castings are used, classified by industries, is given in Table 3-XI. It is estimated that there are about 150 plants in the malleable iron industry in the United States and that their combined annual capacity is about 1,350,000 tons.

Short-cycle Malleable.—Owing to the expense involved in long annealing treatments and the time consumed a great deal of work has been done in the last few years in developing methods by which malleable iron may be made with a much shorter annealing time. The first step in this direction was the development of the continuous tunnel kiln but it is not so effective as some other methods now in use.

The rocking arc furnace has come into considerable prominence in recent years for the purpose of producing iron that can be annealed to produce high-quality malleable castings in a very short time. Thorough mixing of the iron and a high degree of superheating of the molten metal tend to retard graphitization of the white iron on casting to a considerable degree without affecting its ability to malleablize on annealing; if anything, the rate of decomposition of cementite on annealing is increased. It is possible, therefore, to raise the silicon content of these irons markedly and still have them remain perfectly white on casting, thus making them more amenable to a sub-

sequent malleablizing treatment. The iron is cooled in the furnace from the high superheat temperature to a normal casting temperature before being poured into castings.

TABLE 3-XI.—PRODUCTS IN WHICH MALLEABLE CASTINGS ARE USED*

Agricultural Implements:
Plows, tractors, harrows, reapers, mowers, binders, cultivators, rakes, spreaders, dairy and poultry equipment, presses, tools, pumps, wagons, fence parts.

Automobiles:
Parts for frame, wheels, springs, brakes, motor transmission, axles, steering gear, body, accessories.

Boilers, Tanks, and Engines:
Boilers, tanks, fittings, engine parts, outboard motors, Diesel engines.

Building Equipment:
Hardware for windows, doors, garage equipment, awning hardware.

Conveyer and Elevator Equipment:
Chains, buckets, pulleys, rollers, cranes, hoist, fittings.

Electrical and Industrial Power Equipment:
Motor and generator parts, pumps, stokers, electric locomotives and tractors, steam specialties, outlet and switch boxes.

Hardware and Small Tools:
Pneumatic and portable tools, miscellaneous tools, saddlery, hardware, table and kitchen utensils.

Household Appliances:
Stoves, sewing machines, refrigerators, washing and ironing machines, vacuum cleaners, dishwashing machines, oil burners, electric fans and toasters, radios.

Machine Tools:
Lathes, planers, shapers, grinders, screw machines, gear cutters, drills.

Machinery for Special Uses:
Textile, cement, rubber, shoe, mining and quarrying, grinding, forging, foundry, bakery, woodworking, bottling, ice, laundry industries.

Marine Equipment:
Anchors, chains, capstans, fastenings, towing bits, hardware.

Metal Furniture and Fixtures:
Stoves, beds, desks, filing cabinets, shelving, hotel supply equipment.

Municipal, State, and Public Service:
Manhole covers, posts, guard-rail equipment, highway markers, transmission and telephone line fittings, electric railway fittings.

Pipe Fittings and Plumbing Supplies:
Elbows, unions, reducers, flanges, valves, bolts, nuts.

Railroads:
Wide variety of parts for construction of locomotives, freight and passenger cars, guard rails, miscellaneous.

Road and Contractor's Machinery:
Roller, excavators, cranes, hoists, tractors, graders, scarifiers, mixers, pavers.

Toys and Specialties:
Sleds, wagons, automobiles, bicycles, carriages, gun parts.

* "Symposium on Malleable Iron Castings," issued jointly by American Society for Testing Materials and American Foundrymen's Association, 1931.

The following is a typical composition used in producing electric furnace white iron for short-cycle malleable:

	Per Cent
Carbon	2.40
Silicon	1.65
Manganese	0 25
Phosphorus	0 05
Sulfur	0 05

It can be seen that the silicon content, is well above that used in air furnace irons and the phosphorus is lower, thus promoting strength. In order to anneal castings of this composition rapidly, it is necessary to heat-treat them in small batches. In batch-type ovens, lots of from 1,500 lb. to 5 tons are annealed at once by using the following cycle:

	Time, Hr.
(1) Heat to 1750°F	3
(2) Hold at 1750°F	4
(3) Cool to 1250°F	14

The annealing time for complete malleabilization is thus reduced from over 6 days to less than a single day. Other cycles for annealing this white iron are in use in which the temperature is held constant at or just below the critical (1300 to 1325°F.) for sufficient time to decompose the cementite in the pearlite. This permits much more rapid cooling from the temperature of the first stage of cementite decomposition but, since the temperature is held at the lower point for from 10 to 12 hr., no time is saved.

The mechanical properties to be expected from the malleable iron of the foregoing composition and annealed according to the foregoing cycle, are[1]

Tensile strength	60,000 p.s.i.
Yield point	40,000 p.s.i.
Elongation in 2 in	15 per cent
Impact strength (Charpy)	7 ft.-lb.
Hardness (Brinell)	150

These figures show that short-cycle malleable castings compare very favorably in properties with the long-cycle material previously discussed.

Suggested Questions for Study and Class Discussion

1. Describe the construction and operation of the air furnace.

2. Describe the method of testing the iron previous to tapping from the air furnace.

[1] MORKEN, C. H., *Trans. A.S.M.*, **22**, (3), (1934).

3. Discuss briefly the tapping and casting of white iron castings for malleablizing.

4. What are the advantages and disadvantages of the air furnace as a melting medium in the malleable foundry?

5. What are the advantages and disadvantages of the (*a*) cupola, (*b*) open hearth, and (*c*) electric furnace in the malleable foundry? What economic conditions favor the use of each?

6. Why must conditions be so closely watched in producing white cast iron for malleablizing? What factors are controlled?

7. Give a typical composition for malleable iron castings melted in (*a*) the cupola and (*b*) in the air furnace. Why does a difference between them exist?

8. Why are the limits of composition listed in Table 1-XI so necessary?

9. What types of malleable castings are produced? What are the important differences between them? List them in order of decreasing strength.

10. Discuss in detail the constitution of malleable cast iron. Why is the theoretical annealing cycle necessary?

11. Compare the construction, operation, and relative advantages of batch-type annealing ovens and continuous tunnel kilns

12. Describe the annealing operation for long-cycle malleable, giving times and temperature used.

13. Discuss the effects of the following factors from the standpoint of their effect on the structure and properties of annealed malleable castings:

a. Annealing time.
b. Annealing temperature.
c. Supervision of the operation.

14. Show how the decarburized rim is produced on blackheart malleable castings. What is its effect on the strength?

15. Compare the physical properties of malleable cast iron with gray cast iron.

16. How is short-cycle malleable produced? What are its advantages?

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CHAPTER XII

WROUGHT IRON

A crude form of wrought iron was probably the first ferrous material known to man and was made by the Egyptians possibly as early as 3000 B.C. In the early days, the iron was made by direct reduction of the ore. This was made possible by the fact that the common ores of iron, Fe_2O_3 and Fe_3O_4, can be readily reduced by CO_2, H_2, and C at comparatively low temperatures. Thus, a brisk charcoal fire which was blown by a crude form of bellows or blowpipe and into which a quantity of the ore was thrown, was all that was needed by the ancients in order to produce lumps of hot metal out of any fairly pure iron ore. The metal could not be produced in a liquid condition at the temperature of the charcoal fire but could be removed in a pasty or spongy mass consisting of iron, slag, and unreduced ore and hot enough to be hammer-welded to other similar masses. This method was later improved somewhat by using a small shaft furnace into which layers of charcoal and ore were charged. After repeated smeltings of the mass, the product was fused with wood in clay crucibles to make "Wootz steel."

These early methods of ore reduction to produce iron intermingled with particles of slag persisted until comparatively recent times. In fact, no major changes occurred until about the end of the thirteenth century when the Catalan forge was developed by the ironworkers of the Pyrenees Mountains in Spain. This forge was an improvement on the ancient pit furnace in that better working of the charge could be obtained in order to reduce all the ore at one smelting, thereby making repeated smeltings unnecessary. Crude ore was still reduced in these forges, and they were capable of producing about 140 lb. of wrought iron in a 5-hr. period. This was removed from the forge in the form of a pasty ball and hammered vigorously to squeeze out as much of the slag as possible. The temperatures attained were still insufficient to melt the iron but were high

enough to melt the slag so that it could be more thoroughly hammered out of the red-hot iron.

The first major change in the method of making wrought iron came as a result of the development of the blast furnace which was able to reduce the ore and then melt it so that it could be cast into shape. Because of the impurities cast iron contains it is brittle, while wrought iron, being almost entirely composed of nearly pure, malleable, and ductile iron, is capable of being wrought or hammered into shape either hot or cold;

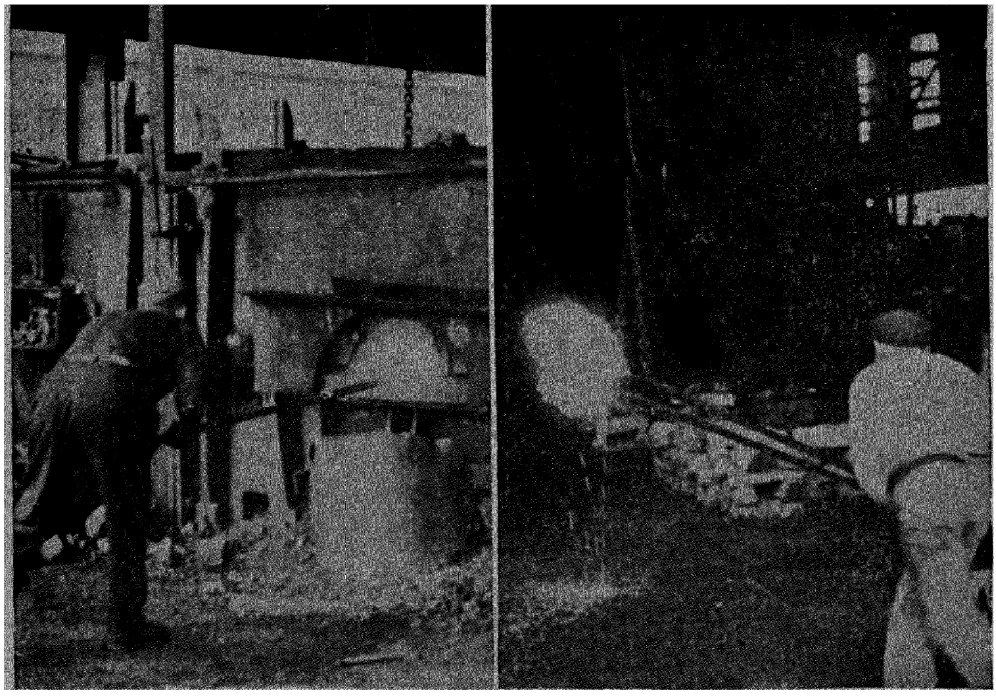


FIG. 1-XII.—The puddling process in operation. At the left, the puddler is rabbling the bath while, at the right, the puddle ball is being transferred from the furnace to the squeezer. (*Courtesy of A. M. Byers Company.*)

hence the names "cast iron" and "wrought iron." As pig iron from the blast furnace became lower and lower in price, the English ironmasters, who had long led the world in the production of the largest amount as well as the highest quality of iron and steel, turned their attention to making wrought iron from pig iron instead of direct from the ore. This change complicates the process to some extent. We know that in the upper part of the blast furnace the old direct reduction process is repeated, producing fairly pure iron direct from the ore without melting. This reduction is followed, however, by a melting of the iron and

its absorption of impurities in the lower part of the stack. These impurities, and particularly carbon, make it incapable of being wrought into shape either hot or cold. In order to make wrought iron out of this brittle pig iron, it was necessary to free the iron of its objectionable impurities.

A process for producing wrought iron from pig iron was finally developed by Henry Cort in England in 1784 and was known as the *puddling process* because of the fact that during the refining of the pig in the type of furnace used, it was necessary for the ironworker constantly to agitate the molten pool or "puddle" of liquid iron and slag on the shallow hearth with a tool known as a *rabble.* The furnace used was later improved by S. B. Rogers and Joseph Hall in 1830 but the principle of operation has remained the same from the days of Henry Cort to the present. At the time of the development of the puddling process, the only known methods of making steel (an alloy principally of iron and carbon but capable of being hardened on sudden cooling) were by the cementation and crucible processes. Since both of these processes were costly and could make the steel only in small lots, wrought iron was the only ferrous material of construction in rolled form until about 1860. With the invention of the Bessemer and open-hearth steelmaking processes, the cost of rolled steel for construction purposes dropped rapidly to below the cost of manufacture of wrought iron until, at the present time, wrought iron costs about 10 to 20 per cent more than the cheapest steel. This caused a correspondingly rapid drop in the amount of wrought iron produced because of the better properties of steel, for construction purposes at least, until in a normal year in the United States only about 500,000 tons are produced at present.

The principal causes for the high cost of manufacture of hand-puddled wrought iron are the low efficiency of the process, the high cost of labor for the severe working conditions encountered, and the small amount of iron produced per heat. These factors led to the development of a new process for the production of wrought iron, based on more scientific principles. This process, known as the *Byers* or *Aston* process, is able to produce wrought iron identical in composition and properties with hand-puddled iron but at a lower cost and in much larger batches.

The wrought iron of today is composed of a mixture of practically pure iron and from 3 to 4 per cent of a ferrous silicate slag.

The iron is very pure and contains only very small amounts of impurities either in chemical combination with or in solid solution in it. The chemical analysis of wrought iron usually falls within the limits given in Table 1-XII and most of even the small amounts of impurities present are contained in the slag and are not associated with the iron matrix itself.

THE PUDDLING PROCESS

The puddling process for the manufacture of wrought iron consists essentially of the following operations: A small charge of pig iron is melted in the shallow hearth of a small reverberatory furnace, the hearth being lined with iron oxide (usually mill scale). During melting there is an oxidation of silicon, manganese, and iron, and these oxides form a basic slag which automatically maintains a very high iron oxide content by absorption from the lining. After the heat is melted, the temperature is reduced and most of the remaining impurities (C, Si, Mn, P, and

TABLE 1-XII.—TYPICAL ANALYSIS OF WROUGHT IRON

	Per Cent
Carbon	0 04 or under
Manganese	0 05 or under
Phosphorus	0 10–0 12
Sulfur	0 03 or under
Silicon	0 10–0.15
Iron silicate slag, by weight	3 0–4.0

S) are oxidized, enter, and are retained in the slag. The oxidation is accomplished mainly by the iron oxide in the slag and lining, although the excess oxygen in the furnace gases probably helps to some extent. Owing to the fact that the melting point of the metal rises rapidly with decreasing content of impurities, the purification finally reaches a stage where the highest temperature attainable in the furnace is not sufficient to keep the metal molten. The metal, therefore, assumes a pasty state—"comes to nature," as it is called—and is rolled up into several balls by the puddler. These balls are removed from the furnace while still dripping with slag and run through a squeezer which eliminates most of the slag contained in the metal and reduces the size of the puddle ball. The resulting ball is rolled between grooved rolls to a bar and further treated in a manner to be described later.

The Pig Iron Charged.—The pig iron charged into the puddling furnace in making wrought iron is of the grade known as *forge iron* or *mill iron*. A medium amount of silicon—about 1 per cent—is desired in the pig because if the silicon is too high, a large amount of slag will be made which carries away a large quantity of oxidized iron; if the silicon is too low, on the other hand, not enough slag will be made and the pig iron will be excessively oxidized owing to inadequate protection from the furnace gases. The manganese content is not so important and varies from about 0.25 to over 1.0 per cent, although a good average is probably about 0.50 per cent. Phosphorus is preferred to be less than 1.0 per cent, but pig iron containing much greater percentages than this is sometimes used. Phosphorus can be largely eliminated in the puddling process because the slag is basic (high in FeO) and, furthermore, phosphorus is not so objectionable in wrought iron as it is in steel because it is contained very largely in the slag and cannot embrittle the iron. Sulfur can also be partly eliminated, but its elimination is not as easily controlled as that of phosphorus. Hence its percentage in the pig charged is usually kept below 0.10 per cent. The carbon content is relatively unimportant and usually varies between 3 and 4 per cent. It must be remembered that the larger the percentage of impurities in the pig, excepting carbon, the larger will be the iron loss, because the slag volume is larger and it carries away a correspondingly larger amount of oxidized iron.

The Puddling Furnace.—The puddling furnace is essentially a low, refractory brick, reverberatory furnace with a cinder-lined hearth of the general shape of a shallow bowl. The furnace is usually coal-fired and the grates are located at one end of the furnace, separated from the hearth by a low bridge wall. A large grate area is provided in comparison to the hearth area in order that high temperatures may be attained. The low roof of the furnace slopes downward from the bridge wall to the back end, at which point the stack is located. This forces the hot gases sweeping over the bridge wall down close to the hearth so that the maximum amount of heat may be extracted from them. Owing to the fact that the gases have only a short distance to travel from the grates to the stack, they leave the furnace while still at quite a high temperature, thus making the thermal efficiency of the furnace very low. To counteract this, waste-heat boilers are

installed in the stacks of many puddling furnaces to recover the heat in the stack gases. The working door is located at about the middle of the side of the furnace and opposite the center of the hearth.

The foregoing description refers to the single furnace, which is the more common and has an average capacity of about 600 lb. of pig iron, being worked by two men. These furnaces are either built singly or in pairs, side by side, to eliminate heat conduction and radiation from the wall of each furnace opposite from the working door. The two furnaces are therefore worked from opposite sides. In double furnaces, which are used to some extent on the eastern seaboard, this dividing wall is knocked out and a single grate and stack are used, making a furnace capable of holding about 1,500 lb. of pig iron at a charge. The hearth of the double furnace is about 4½ ft. wide by 7 ft. between the two working doors. These furnaces are operated by four men. The operation of the double furnace is the same as for the single furnace. The operation of the latter will be considered in detail.

The hearth is lined or fettled with iron oxide in the form of high-grade iron ore, rolling mill scale, or roasted puddled cinder known as "bulldog." This lining is worn away because it enters the slag to help maintain the basicity of the latter and is repaired as often as is necessary between operations.

The usual fuel used is a bituminous coal, rich in volatile matter, which is burned with a long yellow flame. About 1 ton of coal is burned per ton of iron produced, although slightly lower figures have been obtained in some few cases. The process can be readily seen to be quite wasteful of fuel.

Operation of the Process.—The pig iron is charged by hand through the working door and the furnace is fired rapidly in order to melt the heat as quickly as possible and thus minimize iron oxidation. The usual melting time is from 30 to 35 min. As soon as the pig is melted, roll scale or high-grade iron ore is added to the bath in order to make a very basic slag. During a period of from 7 to 10 min., the charge is thoroughly mixed and cooled to some extent. In order to do this, the dampers are closed and sometimes even water is thrown on the bath. The object is to reduce the temperature to a point where the slag will begin to oxidize the impurities. It is essential that the phos-

phorus and sulfur be oxidized before the carbon because the latter protects the iron from oxidation. The reduction in temperature is necessary because only at comparatively low temperatures can phosphorus be oxidized in preference to carbon. This low temperature stage of the process, called the *clearing stage*, is continued until the oxidation of carbon begins, indicating that a considerable portion of the phosphorus has been removed. During this portion of the process, the heat is thoroughly rabbled by the puddler for the purpose of mixing the metal and slag intimately so that oxidation of the impurities may be effected rapidly.

The beginning of the oxidation of carbon can be easily recognized by the appearance of flames that burn at the surface of the slag. These flames are the result of oxidation of the carbon in the charge to carbon monoxide gas which breaks through the slag covering and burns to CO_2 when it comes in contact with the excess oxygen in the furnace atmosphere. The furnace is immediately fired vigorously again to the maximum temperature attainable, in order to prevent the metal from solidifying as long as possible and to oxidize the carbon rapidly. The slag must be very basic during this period in order to prevent the carbon monoxide from reducing the phosphorus and sulfur combined with the slag, because any reduction of these elements would cause them to reenter the metal.

As the formation of carbon monoxide becomes more and more abundant, the charge is violently agitated by its escape and the *boil*, as it is called, is in progress. The charge swells greatly from the gas in its interior and rises in the furnace, causing a large amount of slag to pour out of the slag hole into a slag receptacle. About one-half of the slag produced in the process flows out during this period. The boil continues for from 20 to 25 min. During this time the puddler rabbles the heat vigorously with a long iron tool shaped like a hoe. As the boil begins to decrease in intensity, the metal becomes so pure that the highest temperature attainable (about 2600°F.) becomes insufficient to keep the metal entirely molten and it begins to solidify.

When the metal begins to "come to nature," solid points of metal start to project through the slag in places while other pasty masses form on the cooler furnace bottom. The puddler

attempts to keep the heat uniform in temperature and composition by thoroughly rabbling the heat with a long-handled paddle. He must prevent the iron from projecting through the slag because it will oxidize rapidly and must also prevent it from sticking to the bottom because it chills rapidly. As the heat continues to come to nature it becomes stiffer and more pasty and is very hard to work. During this period the metal becomes thoroughly mixed with the slag because of the rabbling action and the vigorous agitation of the bath itself as it continues to give off gases.

When all of the charge comes to nature, the *balling* period begins, a period which requires from 15 to 20 min. The heat of pasty metal and liquid slag is divided into four portions and each portion is worked into a ball, weighing about 150 lb., which consists of a large number of small iron particles partly welded together by the heat of the furnace and a large amount of liquid slag. The puddle balls are worked into shape and placed against the bridge wall to protect them from the oxidizing action of direct contact with the flame and, at the same time, keep them as hot as possible so that the slag may be easily squeezed out. The balls are removed one by one and delivered to the squeezer, after which the furnace hearth is repaired and relined for another charge. The entire operation usually requires from 70 to 100 min.

Chemistry of the Process.—The oxidation of the elements carbon, silicon, phosphorus, sulfur, and manganese is accomplished by means of free FeO in the slag, the oxygen in the furnace gases playing only a very minor part in this oxidation. This accounts for the necessity of keeping the metal and slag in intimate contact at all times by thorough rabbling of the charge. The FeO is formed by the reduction of Fe_3O_4 and Fe_2O_3 by the furnace gases, according to the reactions:

$$3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2 \quad (1)$$

$$Fe_3O_4 + CO \rightarrow 3FeO + CO_2 \quad (2)$$

Since Fe_3O_4 can be considered to be a mixture of FeO and Fe_2O_3 according to the equation

$$FeO + Fe_2O_3 = Fe_3O_4 \quad (3)$$

Equation (1) is unnecessary and may be replaced by the following

$$Fe_2O_3 + CO \rightarrow 2FeO + CO_2 \quad (4)$$

It is often advantageous, however, to consider Fe_3O_4 as a separate compound. Ferrous oxide, FeO, may also be produced by the action of molten iron on molten Fe_3O_4, according to the reaction:

$$Fe_3O_4 + Fe = 4FeO \quad (5)$$

The result is that by the action of CO and molten iron on the furnace lining and the ore or mill scale thrown in during the clearing stage, as well as by the direct oxidation of iron in the pig by oxygen in the furnace gases according to reaction (6) below, there is always plenty of FeO present in the slag to oxidize the impurities in the pig if the slag and metal are thoroughly mixed.

$$2Fe + O_2 \rightarrow 2FeO \quad (6)$$

The known data on the chemistry of the puddling process are quite incomplete because the process has never been subjected to an intensive metallurgical scrutiny. A partial chemical history of a heat is given in Table 2-XII and illustrates to some extent, at least, the chemical changes that occur in the metal during puddling.

TABLE 2-XII.—ELIMINATION OF IMPURITIES FROM PIG DURING HAND PUDDLING*

Stage of process	C, %	Mn, %	P, %	S, %	Si, %
Pig iron charged (ave.)	4 12	0.70	0 764	0 028	1.55
After clearing	3.43	0.22	0 425	0 033	0.40
Muck bar, ball No. 1	0.05	0 04	0.194	0.026	0.19
Muck bar, ball No. 2	0 05	0 07	0 291	0.025	0.25
Muck bar, ball No. 3	0 05	0.08	0.230	0.025	0.18
Merchant bar, single rolled, ball No. 3	0.05	0.06	0.182	0.020	0 24

* CAMP and FRANCIS, "Making, Shaping and Treating of Steel," 5th ed., 2d impression, Carnegie-Illinois Steel Corp., 1940.

Muck bar is produced by the first rolling treatment on the puddle ball and merchant bar by the second rolling treatment. The difference between them is due to the further removal of slag during the extra rolling treatment. The nonuniformity in analysis of the muck bars from the various puddle balls illustrates

the impossibility of uniformity of hand-puddled iron, although much of the difference is due to variations in slag content. It can be seen from Table 2-XII that by the end of the clearing stage about three-quarters of the silicon, one-third of the manganese, and a little less than one-half of the phosphorus have been removed from the metal, while the carbon and sulfur show slight increases. In this heat, mill scale was not added to the bath until the temperature was raised to start the boil and accounts for the small removal of phosphorus during the clearing stage. The increases in carbon and sulfur are due partly to a decrease in the total weight of the metal because of oxidation of other impurities and partly to absorption of these elements from the furnace gases. If the pig iron carries a very high percentage of sulfur, a decrease will sometimes be noticed at this stage. Slag analyses taken at several stages of the same heat as reported in Table 2-XII are given in Table 3-XII. The small amounts of Al_2O_3, CaO, and MgO have crept into the furnace accidentally and were not intentionally added.

TABLE 3-XII.—SLAG ANALYSES IN HAND PUDDLING PROCESS*

Component	Clearing stage	Start of boil	Middle of boil
SiO_2	20 70	15 11	14 80
Fe_2O_3†	6 22	8 58	8 72
P_2O_5	4 68	4 26	3 82
FeO	59 40	64 74	63 85
MnO	.....	. . .	2.22
SO_3	.. .	.....	0 65
Al_2O_3	.....	.....	2 62
MgO	.....	.. .	1.30
S (as sulfide)	.. ..	.. ..	0 07
CaO	.. ..	. ..	Trace

* CAMP and FRANCIS, "Making, Shaping and Treating of Steel," 5th ed., 2d impression, Carnegie-Illinois Steel Corp., 1940.

† In the analysis, iron is analyzed as ferrous and ferric iron and calculated and reported as FeO and Fe_2O_3. The Fe_2O_3 is really a part of the unreduced Fe_3O_4.

As we have seen, the oxidation of silicon takes place, for the most part, in the early stages of the process. It is first oxidized by the free FeO in the slag as follows:

$$Si + 2FeO = SiO_2 + 2Fe \qquad (7)$$

and the SiO_2 immediately combines with FeO to form ferrous silicate, which is the basis of the puddling slag.

$$SiO_2 + 2FeO = 2FeO \cdot SiO_2 \quad (8)$$

Equations (7) and (8) may be combined by addition and the two-step reaction expressed as follows:

$$Si + 4FeO = 2FeO \cdot SiO_2 + 2Fe \quad (9)$$

The FeO combined as ferrous silicate is no longer able to effect oxidation of other impurities so that an excess of FeO over that combined with other oxides must be present in the slag to bring about their oxidation. It is obtained from the sources and in the manner outlined above. If there is a deficiency in free FeO at any point in the bath, $FeO \cdot SiO_2$ may be formed instead and later combine with more FeO to form $2FeO \cdot SiO_2$ as it comes in contact with it.

The elimination of manganese occurs simultaneously with the oxidation of silicon and can be represented by the following equation:

$$Mn + FeO = MnO + Fe \quad (10)$$

Since MnO is insoluble in the metal, it rises into the slag and, being basic in nature, combines with SiO_2.

$$2MnO + SiO_2 = 2MnO \cdot SiO_2 \quad (11)$$

In fact, it is possible that the following reaction, involving both manganese and silicon, may occur:

$$Mn + Si + 4FeO = MnO \cdot FeO \cdot SiO_2 + 3Fe \quad (12)$$

Since the sulfur in the pig is combined principally as MnS, a little manganese probably reaches the slag as MnS where it is oxidized in the following manner:

$$MnS + 3FeO \rightarrow MnO + SO_2 + 3Fe \quad (13)$$

The SO_2 escapes as a gas and is probably the principal method by which sulfur is eliminated from the metal in the puddling process because it is known that unless the manganese content of the pig iron is high, very little sulfur is eliminated. If the sulfur content is much above 0.1 per cent, it may be reduced considerably in amount, but its reduction below 0.06 per cent

is very uncertain and the only sure way of producing low-sulfur wrought iron is to start with a low-sulfur pig iron.

The oxidation of phosphorus produces P_2O_5, which is an acid and must be neutralized by a base (FeO) in order to remain in the slag in a stable condition. The oxidation and combination can be represented by the equations:

$$5FeO + 2P = P_2O_5 + 5Fe \quad (14)$$

$$3FeO + P_2O_5 = 3FeO \cdot P_2O_5 \quad (15)$$

or equations (14) and (15) can be combined as in (16):

$$2P + 8FeO = 3FeO \cdot P_2O_5 + 5Fe \quad (16)$$

This ferrous phosphate is a stable constituent of the slag only in the presence of excess free FeO which prevents equation (16) from going in the reverse direction with the reduction of phosphorus. Also, if the free FeO content of the slag is not sufficiently high, CO will reduce phosphorus during the boil as shown in equation (17).

$$FeO \cdot P_2O_5 + 5CO = 2P + FeO + 5CO_2 \quad (17)$$

Reaction (16) is favored by low temperatures because it is exothermic, and lower temperatures drive the equilibrium to the right. On the other hand, the oxidation of carbon is endothermic and is consequently favored by high temperatures. The equation for the removal of carbon is

$$FeO + C \rightarrow CO + Fe \quad (18)$$

Thus, we can readily see why it is necessary to lower the bath temperature and charge iron oxide in order to effect the removal of phosphorus before carbon.

The phosphorus elimination occurs during the clearing stage and the early part of the boil. Since the reactions involving the oxidation of both silicon and manganese are more strongly exothermic than that of phosphorus, they are more strongly favored by low temperatures and phosphorus has little chance of elimination until both silicon and manganese are largely oxidized and neutralized in the slag. Furthermore, SiO_2 is a stronger acid than P_2O_5 and will displace it from combination with FeO by the following reaction

$$3FeO \cdot P_2O_5 + SiO_2 = 2FeO \cdot SiO_2 + P_2O_5 + FeO \quad (19)$$

if there is an insufficient amount of free FeO to satisfy both of these acidic oxides. Since this free FeO must be obtained largely from the lining before ore or roll scale is added to the bath, there is little chance of oxidation of phosphorus before this addition is made.

When the boil becomes vigorous, hardly any more phosphorus can be removed for the following reasons: (1) There is so much carbon present in comparison to phosphorus that it robs the bath of available FeO and the excess CO reduces any phosphorus oxidized to P_2O_5. (2) As the increasing purity of the metal causes it to solidify, the phosphorus cannot be readily oxidized because it diffuses only slowly to the surface of the small solidified metal particles where FeO can act upon it. If it could diffuse readily to the surface, it could be oxidized because the carbon content is sufficiently reduced by this time to allow phosphorus oxidation by FeO. The oxidation of carbon adds free FeO to the slag because of the action of the CO released upon the slag while it is trapped in it.

$$Fe_3O_4 + CO = CO_2 + 3FeO \qquad (20)$$

This reaction continues until the temperature of dissociation of CO_2 is reached (about 2350°F.). Carbon, on the other hand, continues to be oxidized from the metal after its solidification because it has a high solubility in the metal and therefore diffuses readily to the surface where it can be oxidized by FeO. For these reasons, unless phosphorus is removed during the clearing stage and the early part of the boil, it is liable not to be removed at all. The extent of elimination of phosphorus from a given pig iron is dependent upon the skill of the puddler, the quantity of free FeO present, the heating capacity of the furnace, and the extent to which the furnace temperature can be controlled.

It should be remembered that the reactions involving the removal of the impurities in the pig iron are all reversible with the single exception of the reaction removing carbon [equation (18)]. This means that equation (18) is the only one that can go to completion and remove all of this element from the pig because the CO is the only product of these elimination reactions which, being a gas, escapes from the sphere of action and allows the reaction to complete itself in a forward direction. The reactions involving the removal of the other impurities all reach

an equilibrium, the value of which depends upon the factors controlling the equilibrium in each case. It is, therefore, theoretically impossible entirely to remove these elements from the metal. The reaction involving the oxidation of MnS goes to completion [equation (13)] but so little MnS reaches the slag that this reaction was not considered.

The loss in the puddling process averages from 4 to 6 per cent of the weight of pig iron charged. A typical example of the losses is given in Table 4-XII. Although there is much iron oxidized

TABLE 4-XII.—LOSSES IN HAND PUDDLING*

Element Oxidized	Per Cent of Loss
Silicon.....	1 00
Carbon...	3 50
Sulfur	0 20
Phosphorus	0 50
Manganese.	0 30
Total . ..	5 50
Iron reduced from oxide (gain)	1 00
Net loss	4 50

* STOUGHTON, B., "The Metallurgy of Iron and Steel," McGraw-Hill Book Company, Inc., New York, 1934.

and carried away with the slag, even more is reduced from the lining by impurities. The figure given in the table represents the excess of reduction over oxidation and, in some cases, may be as high as 6 per cent.

Treatment of the Puddle Ball.—The puddle ball, as it is removed from the furnace, is of very irregular shape and contains much slag in the interior in pockets surrounded by metal. It is necessary to form it to a shape that can be later rolled into a bar form and also remove as much of the slag as possible. This treatment is accomplished by means of a *squeezer*, a drawing of which is shown in Fig. 2-XII, although a steam hammer is used for this work in a few localities and the operation is known as *shingling*. The squeezer consists essentially of a short corrugated cylinder *B*, mounted on a vertical shaft so that it will revolve. A larger stationary cylinder, also corrugated, almost entirely surrounds it and is set eccentrically with respect to the inner cylinder so that the clearance between them is constantly decreased around the circumference of the inner cylinder. The puddle ball is inserted at *C*, is gripped by the revolving cylinder,

and carried, also revolving, around the ever-diminishing space enclosed by the two cylinders to *D*, where it emerges and drops on a small table. This kneading action squeezes out much of the slag and delivers the piece in the form of a rough cylinder, which is grasped by the tongs of a workman and immediately taken to the rolling mill.

The *muck mill* or *puddle mill*, as it is variously called, for rolling the squeezed ball into muck bar is a simple pair of rolls

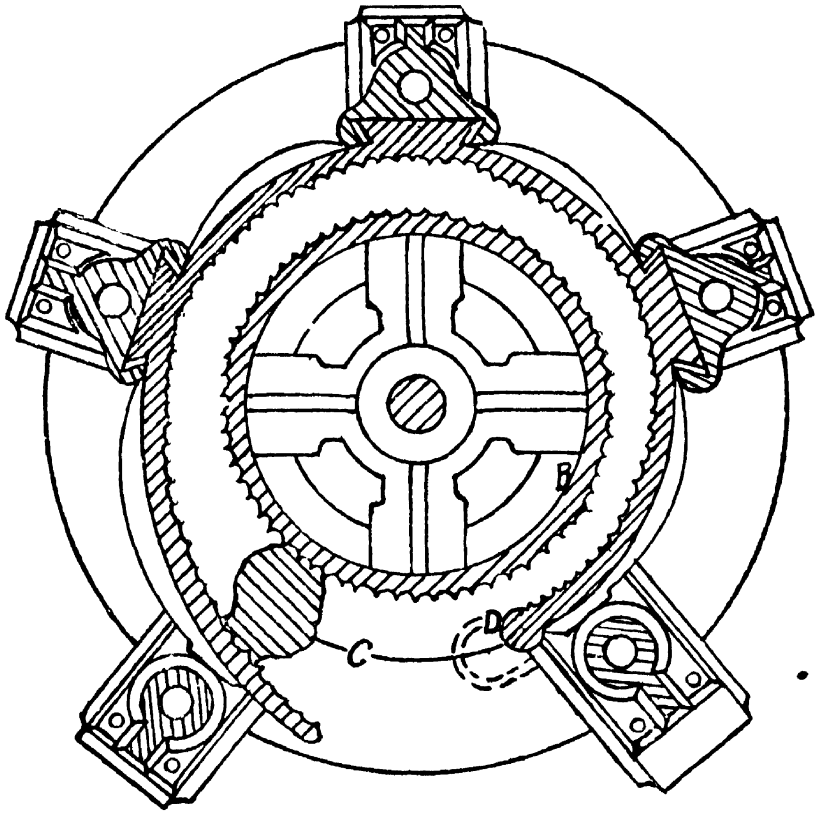


FIG. 2-XII.—Drawing of a rotary squeezer. (*After Stoughton.*)

about 20 in. in diameter with grooves cut in them for forming the bar. The size of the muck bar is dependent upon the product being made but for ordinary bar iron, the principal product, the finished muck bar is $\frac{3}{4}$ in. thick and from $2\frac{1}{2}$ to 8 in. wide. It requires from five to nine passes through the mill to form the bar from the squeezed ball. The first and second passes through the mill form the squeezed ball into a piece of square cross section with rounded corners while the remaining grooves in the mill are of constantly decreasing size to form this piece into the desired

size and shape of muck bar. This treatment also squeezes out much slag, leaving a rough surface on the bar, and elongates the slag remaining in the metal into long streaks, or *stringers*, extending in the direction of rolling. Because of the rapid cooling of the bars in the rolls, about nine passes are all that can be taken before the bar gets so cold that the slag solidifies and can no longer be worked out. After rolling, the muck bar is allowed to cool before being subjected to further treatment.

The final operations carried out on the muck bar depend upon the quality of the iron desired. For the highest quality of hand-puddled product, a process known as *busheling* is used. Owing to the fact that the muck bars are nonuniform in composition (see Table 2-XII), they are sheared into small pieces, mixed with pieces from other muck bars, and portions of from 200 to 600 lb. charged into a reheating furnace, known as a *balling furnace*. They are heated to a self-welding temperature which closely approaches the melting point and the pasty pieces collected into balls with a long-handled paddle in the same manner as the puddle balls are made. The resulting balls are squeezed or shingled, then rolled or hammered into a bloom which is finally reheated and worked into the form desired. This treatment removes much more of the slag and produces wrought iron uniform in composition and of high strength, but the labor costs are very high and the iron must sell for a higher price. This method is also used in reworking scrap wrought iron into bar stock but the product is usually inferior because steel scrap creeps into the charge. The carbon in this steel scrap is not burned out in the balling furnace and steel streaks are found in the finished bars and materially lower their strength, ductility, and resistance to corrosion.

The most common practice is to shear the muck bar into 2- to 3-ft. lengths, arrange the pieces into piles of from 5 to 7 each, and bind the pieces together with wires. The piles are then charged into a reheating furnace and heated to a self-welding temperature. The pieces in the pile weld together and each pile is removed and rolled to produce a single bar of wrought iron. The first two or three passes through the rolling mill squeeze out more slag, but in the last passes the bar has cooled to a point where the slag is merely plastic and can no longer be removed. A fairly smooth, uniform bar is produced but it is

lacking in uniformity and, while its slag particles are very much elongated, they are of comparatively large cross section. Furthermore, since it is built up of flat bars, it does not offer the same resistance to bending in all directions. This product is known variously as *merchant bar*, *single-rolled iron*, and *No. 2 iron*.

In order to remedy the above defects, No. 2 iron may be further treated by cutting into short lengths, piling, reheating, and rerolling to produce a product known as *double-rolled iron*, *double-refined iron*, *best bar*, or *No. 3 bar*. The manner of piling or *faggoting*, as it is often called, is done in a number of ways, depending upon the manufacturer's choice. The object is to produce uniformity and, in practically all of the piling methods in use, some of the bars in the pile are laid crosswise to the rest. More slag is expelled in rolling the piles, the bar is made more uniform in composition, and the slag stringers are much more elongated and reduced in size.

THE BYERS PROCESS

With the rise of the large-tonnage steelmaking processes, the antiquated hand-puddling process became less and less able to compete with steel from a cost standpoint as well as from several others. A few of the more important reasons follow:

1. Owing to the small furnace used and the high temperatures necessary, the thermal efficiency of the process is very low as can be seen from the figures on fuel consumption already given.

2. The labor at puddling furnaces is very severe, owing to the large amount of heat radiated by the furnace and the fact that heavy physical labor is required, practically without intermission. Indeed, the work is so difficult that it is hard to find intelligent men to work at puddling furnaces and they must be paid very high wages.

3. The output of a puddling furnace is too small to compete with the large-tonnage steel processes. For example, two men working at a puddling furnace can produce between them only about 2,800 lb. of wrought iron in a 10-hr. turn while over 100 tons of steel can be made in the open-hearth furnace in less than this time and at a lower cost. In addition, the steel has better mechanical properties, from a construction standpoint at least.

4. The finished wrought iron is a variable product and its nonuniformity is due to the following causes: (*a*) differences in

manipulation by different operators and at different furnaces, (*b*) irregularities in the pig iron charged, (*c*) the small quantity produced in each heat, and (*d*) the fact that the metal solidifies before purification of the whole bath is complete.

5. The fact that the quality of the product is more dependent upon the individual skill of the puddler and the care and judgment that he exercises in carrying out the process, than on any other single factor.

For these reasons, many attempts have been made to improve the process and at the same time lower the cost of making wrought iron. Most of these attempts consisted in building puddle furnaces that could be rocked, tilted, or rotated in order to simulate mechanically the efforts of the puddler in mixing the metal and slag. Although some of these have been partly successful, none ever attained widespread use for one reason or another. These attempts were all in the wrong direction because, from a metallurgical standpoint, the problem consisted essentially in incorporating small particles of slag in a refined base metal. Finally, an entirely different process was developed by the A. M. Byers Company, under the direction of James Aston, and was put into commercial operation in 1927. This method is able to produce much larger batches of wrought iron under close control, with excellent uniformity and at a lower cost.

The process[1] consists essentially in melting pig iron in a cupola and refining it in a Bessemer converter until the carbon, silicon, and manganese are almost entirely removed. In the meantime a ferrous silicate slag of the same composition as that which is produced in the puddling furnace is melted in an open-hearth furnace and then poured into a receptacle called a *thimble*. The essential step in the process consists in pouring the refined metal into the slag, the latter being at a temperature below the melting point of the refined metal. This treatment solidifies the metal and disintegrates it into small particles which sink to the bottom of the slag thimble. For that reason, this step in the process is known as *shotting*. The metal, incorporated with liquid slag, welds itself together at the bottom of the thimble and, after the excess slag is decanted, the ball of metal is dumped on a platform and is identical in composition and appearance with the puddle ball except that it is much larger.

[1] ASTON, J., *A.I.M.M.E.*, Iron and Steel Division, **84**, 1929.

This method of making wrought iron can be seen to be much more efficient than the hand-puddling process from all standpoints, and it produces a material that is the equal of high-quality hand-puddled iron. The details of the process will now be taken up.

Melting the Pig.—As the process is carried out at present, Bessemer grade pig iron (see Table 9-IX) is melted in cupolas of a melting capacity of 15 tons per hour. The cupolas operate continuously for about a week, when they must be shut down for lining repairs. A characteristic pickup of about 0.04 per cent sulfur is adequately eliminated by the addition of about 20 lb. of soda ash per ton of metal which is added in the ladle on tapping. The full requirement for each converter heat is tapped at one time and taken in a ladle to the converter house by an overhead crane. It is possible that blast furnaces may ultimately be used to make the pig iron so that it may be transferred to the converters without casting and remelting.

Refining the Pig.—The molten pig iron is refined in 10-ton, bottom-blown, acid-lined Bessemer converters. The converter is a ganister-lined cylindrical vessel into which the molten metal is poured. An air blast is admitted through tuyères in the bottom of the converter and the pressure of the blast supports the metal and keeps it from running down into the tuyères. The blast oxidizes iron to FeO which, in turn, oxidizes manganese and silicon and then carbon in much the same manner as these impurities are eliminated in the puddling process, although much faster as a 10-ton batch can be purified in from about 12 to 16 min. The heat to keep the metal molten is furnished by the heat of oxidation of the impurities. A detailed account of the operation and theory of the Bessemer converter is given in Vol. II of this series. The converters are well adapted to the refining stage of the process because they afford an almost continuous supply of metal in batches of moderate size on a relatively brief, steady tapping cycle. It has the possible disadvantage of not being able to reduce the phosphorus and sulfur content of the metal; in fact, owing to metal loss in the refining process, the percentages of these elements actually increase. The average composition of the refined metal is given in Table 5-XII. It is poured from the converter into a ladle and taken to the processing machine for shotting.

TABLE 5-XII.—COMPOSITION OF REFINED METAL

Element	Per Cent
Carbon	0.06
Manganese	0 03
Phosphorus	0 10
Silicon	0 02
Sulfur	0 05
Iron	Balance

Slag Preparation.—The slag is prepared by melting a mixture of the desired ingredients in a tilting open-hearth furnace. The slag is made to conform in composition to the slag found in good wrought iron. Puddle-furnace tapping slag (where available), heating furnace scale, roll scale, iron ore, and sand represent available sources of supply. The range of composition given in Table 6-XII is approximately adhered to in making up the slag.

TABLE 6-XII.—APPROXIMATE SLAG COMPOSITION

Constituent	Per Cent
FeO	70–75
Fe_2O_3	5–10
SiO_2	10–12

Small amounts of MnO, Al_2O_3, and P_2O_5 may or may not be added (about 2 per cent of each) in order to simulate the puddle slag more completely although, as we have seen, the constituents of Table 6-XII are the only important ones. The open hearth is of standard steel works design (see chapter on the Basic Open Hearth, Vol. II) except that additional water cooling is used to protect the hearth from the severe scouring action of the molten slag. The molten slag of correct composition is tapped into a ladle and taken to the processing machine.

Shotting.—The operation of shotting is shown in Fig. 3-XII. The metal in the ladle brought from the converter is poured into the ladle of the processing machine shown in the figure. The ladle car containing the slag is spotted in the pit directly under the lip of the ladle. The metal ladle is then tipped and the metal poured at a predetermined rate into the slag below. The machine automatically oscillates as well as moves the ladle backward and forward during pouring to distribute the refined metal through the slag.

The metal, as it pours from the ladle, is at a temperature in excess of its melting point 2750°F., while the slag, liquid through-

out the operation, has a general working temperature of from 2300 to 2400°F. The ratio of slag volume to volume of metal poured is from 6 or 8 to 1. This is quite a bit more than is necessary to absorb the heat of solidification of the metal without the slag becoming heated to a point dangerously near the fusion point of the iron. Under these conditions, the slag is an effective quenching medium which solidifies the metal promptly and continuously as it is poured in. The average

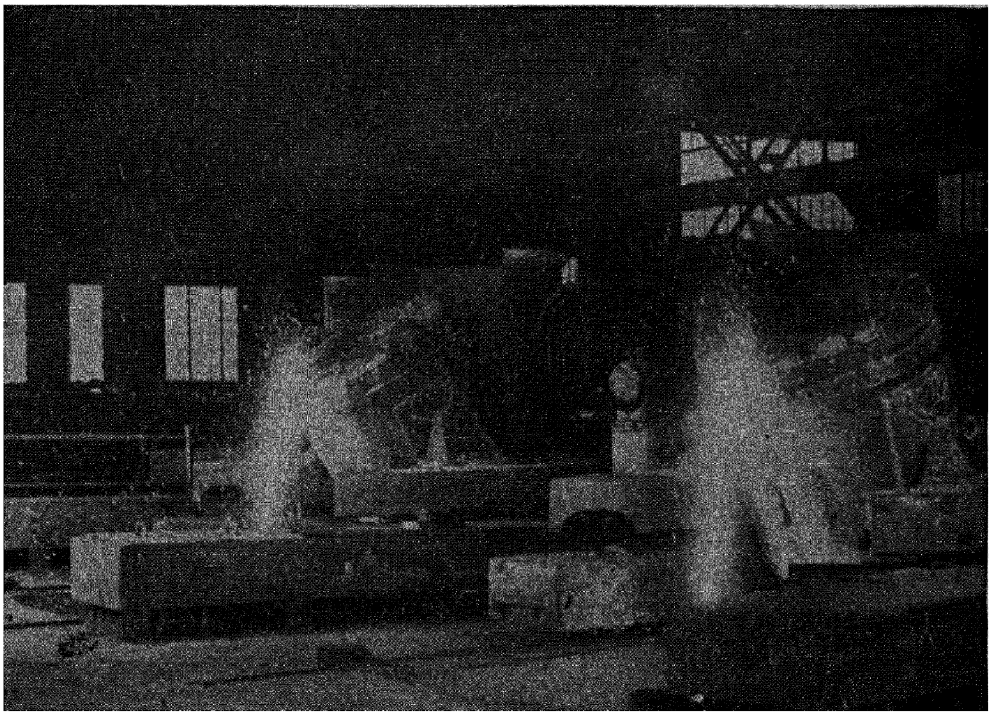


FIG. 3-XII.—The shotting operation. (*Courtesy of A. M. Byers Company.*)

pouring time for 6,000 lb. of metal is in the neighborhood of 6 min., and the slag in the thimble has a depth of several feet.

During the shotting process, there is a marked churning and agitation of the slag, and a boiling action, due to gas elimination from the metal, causes it to foam and rise to the top of the thimble. From time to time, moderate amounts of cold granulated slag are thrown into the ladle in order to quiet the boil somewhat and prevent the rising slag from flowing over the rim of the ladle. The rapid quenching of metal from the liquid state, together with the release of gas, causes the metal to disintegrate into very small solid pellets which sink through the slag and, in so doing, are further purified of impurities. Because

the temperature of the solid metal is at a good welding heat, these small metal particles collect at the bottom and loosely weld themselves together into a ball in which liquid slag is thoroughly intermingled.

Processing the Ball.—Immediately after the pour is completed, the slag thimble is transferred to a point where a crane picks it up and pours off the excess slag into a ladle, and the ladle is returned to the open hearth where enough slag is added to make up for

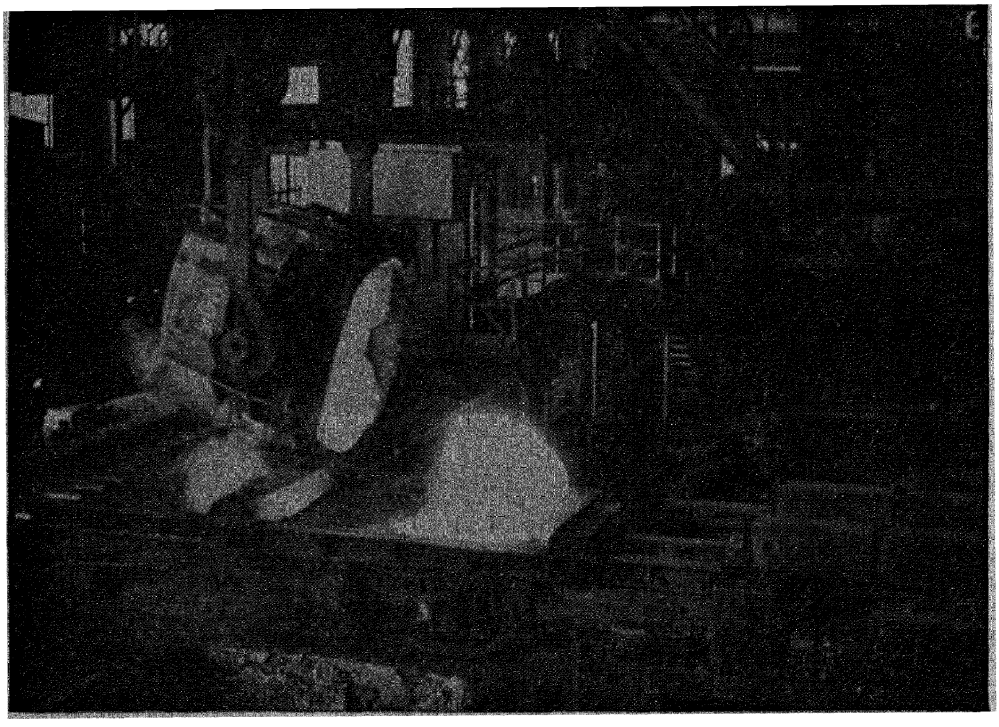


FIG. 4-XII.—Dumping the ball on the press. (*Courtesy of A. M. Byers Company.*)

the amount contained in the metal ball. About 600 lb. of slag per ton of metal poured is contained in the ball, but much of this is recovered on squeezing and rolling. The ball, similar in every respect to the product of the best puddling practice except for weight, which varies from 6,000 to 8,000 lb., is dumped on the platform of a 900-ton electrically driven press (see Fig. 4-XII), which squeezes out most of the slag and compacts the metal into the form of an ingot. The ingot is immediately transferred to a blooming mill where it is rolled into a bloom and then, without reheating but on a different mill, is rolled to produce either billets or standard muck bar. The billets are suitable for

forging or rolling into skelp for the manufacture of lap- and butt-welded wrought iron pipe.

Theory of the Process.—As has been said before, the crux of the process lies in the shotting operation where the metal is disintegrated upon solidification. The refined metal that was treated in the Bessemer converter is saturated with gases (principally CO, H_2, and N_2) at the temperature at which the metal is shotted. This is owing to the fact that the metal in the converter is in intimate contact with the air blast being blown through it. Now these gases have quite a high solubility in liquid iron, but this solubility drops to practically zero when the metal solidifies. Also, the rate of gas evolution is greater, the faster the speed of solidification. Hence, when the liquid metal is rapidly solidified by quenching it in the liquid slag, the metal is shattered by the rapid gas evolution on solidification. The gas evolution also accounts for the boiling action of the slag.

Since the metal is heavier than the slag, the small particles of metal sink through the bath of slag and, in so doing, undergo a further reduction in the amount of impurities contained in them, particularly carbon, manganese, and sulfur. The reactions by which this is accomplished are the same as those already considered in the puddling process, but the extreme speed with which it is accomplished is due to the very large surface area of contact of the metal and slag on account of the small size of the individual metal particles. The refined metal is also saturated with FeO before shotting, and the solubility of FeO also decreases to practically zero when the iron changes from the liquid to the solid state. This FeO is taken up by the slag as it comes out of solution. This can be done only when the metal particle size is extremely small. The shotting operation therefore quite thoroughly frees the metal from oxygen (as FeO) or, in other words, deoxidizes the metal.

STRUCTURE AND PROPERTIES OF WROUGHT IRON

A photomicrograph of a polished and etched specimen of wrought iron is shown in Fig. 5-XII and, since the sample was cut in a longitudinal direction, it shows the slag stringers in their elongated form. The dark lines throughout the matrix mark the boundaries of the iron crystals. The structure can be seen to be that of a mixture of practically pure iron and small

stringers of slag elongated in the direction of rolling. In the best quality of wrought iron there may be as many as 250,000 slag stringers to the cross-sectional square inch. When broken, it has a fibrous structure which is due to the slag stringers and the fracture looks somewhat like a broken piece of wood.



FIG. 5-XII.—Photomicrograph of a longitudinal etched section of hand-puddled wrought iron. 100 diameters magnification.

For wrought iron to be made into chain, the approximate physical properties required are about as given in Table 7-XII.

TABLE 7-XII.—PHYSICAL PROPERTIES OF WROUGHT IRON FOR CHAIN

Property	Value
Tensile strength	46,000 p.s.i.
Yield point	23,000 p.s.i.
Elongation (per cent in 8 in.)	26 per cent
Reduction of area	40 per cent

It is a little stronger than the purest iron, owing to the small amounts of impurities contained in solid solution in the iron. It is also quite ductile and tough when compared to cast iron and malleable iron.

Since wrought iron must compete with low carbon steel in both cost and physical properties for all of the types of service for which wrought iron is used, the comparative properties of wrought iron and low carbon steel will now be considered. From the standpoint of the common physical properties, such as strength and ductility, wrought iron is probably inferior to steel, but, with regard to some other particular properties, it is equally as good and is believed by some to be considerably better. The makers of wrought iron advance the claim that wrought iron is superior to low carbon steel from the following standpoints:

1. Ability to withstand the stresses of shock (impact) and vibration (fatigue or endurance strength).
2. Corrosion resistance.
3. Ability to hold protective coatings, such as tin and zinc.
4. Ease of welding, particularly pressure welding.

The superiority of wrought iron over steel from the first two standpoints has never been proved to the entire satisfaction of many unbiased metallurgists, but its superiority is generally admitted from the last two standpoints. The lower the carbon and silicon content of the metal, the more tightly a zinc (galvanized) coating will stick to it, and, of course, wrought iron shines in this regard. In pressure welding, where the two pieces are heated to a self-welding temperature and welded by being pressed or hammered together, wrought iron is superior because the slag becomes liquid and acts as a flux in carrying away the FeO produced by oxidation on heating. In the various electric fusion-welding processes, the difference between wrought iron and steel becomes much less marked.

The question of the relative superiority of wrought iron and steel with regard to corrosion resistance has been argued back and forth for many years without the question's being fully decided. Corrosion testing is very difficult because so much depends upon the conditions under which the tests are carried out and the uniformity of the material being tested. A number of scientific tests carried out over a period of several years have indicated that there was no great difference between steel and

wrought iron with regard to speed of corrosion, although the results showed that wrought iron was slightly better in resisting the corrosive influences of sea water and alkaline water and that steel was better in resistance to dilute acids and acidulated water. Much of the corrosion of pipe in service comes through the formation of holes or pits in the metal, *i.e.*, corrosion is localized at certain points in the metal and it corrodes entirely through the pipe at these places. The makers of wrought iron insist that the presence of thousands of noncorroding slag stringers effectively obstructs this pitting action.

Wrought iron is claimed to be superior to low carbon steel in resistance to shock and fatigue because of the slag it contains. It is known that failure of a metal under rapid alternations of stress begins as a crack at or near the surface and that this crack slowly spreads through the cross section of the piece until it fails. The presence of the slag stringers is supposed materially to reduce the rate of spreading of this crack.

Wrought iron finds use in the following fields of service:

1. Pipe, where its possible advantages are superior corrosion and fatigue resistance, welding, and threading qualities.
2. Bar iron for staybolts, engine bolts, and rivets where the properties demanded are corrosion and fatigue resistance.
3. Plates, where corrosion resistance is demanded.
4. Chains, where weldability and impact strength are desired.

Suggested Questions

1. Describe briefly the history of wrought iron from earliest times to the present day.

2. What are the requirements of the pig iron for the puddling process?

3. Describe the construction and fettling of the puddling furnace.

4. Describe in detail the operation of the puddling process.

5. Discuss in detail the chemistry of the puddling process. Include all important equations.

6. What are the effects of the other impurities in the pig iron and the temperature on the removal of phosphorus?

7. Describe in detail the various methods of treating the puddle ball.

8. Discuss the factors that led to the development of the Byers process for the manufacture of wrought iron.

9. Describe the operation of the Byers process.

10. Discuss in detail the theory of the Byers process.

11. How is the ball treated after dumping from the ladle?

12. Describe the structure of wrought iron.

13. What are the claims for superiority of wrought iron over low carbon steel?

14. List the uses of wrought iron.

Suggested Reading

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CHAPTER XIII

THE CEMENTATION AND CRUCIBLE STEEL PROCESSES

The cementation and crucible steel processes are included at this point instead of with the steelmaking processes in Vol. II of this series principally for two reasons: (1) both processes originally involved the making of steel from wrought iron and (2) both are so insignificant as steelmaking methods from the tonnage standpoint that they can hardly be classed as steelmaking methods at the present time.

Steel may be roughly defined as an alloy of iron and carbon, but containing other impurities and sometimes alloying elements; it is ductile when cooled slowly but is rendered hard and relatively brittle when cooled rapidly. Steel may be differentiated from cast iron by the fact that steel is ductile and contains less carbon (almost always less than 1.5 per cent), and from malleable iron by the fact that it contains less carbon, no temper carbon, and is more ductile when slowly cooled. It may be differentiated from wrought iron because it contains more carbon than wrought iron and does not contain slag streaks.

THE CEMENTATION PROCESS

It has been known since early times that when wrought iron was heated to a red heat in contact with charcoal or other material high in carbon, the carbon was slowly absorbed by the iron in solid solution up to its limit of solubility. The solubility of carbon in red-hot solid iron increases with the temperature but has a value of about 1.6 per cent at 1900°F. which is the highest temperature it is practicable to use. The famous swords of Damascus and Toledo, as well as other tools, were early made by this process, which came to be known as the cementation process. It was highly developed and flourished during the eighteenth and nineteenth centuries, particularly in England, and was used for making springs, tools, and the highest grades of cutlery steel then obtainable. The process began to decline

with the development of the manufacture of crucible steel direct from wrought iron and shrank to insignificance with the development of the Bessemer and open-hearth steelmaking processes. As far as the author is aware, there is no cemented steel made anywhere today but the principles involved are still used to procure a high carbon rim on low carbon steel, the process being known as carburization.

Operation of the Process.—As the process was carried out at the highest stage of its development, the furnace used was of the muffle type and contained two stone pots, 2½ to 4 ft. wide and deep and from 8 to 15 ft. long. These pots were so situated in the furnace that hot gases from the coal fire were able to pass entirely around them. The wrought iron charged was in the form of bars about 3 in. wide, ⅝ to ¾ in. thick, and 6 to 12 ft. long. Charcoal of about ¼-in. size was used to pack the bars in the pots. In charging the pots, a layer of charcoal 2 or 3 in. thick was spread on the bottom and then alternate layers of bars and charcoal added until the pots were full. The bars were laid flat with their edges at least ½ in. apart so that each bar was completely surrounded by charcoal. After placing the final layer of charcoal, the tops of the pots were covered by clay or other inert material, and every effort was made to make the pots as airtight as possible.

A fire was next lighted in the furnace and the charge gradually heated to a temperature of from 1500 to 1800°F. during a period of from 3 to 4 days. The amount of carbon absorbed by the steel is greater the higher the temperature and the longer the time of contact. Consequently, after the temperature of the bars reached the desired value, the time of heating varied from 7 to 12 days at that temperature, depending upon the size of the bars used and the amount of carbon desired. The degree of carburization was determined by fracture tests on bars which were withdrawn at intervals from the pots through small holes provided for that purpose. When the desired amount of carburization was obtained, the furnace was cooled slowly until the bars were cool enough to be handled.

The Product.—The surfaces of the carburized bars as they come from the pots are covered with irregular "blisters" which are due to the expansive force of the CO formed by carbon reacting with the oxides of the slag. The bars were, therefore,

known as blister or cemented steel. Since the carbon is initially absorbed at the surfaces of the bars, they are nonuniform, the carbon content being higher at the surface and decreasing gradually toward the center. For example, if the carbon content at the outside were 1.50 per cent, the amount at the center would be about 0.85 per cent. In order partly to correct this inhomogeneity, the blister bars were reheated and hammered or rolled, the product being sold for springs, as the raw material for the crucible process, or for the production of shear steel.

In making *shear steel*, the bars were sheared into short lengths, piled, sprinkled with borax, covered with clay, reheated to a welding temperature, and hammered to a single bar which was known as *single-shear steel*. When the highest grade of cementation steel was required, the single-shear bars were broken in the center, the two halves laid together, reheated to the welding temperature, and hammered down to the required size. The effect of the reheating and hammering was to distribute the carbon more evenly and the latter also reduced the crystal size of the metal. These bars were known as *double-shear steel*. Several different grades of cementation steel, given in Table 1-XIII, were made of different carbon contents for different

TABLE 1-XIII.—GRADES OF CEMENTATION STEEL

Grade	Per Cent Carbon
Spring heat	0 50
Country heat	0 60
Single-shear heat	0 75
Double-shear heat	1 00
Steel through heat	1 25
Melting heat	1 50

purposes. The name shear steel was derived from the fact that it was originally used exclusively for cutlery manufacture.

THE CRUCIBLE PROCESS

Wootz steel was the forerunner of the crucible process but it was redeveloped by Benjamin Huntsman, a clockmaker, who realized that the shortcomings of cementation steel for clock springs was due to their nonuniformity in carbon content. He

cut cemented steel of the desired composition into small pieces, packed them in clay crucibles, and melted the metal in a coke fire. After skimming the slag which was liberated by the melting of the iron, he poured the metal in a cast-iron mold. After solidification, the mold was removed and the ingot hammered into the desired shape. This method produced steel of great uniformity, free from slag, dirt, and occluded gases and so superior to cemented steel that it rapidly became the leading method for the production of high-quality steel.

The crucible process maintained this position until recent years. Many changes were made in the details of the process such as the manufacture of crucibles, design of the furnace, and materials charged, but the principles of operation were maintained the same and the process remained the only method for the production of high-speed and other quality tool steel until the introduction of the electric furnace process. The electric furnace process (both the arc and induction types) rapidly superseded the crucible process because it was able to produce steel of equal quality at a lower cost and possessed several other metallurgical advantages. The tonnage produced by the crucible process in this country declined from over 120,000 tons in 1912 to only 1,500 tons in 1931. The author believes that there are no crucible plants in operation in the United States at the present time.

Metal Charged.—The greatest care should be exercised in selecting raw materials for the crucible process because it does not refine or reduce the amount of impurities in the metal, and whatever goes in with the charge comes out in the finished metal. The only exceptions are the elimination of gases, slag, and other nonmetallic inclusions. For many years after the introduction of the process by Huntsman about 1740, cemented steel was the only raw material used. Because of the high cost of this material, attempts were made to utilize wrought iron and provide the carbon by introducing charcoal into the charge. As long as Swedish wrought iron, the purest made at that time, was used, just as good crucible steel could be produced. After the introduction of the Bessemer and open-hearth steelmaking processes, attempts were made to reduce costs by substituting soft steel scrap for a portion of the wrought iron. This did not prove successful unless a large number of chemical analyses were made

on the scrap to be sure that the composition was uniform. This was rarely done.

More recently, washed metal—semipurified pig iron freed from silicon, manganese, and phosphorus—has been used with excellent results when mixed with best quality wrought iron, the washed metal serving to raise the carbon content of the charge to the desired degree. Owing to the competition from the electric furnace process, only carefully analyzed steel scrap was used before this process became obsolete. Even so, steel of good quality cannot be made unless the composition is adjusted by the use of the best quality of wrought iron and washed metal. For the production of alloy tool steels, the major product, ferroalloys are added with the charge. Carefully analyzed tool scrap is used and the remainder of the charge made up and adjusted with wrought iron, washed metal, and ferroalloys.

The Furnace.—The melting furnace is generally of the gas-fired regenerative type. It consists of a number of combustion chambers or "melting holes," built in a row between and above a series of checker chambers which serve to preheat the gas and air for combustion. This preheating is necessary in order to attain the high temperatures required and still maintain good economy of fuel. Each melting hole is built to contain six crucibles, is set with its top level with the working floor, and is covered. Each combustion chamber has its own regenerators, and the direction of the flame is reversed at intervals.

Crucibles.—The crucibles are expensive to make and, as they last for only 12 heats on the average, they are a considerable item of expense in the process. The crucibles have a capacity of from 80 to 125 lb., are barrel-shaped, and vary in size from 13 to 18 in. in height and from 8 to 12 in. in maximum diameter. The wall thickness is about 1½ in. at the bottom and ¾ in. at the top. They are made of 50 per cent ground plastic clay and 50 per cent ground graphite and subjected to a burning treatment lasting several days to drive off all water before being put into use. As they are very fragile, they should be carefully handled in order to give good service.

Operation of the Process.—The materials to be charged are broken or sheared into small pieces and then weighed out in the proper proportions to produce the desired final analysis. They are then packed in the crucible by hand, the base metal of the

charge (wrought iron or steel scrap) being placed on the bottom. The crucibles are tightly covered and introduced into the melting hole and the charge melted as rapidly as possible. The melting time varies from 2½ to 4 hr., depending upon the composition of the charge and the furnace conditions. When the melting of the charge is believed to be complete, the melter removes the covers and inspects the charge by stirring a steel rod through it to be sure that it is entirely melted.

The killing stage of the process now begins and usually lasts from 30 to 40 min. During this stage, the metal evolves gases which finally collect in fairly large bubbles and break on the surface of the metal, causing the phenomenon known in the industry as "cat's eyes." The melter watches the heat closely and when the steel appears to be "dead killed"—free from gas bubbles and any indication of turbulence—the crucibles are removed and placed on the melting floor. This is the most important step in the operation and the knowledge of when to pull the heat requires a lot of experience on the part of the melter. If pulled too soon, the metal will still contain gases which will cause the ingot to be unsound; if allowed to remain in the furnace too long, the heat may be ruined because of too much silicon and carbon absorption from the crucible. Furthermore, the temperature at which the crucibles are removed is important. If poured too hot, the ingot will not be sound; if pulled from the furnace too cold, the metal will freeze before it can be poured.

With the heat killed and at the proper pouring temperature, the cover is removed and the slag skimmed off by means of a ball of slag on the end of an iron rod. The crucible is then picked up with tongs and its contents poured into a cast-iron mold. The pouring requires great strength and considerable skill because the stream of metal entering the mold must not be broken or strike the walls of the mold. The molds are usually square in cross section, about 3 to 4 in. on a side and tall enough to take the contents of one crucible. The mold is of the split type, made in two parts fitted together by rings and wedges so that the ingot may be removed easily.

Since the production of the crucible process is almost entirely limited to high carbon and alloy steels which are very susceptible to cracking if heated or cooled too rapidly, the ingots must be carefully handled in subsequent stages of their treatment. The

ingots are removed from the molds as soon as solidification is complete and buried in ashes or sand so that they will cool very slowly. When cold, they are cleaned and inspected for cracks, slowly reheated to a forging temperature, and forged down to bars of the desired size under a steam hammer. The details of the forging process are reserved for Vol. II of this series.

Chemistry of the Process.—From a chemical standpoint, at least, the crucible process is the simplest of the steelmaking processes. The charge is very pure and contains a little iron oxide in the form of scale and rust, slag in the wrought iron, and the small amount of air trapped in the crucible. On melting, these oxides form a basic and highly oxidizing slag which contains a large percentage of FeO reduced by the carbon in the charge or that in the crucible. The liquid metal becomes saturated with FeO and the remainder reacts with SiO_2 in the clay of the crucible to form $2FeO \cdot SiO_2$. As the metal absorbs carbon from the crucible and the charcoal in the charge (if any), the conditions in the crucible become strongly reducing. Any oxides dissolved or suspended in the metal react with the carbon and are reduced to the metallic form with the formation of CO which rises through the slag, forming the "cat's eyes." The slag rapidly becomes acid from absorption of a large amount of SiO_2 from the crucible, and the free SiO_2 is reduced, probably by CO, to produce metallic silicon which dissolves in the metal. This silicon thoroughly deoxidizes the metal (frees it of FeO) by reaction with FeO according to the equation:

$$2FeO + Si = 2Fe + SiO_2$$

When the metal is entirely deoxidized, SiO_2 continues to be reduced from the acid slag by the strongly reducing influence in the crucible and the silicon content of the metal begins to build up toward the end of the killing stage of the process. The reason why the time for removing the heat from the furnace is so important is that, if the silicon content is allowed to increase beyond 0.50 per cent in most steels, it produces an embrittling effect which is highly undesirable. The temperature of the metal also affects the rate of silicon pickup, being faster the higher the temperature. Hence, the time of killing and the temperature must be closely watched, but close control of either is manifestly impossible under the existing operating conditions

The result is that both the silicon and carbon contents of the metal vary over relatively wide limits, making it very difficult to produce crucible steel of uniform composition in quantities of more than about one ton.

Suggested Questions for Study and Class Discussion

1. How may steel be differentiated from cast iron, wrought iron, and malleable iron?

2. Describe the history of the cementation process.

3. Why is the cementation process no longer used?

4. Describe the operation of the cementation process.

5. Why is it impossible to produce absolute uniformity of composition in cemented steel?

6. What treatment was carried out on the product of the cementation furnace?

7. Why was the crucible process used for making the highest quality of steel? Why is it used so little at present?

8. How is the crucible charge made up and what raw materials are used?

9. Describe the operation of the crucible process.

10. Why is the killing stage the most important step in the process?

11. Describe briefly the important steps in the treatment of the ingot.

12. Discuss the chemistry of the process.

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SUGGESTED PERIODICALS

The student is strongly urged to consult the following metallurgical journals and read articles of interest to him because in them appear practically all the most recent information available in English on present theory and practice in the field of ferrous metallurgy:

The Journal of the Iron and Steel Institute (British).

Transactions of the American Institute of Mining and Metallurgical Engineers. Iron and Steel Division.

Transactions of the American Society for Metals. (Formerly the American Society for Steel Treating.)

Mining and Metallurgy.

Metal Progress.

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