# AN INTRODUCTION TO METALLURGY

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BY

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# PREFACE

The material in this book is largely a development of lecture notes which have been used for several years in a class in principles of metallurgy. It is the author's belief that an introduction such as this should serve two primary purposes, *viz.*: (1) it should give a comprehensive view of the field of metallurgy as a whole, and (2) it should acquaint the student with the metallurgical idiom and give him the necessary vocabulary for the understanding of specialized treatises on the various branches of metallurgy. It is evident that the important problem in the assembling of a book such as this is the selection of the proper material from the vast field of metallurgical literature and the compression of this material between the covers of a book of reasonable size. The guiding thought which has been in the author's mind while writing this manuscript might be put as a question: "If I were teaching an advanced course in any one of the branches of metallurgy, what preparation would I like my students to have?" This book is the author's answer.

With such a purpose in mind, it is necessary that the book must deal with principles rather than practice, and with generalities rather than specific instances. The choice has been difficult to make at times, but in all cases the selection was finally based upon the author's conception of the thesis outlined in the preceding paragraph.

Contrary to the procedure frequently adopted, the chapters on the structure of metals and alloys are given first. This appears to be logical because metallurgy is a study of metals, and the beginner should first of all find out what a metal is. This arrangement also has secondary advantages; for instance, it permits a discussion of slags from the standpoint of the constitutional diagrams involved.

The author is a firm believer in the value of problem work in the study of any engineering subject, and therefore a number of examples of typical calculations are included in the text, and a list of problems is appended to each chapter. The solution of illustrative problems is the best method of fixing the principles in mind, and it is the only way to gain a proper conception of the quantitative aspect of the science. No student who has "trouble" with problems really understands the basic principles involved. It is impossible in a book of this kind to include tables of all the physical and chemical data necessary to solve the problems relating to such a wide variety of topics. Although it would have been easy enough to give the data necessary to work the specific problems quoted in the text, it was thought to be better to require the student to obtain his data from other sources; this book cannot be regarded as a handbook, and the student should become familiar with the standard sources of information on physical and chemical constants.

In the bibliographies at the end of the various chapters are included a number of references to articles in current periodicals; where this book is used as a textbook the instructor should augment these lists with other suitable material as it appears. Much of the current literature is not beyond the powers of a beginning student, and he should be encouraged to read as much of it as possible. This will not only serve to introduce the student to the literature in the metallurgical field, but it will also give him a glimpse of the advances which are continually being made on the different fronts. If we may be permitted to use a rather far-fetched comparison, we might liken the study of metallurgy to a human body—a book such as this is the skeleton, and specialized textbooks are the flesh which clothes its bones; the current literature is its life's blood.

The author is especially indebted to Dr. Curtis L. Wilson of the Montana School of Mines, who was kind enough to read and criticize the first draft of the manuscript. Much of the material in the text is based on lecture notes taken in courses given by Dr. Wilson. Much credit is also due to Dean A. W. Fahrenwald of the School of Mines, University of Idaho, for his kind cooperation and encouragement.

The list of books and periodicals to which credit is due includes all those listed in the bibliographies and footnotes in the various chapters; all of these have contributed in greater or less degree to the material found in this book. For physical and chemical data, most credit is due to "The Handbook of Chemistry and Physics," "The International Critical Tables," and the "Textbook of Metallurgical Calculations" by Allison Butts. Statistical data are largely from the *Mineral Industry* (McGraw-Hill) and the *Minerals Yearbook* (U.S. Bureau of Mines). Most of the problems and calculations are adapted from those in Professor Butts' "Textbook," and from "Heat" by Dr. James M. Cork. For much of the general discussion the author is particularly indebted to the various textbooks in the McGraw-Hill Metallurgical Series. An attempt has been made to indicate the source of all material for which credit is due, and the author wishes to express his thanks to the authors and publishers for their kind permission to use this.

Many of the tables and illustrations are reproduced through the courtesy of various manufacturing, mining, and metallurgical concerns; to all these the author wishes to express his thanks for their kindness and willing cooperation.

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# AN INTRODUCTION TO METALLURGY

## CHAPTER I

## INTRODUCTION

The earth which we inhabit is a rigid spheroid about 8000 miles in diameter, spinning about the sun as one member of its planetary family. We believe that our earth consists of certain definite types of matter, arranged in roughly concentric shells;[1] the central core is composed of a complex iron alloy, containing a large amount of nickel and smaller amounts of other elements. This core is about 4200 miles in diameter and has a density equal to ten times that of water. Surrounding the central core is another shell about 1800 miles thick, which has a density of about 4.0, and which is probably composed of such heavy rocks as metallic oxides, sulfides, and silicates. The outer layer is composed principally of the lighter rocks, such as granite, and has a density of about 2.8. It is approximately 100 miles in thickness.

All our information about the internal composition of the earth is obtained from indirect evidence. We can calculate the density of the entire globe from application of the law of gravity; from the speed of sound vibrations passing through the earth we obtain information about the properties and distribution of the central layers. We assume that the composition of the central core is about the same as that of the metallic meteorites which reach us from the space beyond our earth. The temperature gradient in deep mines and bore holes, and the fact that from time to time molten lava wells out onto the earth's surface, show that the internal temperature of the earth must be quite high. Certainly the matter on the interior of the planet is under enormous pressure, and it is likely that this combination of temperature and pressure means that the central portion of the earth is in the liquid state. Many other physical observations also lead us to believe that the earth behaves as a liquid sphere.

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[1] Lindgren, W.: Mineral Deposits, Edition 4, p. 2, 1933, McGraw-Hill Book Co., New York.

Of the actual properties of matter under high temperature and tremendous pressure, we know very little. Undoubtedly many combinations can exist which would seem strange to our experience—solutions, for example, containing such "immiscible" materials as silica, water, metallic sulfides, and gold. Geological studies lead us to believe that such solutions do exist, and that their decomposition as they rise to regions of lower temperature and pressure is responsible for many of our important *ore deposits.*

Whatever may be the composition of the interior of the planet, our first-hand knowledge of the earth is confined to the crust of the outer siliceous shell, a crust not more than 10 miles in thickness. If we think of a 6-inch globe, such as is commonly used to represent the map of the world, our 10-mile shell would correspond roughly to the thickness of the paper upon which the map is printed. It is this external shell, with a depth of about 10 miles, to which we shall refer as the "earth's crust."

**Composition of the Earth's Crust.**—By computing weighted averages of a large number of analyses of igneous rocks from all parts of the world, F. W. Clarke and H. S. Washington[2] have arrived at the probable percentages of various elements in the earth's crust. They find that eight elements account for over 98.5 per cent of the total, as follows:

| | |
|---|---|
| Oxygen | 46.59% |
| Silicon | 27.72% |
| Aluminum | 8.13% |
| Iron | 5.01% |
| Calcium | 3.63% |
| Sodium | 2.85% |
| Potassium | 2.60% |
| Magnesium | 2.09% |

The amounts of some of the "common" metals are very small, as shown by the following percentages:

| | |
|---|---|
| Nickel | 0.02% |
| Copper | 0.01% |
| Tungsten | 0.005% |
| Zinc | 0.004% |
| Lead | 0.002% |
| Tin | 0.000*n*% |
| Silver | 0.000,00*n*% |
| Gold and platinum | 0.000,00*n*% |
| Radium | 0.000,000,000*n*% |

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[2] Clarke, F. W., and Washington, H. S.: Composition of the Earth's Crust, U. S. Geol. Survey Prof. Paper 127 (1924).

where *n* indicates the position of the first significant figure and also indicates that its exact value is unknown.

The above figures represent the average composition of igneous rocks, which are probably the parent substances of all terrestrial matter. Fortunately, however, certain geological processes result in the concentration of metals in ore deposits; and it is from these metal-bearing beds, veins, or placer deposits that metals are extracted. The amount of gold, lead, or tin in an ordinary igneous rock is so small that it can be detected only by extremely delicate analytical methods, and the commercial recovery of these metals from such a rock is completely out of the question. From the figures given above, it might be thought that aluminum should be one of the most common and cheapest of metals, because it is so abundant. Actually, aluminum is a comparatively rare metal, because it can be extracted commercially only from bauxite, which is a relatively rare mineral; and most of the aluminum found in nature is in igneous rocks, clays, and shales from which it cannot be extracted profitably. Iron is the most important and the cheapest of all the metals, not because it occurs in such abundance, but because there exist vast deposits of commercial ores of iron. Even these great ore deposits, however, represent only a small fraction of the total amount of iron in the earth's crust; most of it is locked up in igneous and sedimentary rocks and, at least with our present technique, is hopelessly out of reach of commercial extraction.

## THE METALS AND CIVILIZATION

Man's physical existence is confined to the shallow upper crust of the earth's surface. He has at his disposal whatever materials are found there with which to support himself and to construct his buildings, tools, and machinery. In addition to the inorganic substances present on this planet, radiant energy from the sun is continually pouring down upon the surface of the earth at a rate equivalent to about 200 trillion ($2 \times 10^{14}$) horsepower; and this radiation provides the energy which supports life on the earth and supplies the necessary energy for dynamic geologic processes.

In man's struggle for existence in his environment, he has established two fundamental industries upon which all human activities and efforts are based. These are: first, the exploitation of living plants and animals for food, clothing, and shelter; and second, the *mineral industry*. The first of these includes such highly important fields as agriculture, lumbering, and fishing; the second includes all operations in which the lifeless material in the earth's crust is utilized to man's advantage. *Metallurgy,* with which we are concerned in this book, is a branch of the mineral industry; it deals with the recovery of metals from the ores found in the earth and with the various treatments necessary to adapt these metals for specific uses. The actual extraction of metal-bearing rock is called *mining,* and metallurgical processes do not begin until the metal-bearing ore has been mined and brought to the surface.

The importance of metals and metallurgy to modern civilization is self-evident. Without our metal products, we should still be living in the Stone Age with caves and skin tents for dwelling places, crude wooden implements for tilling the soil, and stone hammers and axes for tools. Our modern civilization with its great skyscrapers, automobiles, airplanes, refrigerators, radio sets, and ten thousand other devices with which we come in daily contact, would be impossible without the use of metals.

The metal industry was originally fairly simple. Undoubtedly, the first metals to be used by man were those which he found in the native or metallic state, such as gold nuggets in stream gravels, native copper, or meteoric iron. The first smelting, or extraction of a metal from a chemical compound, probably took place by accident rather than by design; some prehistoric man built a fire upon a metal-bearing outcrop and found a lump of metal in the ashes. Such experiences soon led to the construction of crude furnaces for smelting, and the art of metallurgy was born.

At first, there was little distinction made between metals, but gradually man came to the realization that there were different kinds of metals—that copper, for example, was not a form of gold, nor lead a form of silver. Later, he began to appreciate the fact that it was possible to have alloys of two or more metals and that these alloys had properties which differed from those of the pure metals. Until the fundamentals of chemistry had been discovered, metallurgy was purely an art; but after it became possible to study the composition of metals and alloys, and the chemical processes involved in extracting metals, the science of metallurgy began to take form. Today we speak of metallurgy as an art and science, because, in spite of the great strides which have been taken by the physical sciences, metallurgy still contains some unexplained phenomena, still makes use of some rule-of-thumb methods, and still finds it necessary to employ artisans to do work which cannot be learned from scientific textbooks.

Today the metal industry has grown to such proportions that it is the second largest enterprise in the world, being exceeded in importance only by agriculture. About five thousand separate metals and alloys are in commercial use at the present time, and new alloys are being developed every day. Metallurgy has broken up into a number of specialized branches, each of which has developed its own voluminous literature.

## THE DIVISIONS OF METALLURGY

Metallurgy may be defined as *the art and science of extracting metals from their ores and other metal-bearing products, and adapting these metals for human utilization.* The field of metallurgy may be divided into two parts for the sake of convenient study: *extractive metallurgy,* which is concerned with the winning of the metals from their sources; and *adaptive metallurgy,* which deals with the problems of converting metals and alloys into useful forms. Extractive metallurgy is naturally rather closely connected with mining and geology; and the metallurgist who intends to specialize in extraction will need a good working knowledge of these other branches of the mineral industry. Adaptive metallurgy, on the other hand, is related to the various manufacturing and engineering fields which employ metals as materials of construction, such as the manufacture of all kinds of machinery, building construction, etc. The distinction between the two divisions is not always well defined. In most steel mills, for example, both extractive and adaptive processes are used side by side.

At this point we shall list the various processes which are included under the heading of metallurgy and give brief definitions of the most important terms.

## CLASSIFICATION OF METALLURGICAL PROCESSES

I. Adaptive metallurgy.
    A. Physical metallurgy.
        1. Microscopic metallography.
        2. Study of the phase relations in metals and alloys (thermal analysis, etc.).
        3. X-ray analysis.
        4. Testing.
        5. Heat-treating.
    B. Mechanical metallurgy.
        1. Alloying.
        2. Casting.
        3. Rolling.
        4. Hammer forging.
        5. Press forging.
        6. Drawing.
        7. Spinning.
        8. Die casting.
        9. Welding.

- C. Chemical metallurgy.
  - 1. Electrometallurgy.
    - *a*. Electrolytic.
      - (1) Electroplating.

- II. Extractive metallurgy.
  - A. Mechanical metallurgy.
    - 1. Ore dressing.
    - 2. Sampling.
  - B. Chemical metallurgy.
    - 1. Pyrometallurgy.
      - *a*. Drying
      - *b*. Calcining.
      - *c*. Roasting.
      - *d*. Smelting.
      - *e*. Converting.
      - *f*. Distillation.
      - *g*. Fire refining.
    - 2. Hydrometallurgy.
      - *a*. Amalgamation.
      - *b*. Leaching.
      - *c*. Evaporation.
      - *d*. Crystallization.
      - *e*. Precipitation.
    - 3. Electrometallurgy.
      - *a*. Electrolytic.
        - (1) From aqueous solution.
          - (*a*) Anodes soluble—refining.
          - (*b*) Anodes insoluble—extraction.
        - (2) Electrolysis of fused salts.
          - (*a*) Extraction.
          - (*b*) Refining.
      - *b*. Electrothermic.
        - (1) Refining.
        - (2) Smelting.

*Adaptive metallurgy* is largely concerned with the physical properties of the metals; *extractive metallurgy,* with their chemical properties. The table given above is intended to serve principally as an outline which will be followed in subsequent chapters as closely as is practicable. Following are a few brief definitions of some of the most important terms.

*Metals* are those chemical elements which have a "metallic" appearance, and include perhaps seventy out of the ninety-odd known elements. Since matter is a fundamental quantity, it cannot be defined; and the nearest we can approach to a "definition" of the metals is to list the various properties which are characteristic of them. In the discussion of adaptive metallurgy the physical properties of metals will be given, and their chemical properties will be considered in the introduction to the extractive processes.

*Alloys* are "metallic" solids containing two or more metals; some may contain small amounts of various non-metals.

A *mineral* is a naturally occurring, homogeneous, inorganic substance with characteristic physical properties and with a chemical composition that is either definite or fixed between definite limits. The *ore minerals* are those minerals which contain metals that can be extracted economically; they may be either native metals or chemical compounds.

An *ore* is a natural aggregate containing ore minerals in sufficient quantity to warrant commercial exploitation.

*Ore dressing* is a process whereby the various minerals present in an ore are mechanically separated into two or more products.

*Chemical metallurgy* includes all extractive processes in which the metals concerned undergo chemical changes. Extractive metallurgy includes ore dressing and chemical metallurgy.

*Ferrous metallurgy* is the metallurgy of iron and steel.

*Non-ferrous metallurgy* is the metallurgy of the non-ferrous metals, or of all metals other than iron.

*Pyrometallurgy* is the branch of extractive metallurgy that involves chemical reactions brought about by means of heat supplied by the burning of fuel.

*Hydrometallurgy* is another important branch of extractive metallurgy. In hydrometallurgical operations, the metal sought is first obtained in an aqueous solution (by leaching) and is then recovered by precipitation.

*Electrometallurgy* includes the various metallurgical operations which depend upon the utilization of electric currents.

*Physical metallurgy* is a study of the physical laws which govern the constitution and properties of metals and alloys.

*Metallography* is the branch of physical metallurgy which deals with the microscopic study of the structure of metals and alloys.

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# PART A

# ADAPTIVE METALLURGY

# CHAPTER II

## THE STRUCTURE OF METALS

We shall begin this chapter with a brief review of some theories of atomic structure. It is believed that atoms are built up of two kinds of material—protons and electrons. The proton has one positive charge of electricity, and the electron one negative charge; and the total number of protons in any one atom must equal the total number of electrons. The simplest atom is the hydrogen atom, which consists of a single electron rotating about a single proton; hence the nucleus is a single proton. In heavier atoms (atoms of higher atomic weight) the nucleus is composed of several protons and electrons closely packed together. This combination acts as a unit. The nucleus always contains more protons than electrons, and consequently carries a net positive charge. Arranged in some fashion around the nucleus is a group of planetary electrons, in number equal to the net positive charge on the nucleus so that the normal atom is electrically neutral.

The extranuclear or planetary electrons appear to rotate in circular or elliptical orbits about the nucleus, and these electrons tend to assemble in concentric shells. In progressing from atom to atom in order of increasing atomic number (the order of atomic numbers corresponds almost exactly to the order of atomic weights), each nucleus has one more positive charge than the nucleus of the preceding atom; and each atom has one more planetary electron. The atom which has two such electrons has the first stable or complete shell, and this element is chemically inert (helium). The second shell consists of eight additional electrons, so that there are ten planetary electrons in all. The element with this configuration is neon. Argon has an atom containing three completed shells (eighteen planetary electrons). In the entire series of elements, these inert elements are found at definite periods. The inert elements resemble one another very much, and all are entirely lacking in chemical activity. The elements which fall between the inert gases show a regular repetition of properties. For example, lithium and sodium are very closely related; lithium has a nucleus carrying three positive charges, one completed shell of two electrons, and one additional electron outside this shell. Sodium has a nucleus carrying eleven positive charges, two completed shells containing respectively two and eight electrons, and one additional electron outside the second shell.

The electrons of the outer, incompleted shell of any atom are called the *valence electrons;* most of the chemical and physical properties of elements are due to the valence electrons of the atom. The lack of chemical activity of the inert gases is ascribed to the fact that their atoms possess no valence electrons. In the Lewis-Langmuir (static) atom model, it is assumed that the shells of electrons are in the form of cubes; and a stable shell or octet consists of a cube with an electron at each of the corners (see Figs. 1 and 2). Although this model does not fit very well with the concept of rotating electrons, it is useful in visualizing the processes of chemical combination and ionization. The nucleus plus the completed electronic shells is called the *kernel* of the atom; for all ordinary properties of the atom, the important parts are the kernel and the valence electrons. As the atomic weight becomes greater, the arrangement of the shells becomes more complex (accounting for the "long periods" in the periodic system), but even the heavier elements may be regarded as composed of a kernel and one or more valence electrons. Although the simpler atoms will be used for purposes of illustration, most of the conclusions that will be drawn are applicable to the more complex atoms.

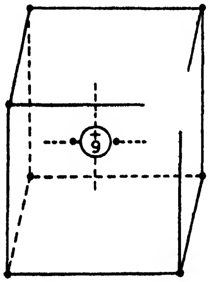

FIG. 1.—The Lewis-Langmuir Model of the Fluorine Atom.

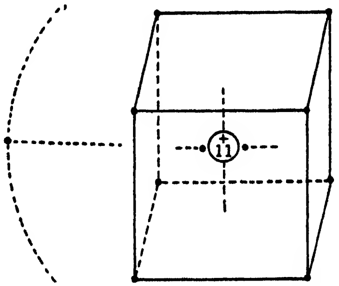

FIG. 2.—The Lewis-Langmuir Model of the Sodium Atom.

The tendency for electrons to group themselves into stable shells or octets is very pronounced; the sodium atom, for instance, which has one electron in excess of a stable shell, may lose its single valence electron to form a sodium *ion.* This is the process of ionization, and the ion itself is nothing but the kernel of the sodium atom. It has the characteristic inert gas structure and carries one positive charge. Fluorine, on the other hand, which has seven valence electrons, has a strong tendency to acquire one electron to form a stable outer shell.

The resulting fluorine ion also has the inert gas structure and carries a negative charge. When the compound sodium fluoride is formed, the single valence electron of the sodium goes to complete the outer shell of the fluorine atom, and the resulting molecule of NaF is essentially two inert gas atoms held together by electrostatic forces, since the two ions have opposite charges. When such a compound is melted or dissolved in water, it ionizes; and here the ionization process is nothing but the separation of ions which were already present in the molecules.

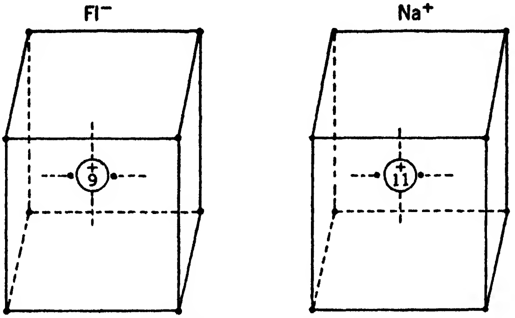

Fig. 3.—The Sodium Fluoride Molecule.

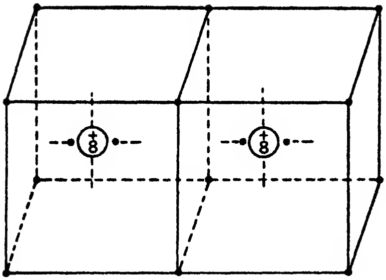

Fig. 4.—The Oxygen Molecule.

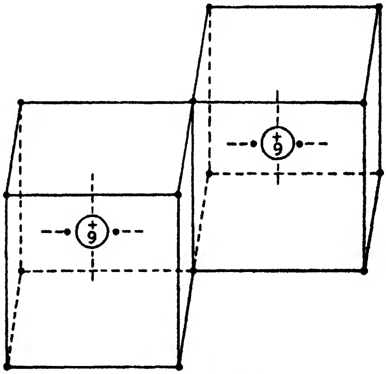

Fig. 5.—The Fluorine Molecule.

If a metal (such as copper) has two valence electrons, it may be singly or doubly ionized, as it loses one or both valence electrons. Aluminum has a valence of three; or, in other words, it loses three valence electrons when it forms a compound.

**Chemical Combination.**—Figures 3, 4, and 5 illustrate diagrammatically how chemical combination and association take place. The governing principle appears to be the tendency for the atoms to arrange themselves so that all the electrons enter into stable shells or octets; this may be done in two ways: either the atoms may share electrons as illustrated by the molecules $O_2$ and $F_2$, or electrons may be transferred from one atom to another as in the NaF molecule. In each of these instances, all the electrons enter into a stable shell; and after the molecule is formed, no more valence electrons are left. The valence of any atom, as determined by the number of electrons that it gains or loses when it combines with other atoms, is called *primary valence;* and this is the valence of elementary chemistry. In some cases atoms may associate by virtue of the oriented attractive forces between the atoms without the interchange or sharing of electrons. This force is called *secondary valence.* The atoms in the crystal lattice of copper, for instance, are held in position by their secondary valences.

**Metallic Atoms.**—From what has been said about the sodium and fluorine atoms (typical metal and non-metal), some generalizations can be made as to the fundamental difference between metals and non-metals. One property of a metal is the fact that it yields positive ions. The same statement may be put in different language by saying that metallic atoms in general tend to satisfy their primary valence demands by losing electrons. Conversely, non-metals are substances whose atoms tend to acquire electrons when they ionize. If an element is amphoteric, it simply means that the number and position of its valence electrons are such that under certain conditions its atoms may lose electrons in an effort to complete a stable shell, while under other conditions they may acquire electrons. In the first instance it will display metallic properties. In the second it will behave as a non-metal. Thus, in the compound $MnO_2$ the manganese atom has lost four electrons and has a valence of $+4$; in $KMnO_4$ it has lost seven electrons and has a valence of $+7$.

When a substance solidifies, the units of the crystal pattern are usually the same as the units of the liquid at the freezing point. If the atoms of the liquid are associated into molecules, then the space lattice of the solid will be built up of molecules. If the atoms in the liquid are free or unassociated, the crystal lattice will be built of the single atoms. The atoms of metals do not associate into molecules in the liquid or gaseous state as do the atoms of fluorine or oxygen, and as a consequence the space lattices of metals are *atomic* rather than *molecular* or *ionic.* This fact is of the utmost importance, and the most of the unique and characteristic properties of solid metals and alloys may be traced to the fact that their space lattices are of the atomic type.

The fact that metallic atoms do not associate into molecules in the gaseous or liquid state may be most simply explained, as we have noted, by considering the geometry of the Lewis-Langmuir atom models. Atoms lacking but one or two electrons to complete their outer shell (e.g., fluorine and oxygen; non-metals) can easily unite by sharing electrons so that every electron is in a stable shell. Atoms which have only one, two, or three electrons in the outer shell (metallic atoms) do not associate into molecules.

**Physical States.**—The units of matter (atoms and molecules) have three important properties upon which the physical state of the substance depends. The following discussion will deal with atoms—the same reasoning may be applied to molecules, although here the problem becomes more complicated.

1. *A force of attraction:* Atoms have a certain force of attraction for one another which seems to be of the nature of gravitational attraction. All atoms and molecules, like and unlike, exert this mutual attractive force, although the magnitude of the force may vary considerably. This force will be referred to as secondary valence.

2. *A force of repulsion:* This appears to be largely due to electrical forces. If atoms approach each other too closely, this force of repulsion comes into play and prevents closer contact, because atoms can never actually collide. "Collision" between atoms means a relatively close approach. The net result of the attractive and repulsive forces is that the atoms in any aggregate strive to maintain an average distance between centers, so that the two opposing forces are balanced. It may seem contradictory to assume that two atoms can at one and the same time exert both attractive and repulsive forces upon each other, but it is known that (1) there is some powerful force which absolutely prohibits actual contact between atoms, and (2) in a liquid, for example, there is some attractive force holding the atoms within a definite volume and preventing them from scattering in all directions. Probably the most logical explanation is that the repulsive force increases much more rapidly than the attractive force as the atoms approach one another closely.

3. *Thermal agitation:* All the constituent atoms (or atomic groups of molecules) of a substance at any temperature above absolute zero are in ceaseless motion, and this motion is *thermal agitation.* This may take the form of motion of translation, in which case the atoms move in straight lines until they "collide" with other atoms, motion of vibration with the atom vibrating about a fixed point, or motion of rotation which occurs when a molecule having a definite moment of inertia spins about an axis. All these various motions involve

energy, and the energy of thermal agitation is *heat*. In a solid the thermal energy is stored as energy of vibration; as the body is heated, more and more energy is absorbed by the vibrating particles, and they vibrate in longer paths. In a liquid most of the energy may be stored as translational energy; as heat is added to the liquid the atoms move faster, since they have more kinetic energy. The addition of heat is in each case attended by a more vigorous motion of the constituent atoms, and this we recognize as a rise in temperature.

Atoms in motion are continually colliding with one another (as closely as the repulsive forces will permit) with perfectly elastic impacts. Because of such impacts, a constant interchange of energy is taking place, and this is the mechanism of heat transfer by conduction.

Finally, the attractive forces of atoms appear to be oriented in certain directions and do not produce a uniform force field about the atom. As a result of these directional forces, atoms may be drawn into a regular arrangement or space lattice; the presence of a space lattice is characteristic of all crystalline material.

Solids are characterized by the fact that their constituent atoms are arranged in a regular space lattice or crystal pattern; i.e., all solids are crystalline. The entire mass may be a single crystal, in which case the outer configuration has the same shape as the lattice itself (perfect crystal), or the mass may be made up of a large number of randomly oriented crystals. In either case, however, the shape and dimensions of the space lattice are invariant and characteristic for a given kind of atom at a given temperature. Solids are sometimes spoken of as crystalline or amorphous (non-crystalline). However, amorphous "solids," such as glass, have properties resembling those of very viscous liquids; and the modern tendency is to class such substances as liquids and restrict the term "solid" to crystalline material. All solid metals and alloys are crystalline—there are no amorphous "solid" metals, so that at least for our purposes there will be no confusion in designating only crystalline material as solid.

Owing to the oriented attractive forces between atoms, the atoms of any metal will arrange themselves in their regular lattice pattern, provided that the temperature is below the melting point of the solid. Some of the types of space lattices characteristic of metals are illustrated in Figs. 6, 7, and 8. In the solid state, then, the atoms are held in fixed places by their attractive forces, and because of thermal agitation they vibrate about the fixed points at the lattice corners. Now as the temperature is raised, the amplitude of these thermal vibrations becomes greater and greater, until it approaches in magnitude the distance between the "rest position" of the atoms in the lattice. When this happens, we have reached the melting point—the lattice breaks down and the substance melts. Since the conditions are the same at all points of the lattice, fusion should take place at a single definite temperature, and for pure metals this is the case. In certain alloys, however, "foreign atoms" may be introduced into a space lattice, and a solid of this type usually has no definite melting point. This would also be expected because the lattice is not uniform, and consequently the breakdown or "melting" of the lattice takes place over a range of temperature.

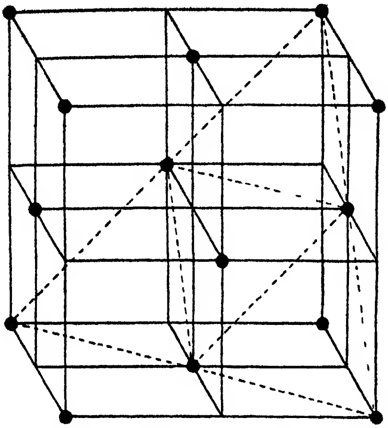
Fig. 6.—Face-Centered Cubic Space Lattice.

The broken lines lie in a crystallographic plane.

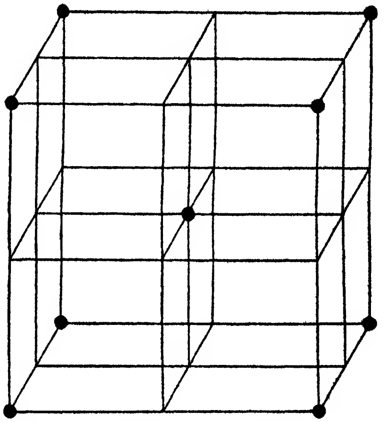
Fig. 7.—Body-Centered Cubic Space Lattice.

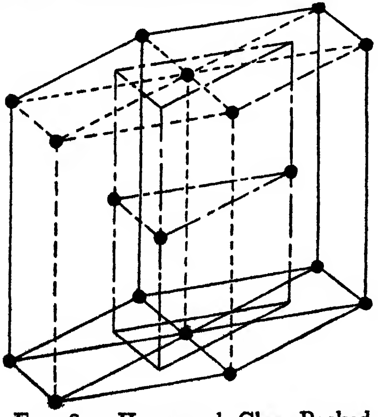
Fig. 8a.—Hexagonal Close-Packed Space Lattice.

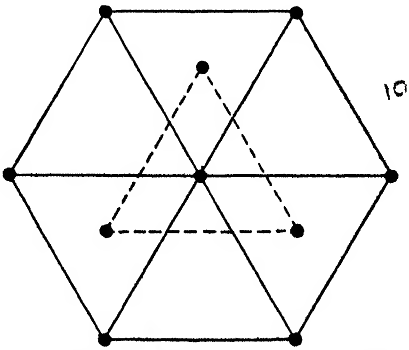
Fig. 8b.—Horizontal Section Through Hexagonal Close-Packed Space Lattice.

10

After the solid has been melted, the atoms are still held together by their attractive forces, but thermal agitation is too intense to permit crystallization. This condition is characteristic of a liquid. A large part of the thermal energy is in the form of translational motion of the atoms, and this random motion accounts for the diffusion which takes place in liquids.

Finally, when the temperature of the liquid is raised still higher, the thermal agitation becomes so great as to overcome entirely the attractive forces, and the atoms fly off from the main body of the liquid to form a gas, or the liquid vaporizes.

It must be borne in mind that the atoms in any system do not all have the same energy—what has been considered above is the average energy of the total number of atoms. There are always some atoms in a liquid which possess (momentarily) more than average energy. If such an atom happens to be near the surface, it may escape as a gaseous atom; likewise, if a gaseous atom happens to strike the surface of a liquid, it may lose some of its translational energy and be held to the body of the liquid. These two phenomena are responsible respectively for evaporation and condensation. Since those atoms which escape as a gas have more energy than the average, the effect of losing them is to diminish the average heat energy remaining in the body of the liquid, and as a result evaporation from a liquid lowers its temperature. To a much lesser extent, there is the probability that some of the atoms of a solid will possess more than the average thermal energy. In this case the atom breaks away from its position in the space lattice and moves about in the solid material, and it may even escape as a gaseous atom. This process whereby a gas is formed directly from the solid phase is called *sublimation.*

Some of the important facts concerning the various states or phases of matter may be summarized:

1. Solids are characterized by the fact that the constituent atoms are arranged in a definite space lattice or crystal pattern.
2. Liquids and gases are amorphous or non-crystalline. Amorphous "solids" are essentially highly viscous liquids.
3. Diffusion depends on temperature, and a rise in temperature means a higher rate of diffusion.
4. Diffusion takes place very readily in gases, quite readily in liquids, and even, to a certain extent, in solids.
5. The only difference between an atom of a solid and an atom of a liquid or gas is the difference in heat energy or thermal agitation.
6. Gaseous atoms or molecules tend to escape from both solids and

liquids (sublimation and evaporation), and the rate at which they escape increases as the temperature rises.

7. The tendency for gas to escape from a liquid or solid is a measurable quantity and is called vapor pressure (for a liquid) or sublimation pressure (for a solid).

8. When the vapor escaping from a liquid is restricted to a space above the liquid, a state of equilibrium is reached, when evaporation and condensation just balance. The space above the liquid is then said to be saturated, and this saturation pressure is independent of the pressure of other gaseous atoms or molecules in the space. The partial pressure of this saturated vapor is the vapor pressure of the liquid. A similar definition applies to sublimation pressure.

9. When a solid changes to a liquid, a certain amount of additional heat energy is required, which does not raise the temperature. This represents the energy difference between solid atoms and liquid atoms at the same temperature (the melting point), and the energy required in calories per gram of substance melted is called the heat of fusion of the substance.

10. If heat is continually added to a liquid, its temperature will rise; but the rise in temperature will be counteracted by the cooling effect of evaporation. When these two balance, the liquid boils, and its temperature will not rise any further. The rate at which the gaseous atoms escape from the vicinity of a liquid is determined by the pressure above the liquid, and therefore the temperature at which a liquid will boil increases with the external pressure. The temperature at which a liquid boils under a pressure of 760 mm. of mercury is called the normal boiling point.

11. The melting point of solids is influenced by pressure, but unless the pressures are very large the effect is negligible. This is due to the fact that solids and liquids are practically incompressible as compared with gases, which are easily compressed.

12. When a liquid vaporizes, the energy content of the gaseous atoms is greater than that of the liquid atoms at the same temperature. This accounts for the heat of vaporization, which is the number of calories of heat required to change 1 gram of liquid to gas at constant temperature. The heat of vaporization is not invariant but depends upon the temperature and pressure at which the vaporization takes place. The values given in tables are usually those for the heat of vaporization at the normal boiling point.

13. A solid has a definite shape and a definite volume. A liquid has a definite volume, but its shape is that of the containing vessel.

A gas has neither shape nor volume, but both are determined by the container.

14. Heat is a form of energy; and since it can exist only as energy of motion of the atoms or molecules of a material substance, the definition of the unit for measuring heat must specify some standard substance (cf. the definition of the calorie).

15. Temperature is the intensity of heat energy.

**Metallic Crystal Lattices.**—Those familiar with crystallography will recall that the various types of crystalline minerals may be classified as belonging to one of six crystal systems. Most metals belong to the isometric system. There are a few metals with hexagonal or tetragonal crystal systems, but none of the space lattices of pure metals belong to the orthorhombic, monoclinic, or triclinic systems. The accompanying table gives the crystal patterns of the more common metals, and Figs. 6, 7, and 8 illustrate the body-centered cubic, face-centered cubic (both isometric), and hexagonal close-packed space lattices. It will be noted that as a rule metallic crystal lattices are geometrically simple, and have a high degree of symmetry.

Since metallic atoms do not associate into molecules in the liquid state, the units which enter into the crystal lattice are single atoms, and this is the reason why the geometry of metallic space lattices is relatively simple. A substance such as a complex silicate mineral, on the other hand, may have such a complicated molecule that an intricate lattice pattern is required in order that the constituent molecules may fit in the proper places. The more complex minerals usually have the most complicated crystal patterns; the simpler compounds such as PbS or ZnS are characterized by a simpler lattice structure. In molecular and ionic lattices the molecules are usually so interlocked that it is impossible to identify the individual molecules which were present in the liquid. A given atom may be thought of as belonging to any one of a number of adjacent molecules. This is illustrated in the simplest case by a diagram of the NaCl space lattice (Fig. 9). Here each sodium atom (ion) is surrounded by six equidistant chlorine atoms, any one of which might be the partner of the sodium atom. Similarly, each chlorine atom is surrounded by six equidistant sodium atoms. Considerations such as this lead to the statement that the term "molecule" has very little meaning when the substance is in the solid state, unless we think of the molecule as being the entire crystal. All chemical compounds and those elements whose atoms associate in the liquid state have molecular or ionic lattices. NaCl has a typical ionic lattice.

Another outcome of the simplicity of metal crystal patterns has to do with the possibility of producing amorphous "solid" metals. Any liquid will crystallize upon freezing, if the proper conditions are present. However, it is often possible to cool through the freezing point so rapidly that the molecules do not have an opportunity to arrange themselves into a crystal pattern, and the result is that an amorphous solid or "glass" is formed. Glass, obsidian, some lavas, and slags are examples of amorphous solids. From the standpoint of atomic structure, such a substance is nothing but an undercooled liquid, in which the atoms are oriented at random (not arranged in space lattice) but in which the cohesive forces are strong enough to give the substance the characteristic appearance of solid material. Amorphous solids are produced only from substances which possess rather large molecules, the reason being simply that it is much easier to inhibit the formation of a crystal composed of cumbersome molecules than to prevent the formation of an atomic space lattice such as metals have. No specimen composed entirely of solid amorphous metal has ever been prepared; and, although some theories postulate the existence of small amounts of amorphous metal in a crystalline aggregate, there is no doubt that practically all the substance of any solid metal or alloy is crystalline.

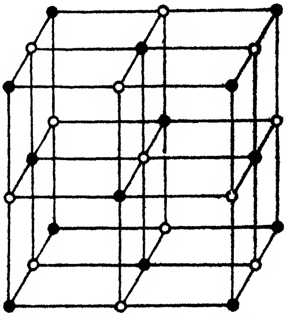

Fig. 9.—The NaCl Space Lattice.

As would be expected, amorphous solids have no definite melting point. As they are heated, they gradually soften until they finally become liquid ("fluid" would be a better term). Likewise, these amorphous substances have no heat of fusion.

Before leaving this subject, it will be well to call attention to another characteristic of metallic crystals. In the diagrams of metallic space lattices (Figs. 6, 7, and 8), the atoms are shown occupying the corners of hypothetical prisms; and these atoms are vibrating back and forth about their rest positions. As a matter of fact, the dots represent the kernels of the atoms rather than the atoms themselves. The valence electrons are so loosely held to the atoms that they are not necessarily constrained to follow the motion of the atom. Because of the electrostatic pull of the kernels on the valence electrons, they are kept uniformly distributed throughout the mass of the solid, but in any solid metal there is a swarm of loosely bound valence electrons which move freely throughout the entire mass, and these are called *free electrons*. The model of the lithium space lattice (Fig. 10) shows how the single valence electrons are located with reference to the kernels. These, however, do not necessarily vibrate about fixed positions as the diagram would indicate, but move freely about inside the crystal.

An electric current is a directed flow of free electrons, and only those substances which possess free electrons can conduct an electric current. Solids such as compounds, or non-metallic elements (since non-metallic atoms usually associate into molecules), are non-conductors, since, as we have seen, in the formation of molecules the valence electrons of the elements are tied up in stable shells, and no longer exist as free or valence electrons. A little consideration will show that, as a class, all metals should be good conductors, whereas almost all other substances should be non-conductors. This is essentially true. Because of the almost universal application of this rule, electrical conduction by the transfer of free electrons is called first-class, or metallic conduction, as distinguished from second-class, or electrolytic conduction.

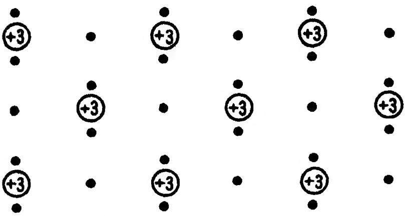

FIG. 10.—Section Through the Lithium Space Lattice.

Some compounds are metallic conductors, and here it may be assumed that the process of chemical combination has not been perfect—not all the electrons are tightly held in stable shells, and consequently some free electrons are available to carry the current. Likewise, non-metals may be electrical conductors if their space lattice is such as to permit the presence of free electrons—graphite is an example of such a non-metallic "metallic" conductor; however, such exceptions are rather rare, and the first-class conductors are generally metals.

**Isotropic and Anisotropic Substances.**—Certain substances have directional properties; these substances are called anisotropic. Substances whose properties are the same in all directions are isotropic. For example, the electrical conductivity of a crystal may be greater if the current passes parallel to one of the crystal axes than if it passes at right angles to this axis. Since the properties of materials depend directly upon internal structure, it follows that liquids, gases, and amorphous solids should be isotropic, since the atoms are oriented at random and are not lined up in a crystal lattice. In crystals, the constituent atoms are arranged in a definite pattern, and for this reason all single crystals are anisotropic—some writers use the terms "isotropic" and "anisotropic" as synonymous with "amorphous" and "crystalline."

Single crystals of metals are anisotropic, but most metal specimens are effectively isotropic, since they are made up of a great number of small crystals oriented at random. Although each of the small crystals is anisotropic, the properties of the aggregate are the same in all directions and represent the average properties of the individual crystals. However, polycrystalline metals and even glass (amorphous solid) may show directional properties, but in this case the anisotropic effect is usually the result of mechanical work done on the material.

**Atomic Mass and Volume.**—The atom was originally thought to be a solid, indivisible particle, and in diagrams of space lattices, etc., the atoms are conventionally represented as small spheres. However, it has been proved that atoms are not solid particles and that the interior of the atom is largely empty space. If an atom consists of a nucleus surrounded by rotating electrons, the conception of the volume of a single atom must necessarily be rather vague, and the volume of a single atom is best regarded as a sphere of influence or as a force field. The diameter of an atom of hydrogen (diameter of the orbit of the rotating electron) is about fifty thousand times the diameter of an electron, and the nucleus, or proton, has a smaller diameter than the electron.

Atoms correspond in many respects to miniature solar systems; if the sun is regarded as a nucleus and the planets as electrons, there results a conception that illustrates fairly accurately the relative magnitude of atoms and their constituent parts, and emphasizes the preponderance of empty space within the atoms.

The mass of an atom is contained almost entirely in the nucleus. In the hydrogen atom the mass of the electron is only about 1/1700 of the mass of the atom, and in the heavier atoms the mass of the planetary electrons is a still smaller fraction of the total mass.

It is difficult to appreciate the extreme minuteness of atoms and their nuclei and electrons. If an atom of copper and a drop of water were assumed to expand at equal rates, the drop of water would be as large as the earth before the nucleus of the copper atom became visible (about 0.01 inch in diameter). In a normal crystal of tungsten (specific gravity 19) there are about one hundred million atoms to the linear inch.

Although the actual volume of an individual atom cannot be defined or measured, it is possible to compute the volume dominated or "occupied" by a single atom in an aggregate. The term *atomic volume* is defined as the volume in cubic centimeters of a gram-atomic weight of a substance. Since the reciprocal of the specific gravity is the specific volume, or the number of cubic centimeters occupied by 1 gram of a substance, the product of the specific volume by the atomic weight gives the atomic volume. In other words, the atomic volume is obtained by dividing the atomic weight by the specific gravity. The atomic volumes of the elements give a series of numbers which are proportional to the actual volume occupied by each particular atom. To obtain the actual volume, the atomic volume must be divided by $6.06 \times 10^{23}$ (Avogadro's number = the number of atoms in a gram-atomic weight).

**Allotropy.**—Some metals (or other crystalline substances) may have more than one type of crystal lattice, and such metals are said to have two or more allotropic modifications. The change from one form of crystal lattice to another takes place at a definite temperature and is accompanied by an energy change; in fact, an allotropic modification represents a change of phase just as the freezing of a liquid does, and the heat of transformation is exactly analogous to the heat of fusion. Allotropic modifications of a metal differ in their physical properties. Alpha iron (stable below 760° C.) is magnetic and crystallizes in a body-centered cubic lattice; gamma iron (stable above 890° C.) is non-magnetic and has a face-centered cubic lattice.

Since the physical properties of a substance depend to a large extent upon its atomic structure, it seems reasonable to associate allotropic modification with changes in crystal structure; but this association is not always obvious. Between alpha and gamma iron (temperature range 760–890° C.) there exists another allotropic modification, beta iron. When alpha iron alters to beta iron, energy is absorbed, and a change in physical properties takes place. Beta iron is non-magnetic, for example, but alpha iron is magnetic. The alteration of properties and the heat of transformation point to an allotropic modification, and yet investigation reveals that alpha and beta iron crystallize identically in the body-centered cubic system. Although the present methods of analysis reveal no difference in the crystal structure of alpha and beta iron, it would be very difficult to explain the heat of transformation and the sudden change in properties without assuming some modification of the internal structure. Consequently, this transformation is called an allotropic change, even though the alteration of the crystal pattern has not been definitely established.

## TABLE 1

### LATTICE PATTERNS OF THE COMMON ALLOY-FORMING ELEMENTS *

| Element | Lattice Constants | Molecules | Element | Lattice Constants | Molecules |
|---|---|---|---|---|---|
| *Face-Centered Cubic (Isometric)* | | | | | |
| Ag | 4.0776 | 4 | Ir | 3.823 | 4 |
| Al | 4.0402 | 4 | Ni (β) | 3.517 | 4 |
| Au | 4.0702 | 4 | Pb | 4.941 | 4 |
| C (Diamond) (18° C.) | 3.5597 | 8 | Pd | 3.879 | 4 |
| Ca | 5.56 | 4 | Pt | 3.9142 | 4 |
| Co (α) | 3.554 | 4 | Rh | 3.7944 | 4 |
| Cu | 3.608 | 4 | Si | 5.418 | 8 |
| Fe (γ) (1100° C.) | 3.63 | 4 | Sn (α, gray) | 6.46 | 8 |
| | | | Sr | 6.075 | 4 |
| *Body-Centered Cubic (Isometric)* | | | | | |
| Ba | 5.015 | 2 | Li (−173° C.) | 3.46 | 2 |
| Cr (α) | 2.878 | 2 | Mn (α) | 8.894 | 58 |
| Cr (γ) | 8.717 | 58 | Mo | 3.1401 | 2 |
| Fe (α) | 2.86106 | 2 | Na (−173° C.) | 4.24 | 2 |
| Fe (β) (800° C.) | 2.90 | 2 | V | 3.011 | 2 |
| Fe (δ) (1425° C.) | 2.93 | 2 | W (α) | 3.1583 | 2 |
| K | 5.333 | 2 | | | |
| *Simple Cubic (Isometric)* | | | | | |
| Mn (β) | 6.300 | 20 | W (β) | 5.04 | 8 |
| *Hexagonal Close-Packed (Hexagonal)* | | | | | |
| Be | 2.2679, 3.5942 | 2 | Ni (α) | 2.66 , 4.29 | 2 |
| Cd | 2.973, 5.606 | 2 | Ti | 2.951, 4.692 | 2 |
| Co (β) | 2.514, 4.105 | 2 | Zn | 2.649, 4.930 | 2 |
| Cr (β) | 2.717, 4.418 | 2 | Zr | 3.223, 5.123 | 2 |
| Mg | 3.203, 5.196 | 2 | | | |
| *Simple Hexagonal (Hexagonal)* | | | | | |
| C (Graphite) | 2.48, 6.78 | 4 | Te | 4.495, 5.912 | 3 |
| Se | 4.337, 4.944 | 3 | | | |
| *Hexagonal Rhombohedral (Hexagonal)* | | | | | |
| As | 4.151 | 2 | P ("metallic") | 5.14 | 2 |
| Bi | 4.749 | 2 | Sb | 4.501 | 2 |
| Hg (−46° C.) | 2.997 | 1 | | | |
| *(Tetragonal)* | | | | | |
| Mn (γ) Face-centered tetragonal | 3.774, 3.526 | 4 | Sn (β, white) Double body-centered tetragonal | 5.818, 3.174 | 4 |

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* Hodgman: Handbook of Chemistry and Physics, Edition 19, 1934, Chemical Rubber Publishing Co., Cleveland, Ohio. Reprinted by permission.

Explanatory note: The column headed "Molecules" refers to the number of molecules (atoms in all cases in this table) contained in a unit cell of the lattice. Figures in parentheses indicate the temperature at which the lattice constants were determined.

In all the isometric crystals the figure in the column headed "Lattice Constants" gives the length of the side of the unit cube. In the simple hexagonal and close-packed hexagonal crystals the first figure gives the side of the hexagonal unit prism, and the second figure gives the "altitude" of the prism. In the hexagonal rhombohedral lattices the number refers to the length of one side of the unit rhombohedron, and in the tetragonal lattices the first number gives the length of the two equal sides, and the second number gives the length of the third side. All measurements are in angstrom units (1 angstrom unit $= 10^{-8}$ cm.).

## CRYSTAL GRAINS

For the benefit of those who are unfamiliar with the properties of crystals, it might be well to point out a few facts concerning them before taking up the subject of metallic crystals or crystal grains.

In ordinary usage, the term "crystal" is often misapplied. "Clear as a crystal" is a common phrase, and to many people the term "crystal" connotes transparency. Crystallinity *per se* has nothing to do with transparency; a crystalline substance, such as calcite, may be transparent; but metallic copper, which is also crystalline, is densely opaque. Glass is transparent, and it is non-crystalline.

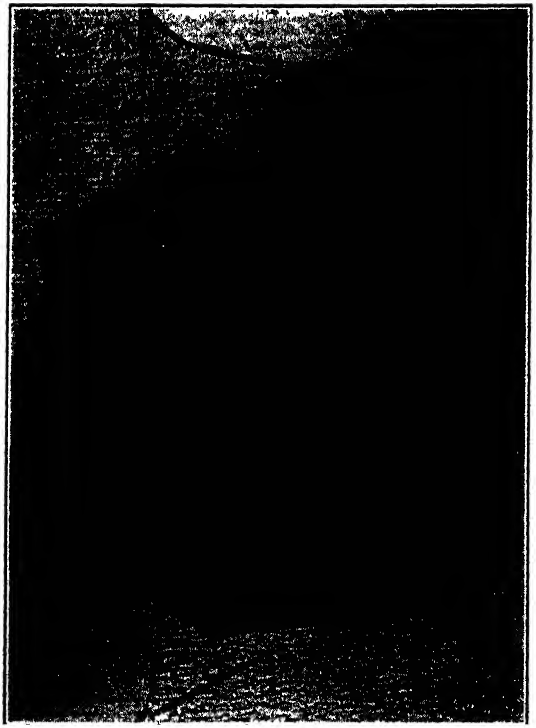
Many people also associate the term "crystal" with the striking geometric forms of certain natural minerals. A section of copper wire is as truly crystalline as the largest and most perfect tourmaline crystal. The difference is that the tourmaline has formed a single large crystal whose exterior form reproduces the lattice pattern, whereas the copper wire is made up of a large number of tiny crystals. Large, perfect crystals are very rare among metals—most individual metallic crystals are microscopic in size.

Often, when a piece of metal fails in service, it is said that it "crystallized"—particularly when the fracture shows a coarse-grained structure. This, of course, is an erroneous statement, because the metal always had been crystalline.

For present purposes, a crystal may be defined as *a homogeneous solid whose constituent atoms or molecules are arranged in a definite and repeating geometric pattern.* Note that no restriction is placed on the size of the crystal or its chemical composition.

**Polished Surfaces.**—In the metallographic examination of metals and alloys a section of the surface is ground and polished until it is perfectly flat and free from all scratches and pits. The polishing produces a "flowed layer" of metal on the surface which has a mirror-like appearance. This prepared surface is then treated with an etching reagent which dissolves away the flowed layer and reveals the structure of the metal.

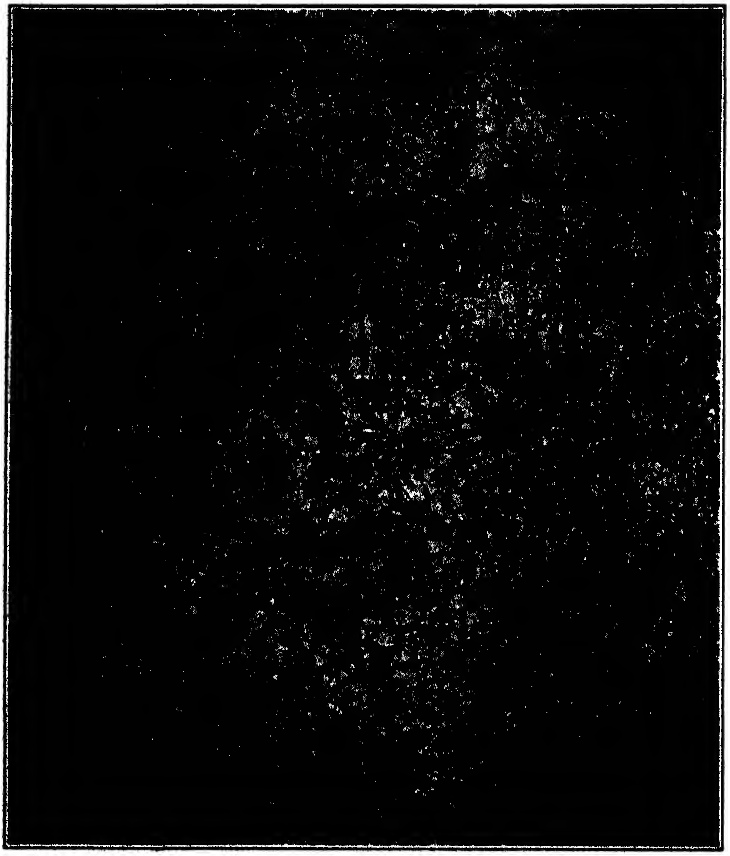
When a properly polished and etched sample is examined under a microscope, it appears to have a cellular structure as if it were composed of closely fitting polyhedral blocks. These small units are individual crystals of the metal or alloy and are called *crystallites, crystal grains,* or simply *grains.* In a pure metal only one kind of grain is present; in alloys there may be two or more distinct types of grains.



*(Courtesy The Dow Chemical Company, Midland, Michigan)*

FIG. 11*a*.—Photomicrograph of Pure Magnesium. (× 200)

As a crystal forms in a liquid, it grows by accretion, and the growth takes place in such a way that the exterior of the crystal assumes its characteristic form. However, if a large number of crystals form simultaneously, each will interfere with the growth of some of the others; and the final shape of any crystal will depend upon the space available rather than upon the geometric form of the crystal pattern. Perfect crystals whose growth has not been hindered in any way are called *idiomorphic* crystals; crystals whose exterior shape is due to the available space are *allotriomorphic* crystals. The grains in metals and alloys are usually allotriomorphic crystals. Figure 11 shows examples of various crystal grains as they appear under the microscope.



*(Courtesy The American Brass Company, Waterbury, Connecticut)*

Fig. 11*b*.—Photomicrograph of Pure Copper.

**The Nature of Crystal Grains.**—All solid metals (and alloys) are composed of these crystal grains. All commercial metals and alloys are polycrystalline; that is, they are composed of large numbers of microscopic crystal grains. Under special conditions, metal objects consisting of a single grain may be prepared in the laboratory, and these single-crystal specimens have been studied by various investigators in an effort to learn more about the properties of metallic grains. A solid metal, no matter how it has been formed—whether by the freezing of a liquid, condensation of a gas, deposition by an electric current, or by the pressing together of particles of a solid metallic powder—has a structure composed of metallic grains. The size of the grains depends upon many factors, such as the rate of freezing of a liquid, the current density and the nature of the electrolyte in electrolytic deposits, and the type and extent of the mechanical working (hammering, forging, etc.) done upon a solid metal.

Cast and hot-worked metals are composed of equiaxed grains having random orientation; that is, the grains have the same average diameter in all directions, and the crystal axes of the grains are disposed in all possible directions. In cold-worked metals, however, the grains are elongated; that is, one dimension of the grains is much greater than the other two, and the long dimension points in a direction determined by the deforming stress. In a cold-rolled sheet, for example, the long dimension of the grains is parallel to the direction of the rolling, since the cold-rolling has the effect of "rolling out" the individual crystals, much as a cook would roll a spherical piece of dough into a long strip with a rolling pin. The fact that a metal has elongated grains does not necessarily mean that the grains are not still randomly oriented, although it appears that in severe cold-working the metal grains actually are forced to line up in such a way that all grains tend to have their principal crystal axis pointing in a definite direction. Such a preferential orientation tends to give the metal object vectorial or anisotropic properties, instead of the effectively isotropic properties of a metal composed of randomly oriented grains. Under certain conditions, electrolytically deposited metal will contain grains which are elongated and which show preferential orientation—evidently the electric current causes the grains to grow more readily when oriented in a definite direction. Other electrolytic deposits, however, are composed of equiaxed, randomly oriented grains.

The size, shape, and orientation of the grains in any metallic object have a pronounced effect upon its physical properties.

Recent studies[1] of crystal structure have indicated that individual metallic crystals or grains do not consist of a continuous and homogeneous lattice, but rather that each grain is a mosaic of small, uniformly oriented, crystalline blocks. These blocks are estimated to be about 50–100 atom diameters on an edge. The nature of the mosaic structure in metal crystals is a matter of great importance in the

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[1] Greninger, Alden B.: Crystallographic Uniformity of Lineage Structure in Copper Single Crystals, A.I.M.E. T.P. 596 (1935).

study of physical metallurgy, but the subject has not yet been completely investigated.

Most metals begin their crystallization as skeleton crystals or dendrites ("fir-tree" crystals). When allotriomorphic crystals are formed, the growth of the skeleton is stopped, and further growth must take place by filling in the spaces between the axes of the dendrites. Figure 12 illustrates the relation of the original dendrites to the final grains. Under certain conditions large natural crystals of metals (iron, for example) may be obtained, and these often have the dendritic form.

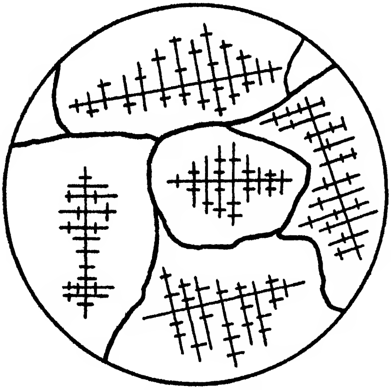

Fig. 12.—Relation of Primary Dendrites to Crystal Grains.

**Evidence of the Crystallinity of Metal Grains.**—There is no longer any doubt that metallic grains are individual crystals, but it would not be out of place to discuss briefly some of the phenomena which led to the discovery of this fact. X-ray analysis, which has presented the most conclusive evidence to establish the crystallinity of metals, is still the most widely used method for studying the crystal structure of metals and alloys.

The anisotropism of metallic grains is well illustrated by the action of the etching reagents used in metallographic examination. The chemical action takes place most rapidly in certain preferred directions. If this direction is not normal to the plane of the polished surface, the etching leaves the exposed face of the grain inclined to the original surface. The greater the inclination, the smaller is the amount of light reflected back into the tube of the microscope, and consequently the darker the grain appears. Suitable etching causes the various grains of a pure metal to appear to have different colorations. This is due to the etching effect just mentioned, and it is called grain-contrast etching as distinguished from grain-boundary etching.

If the etching is prolonged sufficiently, this preferential attack results in the formation of small pits or etch figures on the grain surfaces. These usually have geometric shapes, and all the etch figures on a given grain are similar. Etch figures and grain-contrast etching are direct evidence of the facts that metallic grains are individual crystals (anisotropic) and that the grains have a random orientation.

Shortly after the discovery of X-rays, Professor von Laue at Zurich was speculating upon the unknown nature of these rays. If, as had been suggested, they were electromagnetic waves similar to light waves, then it should be possible to obtain diffraction patterns by passing a beam of X-rays through a suitable diffraction grating. It was suspected that the wave lengths of X-ray beams were so short, however, that they would not be affected by the relatively coarse diffraction gratings which were used with beams of visible light. Von Laue decided that if it were true that the atoms of crystalline objects were lined up in regularly spaced planes, and if the X-rays were electromagnetic waves, then it should be possible to obtain diffraction patterns by passing X-rays through a crystal. Working with "white" (i.e., not "monochromatic") X-rays and a crystal of zinc sulfide, Friedrich and Knipping, who were associates of von Laue, finally obtained a geometrical diffraction pattern on a photographic film placed behind the crystal. This and further work abundantly confirmed von Laue's assumptions both as to the nature of X-rays and as to the spacing of atoms in crystal lattices.

At first it was thought that X-ray analysis could be applied only to single, carefully oriented crystals, but later Hull, and Debye and Scherrer found that the method of X-ray analysis could be applied to the study of crystalline powders containing a large number of randomly oriented crystals, or to the study of such materials as polycrystalline metals.

The development of X-ray analysis has made it possible to determine the lattice pattern and lattice dimensions (see Table 1) of the various types of crystals found in metals and alloys. Study of polycrystalline metals also reveals whether crystals are randomly or preferentially oriented.

As an example of how the distance between atomic planes may be calculated from observed X-ray data, let us briefly consider Bragg's law for the diffraction of X-rays in a crystal. Bragg explained the phenomenon on the basis of the reflection of the primary ray from the lattice planes, and his law is derived as follows:

When a monochromatic beam of X-rays impinges on a crystal grating, a small fraction of the beam is reflected by each crystal plane so that the angle of incidence equals the angle of reflection. The intensity of a single reflected beam is very low; but if the conditions are such that many beams reinforce one another, the total reflected beam may be quite intense. The condition for reinforcement is that the reflected beams must be in phase, or that the total path of any two reflected beams must differ by a whole number of wave lengths.

Figure 13 shows a section through a crystal lattice with reflection of the incident beam taking place from two crystal planes (*AA′* and *BB′*).

Here the beam *CDKE*, incident at the angle $\theta$ is reflected from *AA′* along *DG* and from *BB′* along *EH*. *GH* is perpendicular to *DG* and *EH*; *FK* is perpendicular to *DE*.

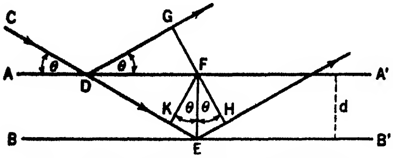

FIG. 13.—Reflection of X-Rays.

The condition for reinforcement is that the paths *DG* and *DEH* shall differ by a whole number of wave lengths, and therefore, since $DG = DK$, we have $KEH = n\lambda$, where $n$ is an integer and $\lambda$ is the wave length of the beam. But

$$KEH = 2d \sin \theta \tag{1}$$

where $d$ is the separation, and thus we are led to Bragg's law:

$$n\lambda = 2d \sin \theta \tag{2}$$

Since $n = 1$ for the strongest reflected beam (first-order reflection), if $\lambda$ is known, the measurement of the angle $\theta$ makes it possible to calculate $d$.

X-rays, besides being used as mentioned above (X-ray analysis), are also used in *radiography*, in which the interior of castings and forgings may be photographed in exactly the same way as fractured bones. Radiography shows the presence of such defects as blow holes, cracks, flaws, inclusions, and faulty welds, while X-ray analysis determines the characteristics of submicroscopic lattice structures. Sections thicker than 4 inches will ordinarily not be penetrated by X-rays, and for thicker sections the more penetrating (shorter-wave-length) gamma rays from radioactive substances are used in radiographic examination.

## GRAIN BOUNDARIES

Figure 14 is a diagram illustrating the formation of crystal grains in molten metal. As the metal is cooled to its freezing point, small groups of atoms begin to assemble into crystalline form. These small crystals or nuclei are scattered throughout the body of the liquid, are oriented in all possible directions, and, as solidification continues, grow by accretion of atoms from the surrounding liquid. Since these crystals are suspended in a liquid, their growth is not impeded; and they are idiomorphic. Often they take the form of dendrites or skeleton crystals. Now, as crystallization continues, the crystals begin to touch one another, their free growth is hampered, and the liquid remaining in the interstices freezes to the adjacent crystals until solidification is complete. The solid is now composed of allotriomorphic crystals or grains—irregular polyhedra which show no vestige of their original form—and each grain is separated from adjacent grains by a *grain boundary*. In photographs the grain boundaries usually appear quite broad, and this is due to the fact that they are more rapidly attacked by the etching reagent than the bodies of the crystallites are. Actually the visible grain boundary is a comparatively deep

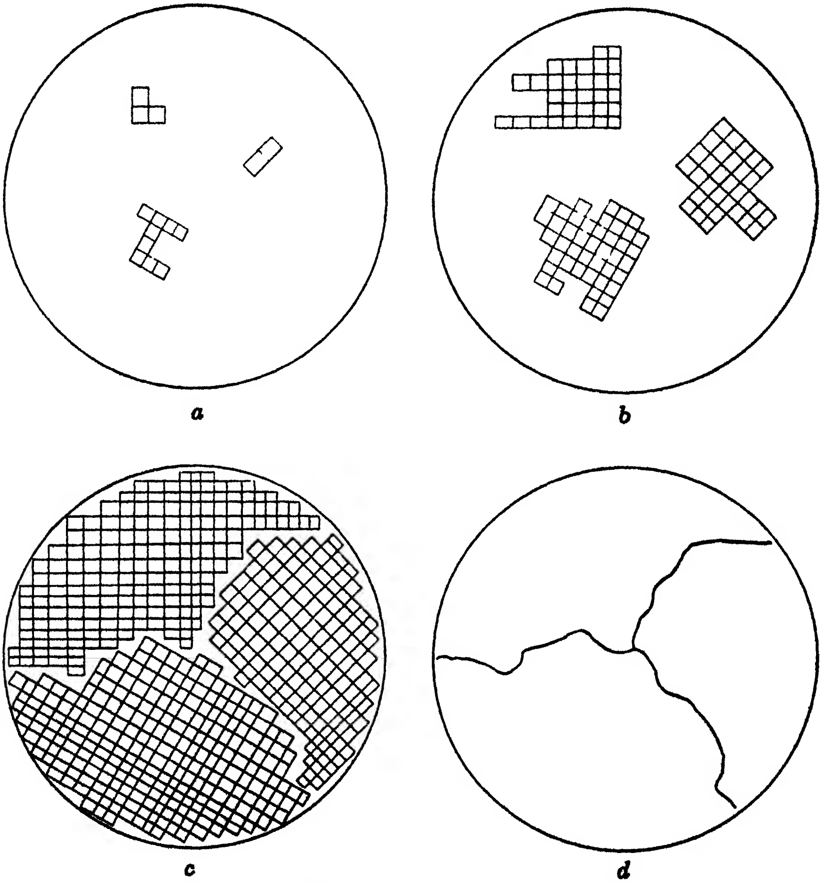

FIG. 14.—Diagram Illustrating the Formation of Crystal Grains.

groove. The true grain boundary is probably only a few atom diameters in thickness and hence would be invisible.

From Fig. 14 it is apparent that a grain boundary is a discontinuity between two crystal lattices, for, if the two lattices had the same orientation, they would merge into a single crystallite, and the grain boundary would disappear. If the two lattices are out of alignment, one of three conditions must obtain: (1) the atoms of the boundary are pulled into either one or the other of the lattices, leaving a void between the grains; or (2) the atoms in the boundary belong to a distorted lattice which acts as a bridge between the two stable lattices; or (3) the atoms in the boundary constitute a phase which differs from the material in the grains. Certain properties of metals point to (3) as being the most likely to give the true picture.

At ordinary temperatures most metals exhibit a transcrystalline fracture; that is, when the metal is broken in tension, the fracture takes place through the grains rather than at the grain boundaries. This would indicate that the material at the grain boundaries is stronger than the crystalline grains, and would appear to rule out the first condition mentioned in the preceding paragraph. However, it also is possible to cause metals to fracture at the grain boundaries if the temperature is high enough; and when this happens, the load required to cause failure is a function of the time—the longer the force is acting, the smaller the force required. This behavior is typical of amorphous substances such as pitch or glass. Lead and a few other metals show this intergranular fracture at room temperature.

Certain types of etching result in much more vigorous chemical action on the grain boundaries than on the crystal grains (grain-boundary etching), which leads to the belief that the properties of the two substances differ. It is beyond the scope of this work to consider all the evidence that has been collected to show that the material at the grain boundaries is different from the material in the grains themselves. There is still considerable difference of opinion as to exactly what this grain boundary material is, but all agree that it is something with properties which do not resemble those of the crystalline material in the metal grains. There is also no doubt that this intercrystalline phase has a marked effect upon the physical properties of the metal.

Bielby[2] postulated that the material between crystal grains was an amorphous metal. His "amorphous cement" theory has been ex-

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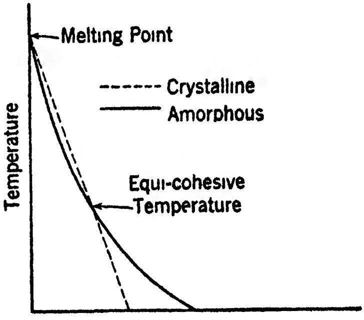
[2] Jeffries and Archer: The Science of Metals, McGraw-Hill Book Co., 1924, New York.

panded and modified by Rosenhain and Jeffries,[3] and it can be used to give a rational explanation of many of the observed properties of metals. Tammann[4] states that the grain boundary material may consist of low-melting impurities which are found in even the "purest" metals. Maier[5] prefers to refer to the intercrystalline material simply as the $\omega$ phase, and he attributes to it certain specifications which fit in with its observed properties. This $\omega$ phase differs in many important respects from the amorphous cement which was considered in earlier theories. As an example of how one of these theories may be applied to interpret the physical behavior of metals, let us briefly consider one of the consequences of the amorphous cement hypothesis (after Jeffries and Archer).



*(After Jeffries and Archer)*

FIG. 15.—The Variation of the Cohesion of Metals with Temperature.

Lead and a few other materials exhibit an intergranular fracture at room temperature; or when the metal is pulled apart, the rupture takes place at the grain boundaries rather than through the grains. Not only is this true for a few metals, but all metals exhibit this intergranular fracture if the temperature is high enough. The curves in Fig. 15 give an explanation of this phenomenon on the basis of the assumed properties of the intergranular cement. At the melting point, the cohesion (essentially the elastic limit) of both the crystalline and amorphous metal is zero; but, as the temperature drops, the cohesion of the two species of metal changes according to the curves shown. At the *equicohesive temperature*, the curves intersect; and at this point the strengths of the crystalline and amorphous varieties are equal. Below this point the amorphous cement is stronger, and the metal has a transcrystalline fracture. Above the equicohesive temperature the crystalline metal is stronger, and the fracture is intergranular as if the grains were being pulled out of a soft matrix. The equicohe-

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[3] Jeffries and Archer: The Science of Metals, McGraw-Hill Book Co., 1924, New York.

[4] From "A Textbook of Metallography" by Gustav Tammann, translated by R. S. Dean and L. G. Swenson (1925), Chemical Catalog Co. (Reinhold Publishing Corp.), New York.

[5] Maier, Charles G.: Theory of Metallic Crystal Aggregates, American Institute of Mining and Metallurgical Engineers, T.P. 701, 1936.

sive temperature is difficult to determine accurately, since it varies with the time rate of loading—corresponding very closely to the equicohesive temperature is the *recrystallization temperature.* This likewise is not a definite point which may be accurately determined; but, as a first approximation, it may be assumed that there is a definite temperature characteristic of a given metal which may be called either the recrystallization temperature or the equicohesive temperature. The significance of the recrystallization temperature will be discussed later.

## PLASTIC FLOW

The manner in which metals and alloys respond to external stresses constitutes their most important physical property. Upon it depend the strength, hardness, ductility, malleability, toughness, and all the other mechanical properties characteristic of metallic substances.

Many metallic shapes are formed by mechanical working; i.e., rails, beams, and plates are rolled to the proper shape and dimensions; crankshafts, axles, and other machine parts are forged; tanks, tubes, and other light shapes are spun or drawn. All such processes involve the mechanical deformation of a solid metal or alloy to give the desired form to the finished product. This property of plastic flow, or the ability of solid material to be permanently deformed without rupture, is unique to metals and alloys, and is one of the fundamental reasons for the universal use of metallic substances as materials of construction. Not only can shapes be produced cheaply and on a large scale by the methods mentioned above, but deformed or mechanically worked metal is in most respects much superior to the cast metal from which it was produced.

**Slip Planes.**—Examination of Figs. 6, 7, and 8 shows that, in the metallic crystal, the atoms are spaced at definite intervals in a repeating pattern and are held in position by the equilibrium of the cohesive and repulsive forces acting between the atoms. The lines connecting the atoms in these diagrams may be thought of as representing atomic bonds, and these bonds act like springs which resist both tensile and compressive forces. When any metallic specimen is subjected to a small stress, the atomic bonds are stretched or contracted. If the external stress is tensile, for example, those bonds normal to the force are in compression, and the bonds parallel to the force are in tension. The atomic bonds behave like springs; while the force is acting, the specimen is deformed. However, as soon as the force is removed, the metal regains its original shape. This deformation, which exists only while the stress is acting, is called *elastic deforma-*

*tion*, and the maximum stress which will permit this type of deformation is the *elastic limit* of the material. When the elastic limit is exceeded, some of the atomic bonds begin to rupture, and the specimen is permanently deformed; that is, it does not return to its original shape after the deforming stress has been removed.

Figures 6, 7, and 8 show that the atoms of a crystal are grouped into natural planes (such as the cube faces in the cubic systems) which are called crystallographic planes. The density of these planes is higher than the density of the crystal; that is, a crystallographic plane contains more atoms per unit area than a plane passed at random through the body of the crystal. Because of the greater density of atomic population, the cohesive forces holding the atoms of a given plane in position are stronger than the forces holding two planes together. As a result, when a crystal is subjected to a stress greater than its elastic limit, the bonds holding the planes together are the first to yield; and deformation takes place by a slipping between two adjacent planes. These planes are *slip planes*, and all permanent deformation of metals and alloys must take place by this slipping motion or "faulting" along slip planes. A single crystallite may have several systems of slip planes intersecting one another; within a given crystal, however, all the slip planes of any system must be parallel.

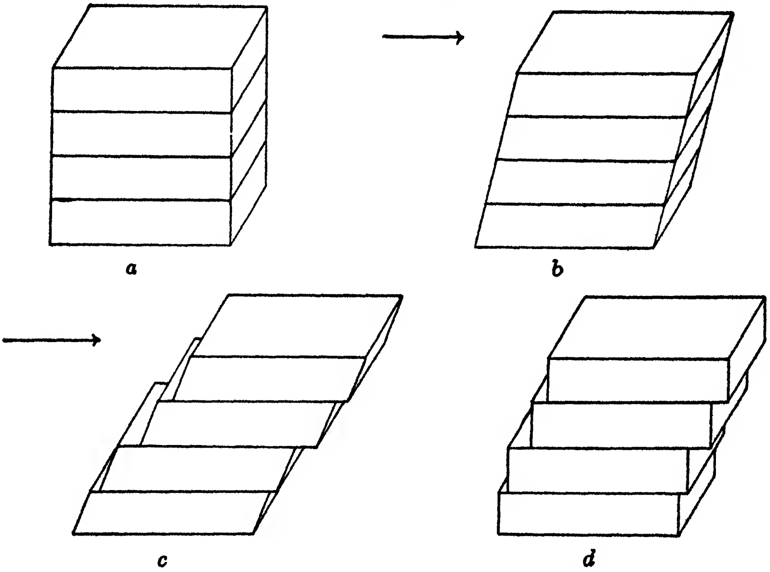

Fig. 16.—Diagram to Illustrate the Deformation of a Simple Cubic Lattice.

The sketches in Fig. 16 represent the action of a deforming force on a simple cubic lattice. In (*a*) the normal crystal form is shown; in (*b*) the entire lattice has been distorted, but the stress is still under the elastic limit. If the stress were removed at this point, the lattice would resume the shape it had in (*a*). As the stress exceeds the elastic limit, motion along the slip planes begins, and the lattice assumes the form (*c*). Finally, when the force is removed, the elastic stresses in the individual blocks are relieved, and the lattice appears as in (*d*). The individual blocks in the strained lattice may be several hundred to several thousand atom diameters in thickness. As the strain becomes more severe, the number of slip planes increases and the blocks between slip planes become thinner. This diagram represents the simplest case possible; actually the forces and the

*(Courtesy The American Brass Company, Waterbury, Connecticut)*

FIG. 17.—Slip Bands in Phosphor Bronze.

**The fine dark lines are slip bands. The short irregular black lines are fatigue cracks.**

motions accompanying them are more complicated, and there will often be two or more sets of slip planes in a single crystal grain.

**Slip Bands.**—If a polished and etched section of a metal is stressed, a number of fine dark lines appear on the surfaces of the grains (Fig. 17). These are *slip bands*, and they represent the traces of slip planes on the plane of the surface. The slip bands in any one grain are generally parallel; but if the strain is very severe, additional sets of parallel lines may appear which intersect the first set. Figure 18 is an ideal section illustrating the formation of slip bands. The arrows indicate the direction of the stress, and the broken line represents the surface of the metal before deformation. The displacement of the blocks must be about one thousand atom diameters before the slip bands become visible.

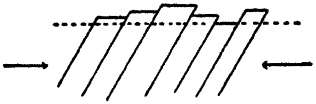

FIG. 18.—Formation of Slip Bands.

**Slip Interference.**—Motion along any slip plane does not continue indefinitely but usually stops after a displacement of a few hundred to several thousand atom diameters. In a polycrystalline metal, it is easy to see why this should be true. Since the crystal grains are oriented at random, a slip plane cannot extend from one grain into the next; but the slip is brought to a halt by the "end resistance" of the relatively rigid grain boundary. However, even in specimens composed of single crystals, it has been found that ultimate failure does not always take place along the original slip plane, but that slips occur on a great number of different planes, and the motion along any particular plane appears to be limited automatically to a certain amount. This "self-stopping" ability is particularly evident in ductile metals and alloys. The total deformation of any metallic specimen is the result of the integration of innumerable small displacements along many slip planes.

The halt which takes place after the displacement on a slip plane has proceeded for a certain distance apparently means that the atomic bonds between the blocks on either side of the slip plane have been re-established. It is as if the cohesive forces between the atoms act as a brake on the motion, and at the first opportunity they again make contact between neighboring atomic groups and "heal" the rupture in the crystal lattice. The actual mechanism of slip-interference has been the subject of much speculation, and several theories have been offered to explain slip-interference in pure metals.

Metals in general have a high specific cohesion; that is, the secondary valence forces holding the atoms together are comparatively strong. This seems to be due to the fact that the atoms of a solid metal are "normal," i.e., their valence electrons are not tied up in stable shells. Atoms and molecules with a stable or "inert gas" structure have low specific cohesions, and we may state as an approximation that secondary valence forces are due to unsatisfied primary valences. The tenacity, or strength, of metals and alloys is due largely to their high specific cohesion.

Associated with the atomic nature of metallic crystal lattices is the fact that the geometry of the space lattices is usually quite simple, and the ability of metallic atoms to re-establish their atomic bonds after slip has taken place is largely due to this. Where the crystal lattice is simple and all the atoms are alike, it is much easier for atoms to fit back into the lattice after they have been moved than if the crystal structure is complicated and composed of two or more kinds of atoms.

*Malleability* and *ductility* are two closely related physical properties peculiar to metals and alloys. Both are concerned with the magnitude of plastic deformation; malleability is the property of a metal which enables it to be beaten into thin sheets, and ductility is the ability of a metal to be drawn into thin wires. Obviously, both depend upon the property mentioned above—the re-establishment of atomic bonds after slip has taken place. The face-centered cubic system is the simplest of all the metallic lattices, and all the metals crystallizing in this system are malleable and ductile. This group also includes the most malleable and ductile metals known. Opposed to these two properties is *brittleness*, or the tendency to rupture as soon as the external stress exceeds the elastic limit. Brittle materials invariably have relatively complex crystal patterns, often containing two or more types of atoms. All solids possessing molecular or ionic lattices are brittle. Of course, the terms malleability, ductility, and brittleness are relative; some metals are brittle as compared with more malleable metals, but they would not be considered brittle if compared with a crystalline compound such as calcite.

It is possible to prepare a zinc rod consisting of a single crystal so oriented that the principal system of slip planes cuts the axis of the rod at an angle of about 90°. Such a specimen exhibits properties which are astonishingly different from those of a similar rod of polycrystalline metal. Layers of metal can be displaced along the slip planes with relatively little effort—the pressure of the thumb nail or the weight of the rod itself is often sufficient to cause deformation. The blocks or plates of metal which are displaced slip on one another almost like a deck of playing cards. The slip planes are perfectly flat surfaces with a bright mirror-like appearance.

## GRAIN SIZE AND GRAIN GROWTH

**Grain Size.**—The size, or average diameter, of the grains in metals may vary between rather wide limits, depending upon the treatment the metal has undergone. In cast metals, the grains will be small, if the metal has been cooled rapidly. However, if the cooling through the freezing point has been slow, fewer nuclei will be formed, and the grains will grow to a larger size. Mechanically worked metals generally have a finer grain than cast metal.

Since deformation of a metal takes place by motion along slip planes, a coarse-grained metal would present more uninterrupted planes of slip than a fine-grained one, because of the interference of the grain boundaries. Likewise, since the material of the grain boundaries is usually stronger than that of the crystallites themselves, a fine-grained metal would be stronger than a coarse-grained one because of the larger amount of intergranular cement present. These considerations lead to the statement, which is supported by experiment, that, all other things being equal, a metal has its greatest strength when the size of its constituent grains is a minimum.

**Strain-Hardening.**—Strain-hardening is due to mechanical working of metal such as rolling, forging, drawing, etc.; but for the present the effects of rolling only will be considered, since they are characteristic of all kinds of mechanical working, and it will simplify matters to deal with a single process.

All metals which are to be rolled are initially cast in the form of an ingot, and this ingot is reduced to the proper shape by passing it through a series of rolls which in appearance and mode of operation somewhat resemble large clothes-wringers. As the metal is forced through the rolls, it acquires a permanent deformation (plastic deformation), and the equiaxed grains of the cast metal are flattened and elongated in the direction of the rolling. The deformation of the individual grains must take place by a series of slip-displacements inside the grains, and each time such a slip occurs, other slip planes are *keyed* or thrown out of alignment, so that slip becomes more and more difficult and the metal becomes progressively harder. After severe cold-rolling, the original grains are greatly elongated, the crystal lattice of the interior of the grains becomes disorganized, and the metal is said to be strain- or work-hardened. Strain-hardening may be produced only by cold-working, that is, working below the recrystallization temperature of the metal concerned.

**Hot-Working.**—When the crystal structure of grains is broken down by mechanical work, the natural tendency is for the atoms to regroup themselves into a normal crystal lattice. Below the recrystallization temperature, however, this does not happen because the thermal energy of the atoms is too low to give them the necessary mobility, and also because of the rigidity of the grain boundaries. At any temperature above the recrystallization temperature, the fractured crystal lattices spontaneously rearrange themselves into new, equiaxed crystal grains; and each deformation of the metal is accompanied by the formation of an entirely new set of crystal grains. Hot-working or mechanical working above the recrystallization temperature does not cause strain-hardening or distortion of the crystal grains. A hot-rolled section has equiaxed crystallites. Usually the grains of hot-rolled material are much smaller than the grains of the cast metal.

Table 2 gives a list of recrystallization temperatures of some representative metals. It will be noted that any mechanical working of lead, zinc, tin, or cadmium at room temperature or above is hot-working, and consequently these metals cannot be strain-hardened. On the other hand, mechanical work done on tungsten at any temperature below 1200° C. is still cold-working. The identity which has been assumed to exist between the recrystallization temperature and the equicohesive temperature explains the intergranular fracture of lead at room temperature.

TABLE 2

RECRYSTALLIZATION TEMPERATURES *

| Metal | Approximate Lowest Recrystallization Temperature, Degrees Centigrade |
|---|---|
| Iron | 450 |
| Nickel | 600 |
| Gold | 200 |
| Silver | 200 |
| Copper | 200 |
| Aluminum | 150 |
| Platinum | 450 |
| Magnesium | 150 |
| Tantalum | 1000 |
| Tungsten | 1200 |
| Molybdenum | 900 |
| Zinc | Room temperature |
| Lead | Below room temperature |
| Tin | Below room temperature |
| Cadmium | About room temperature |

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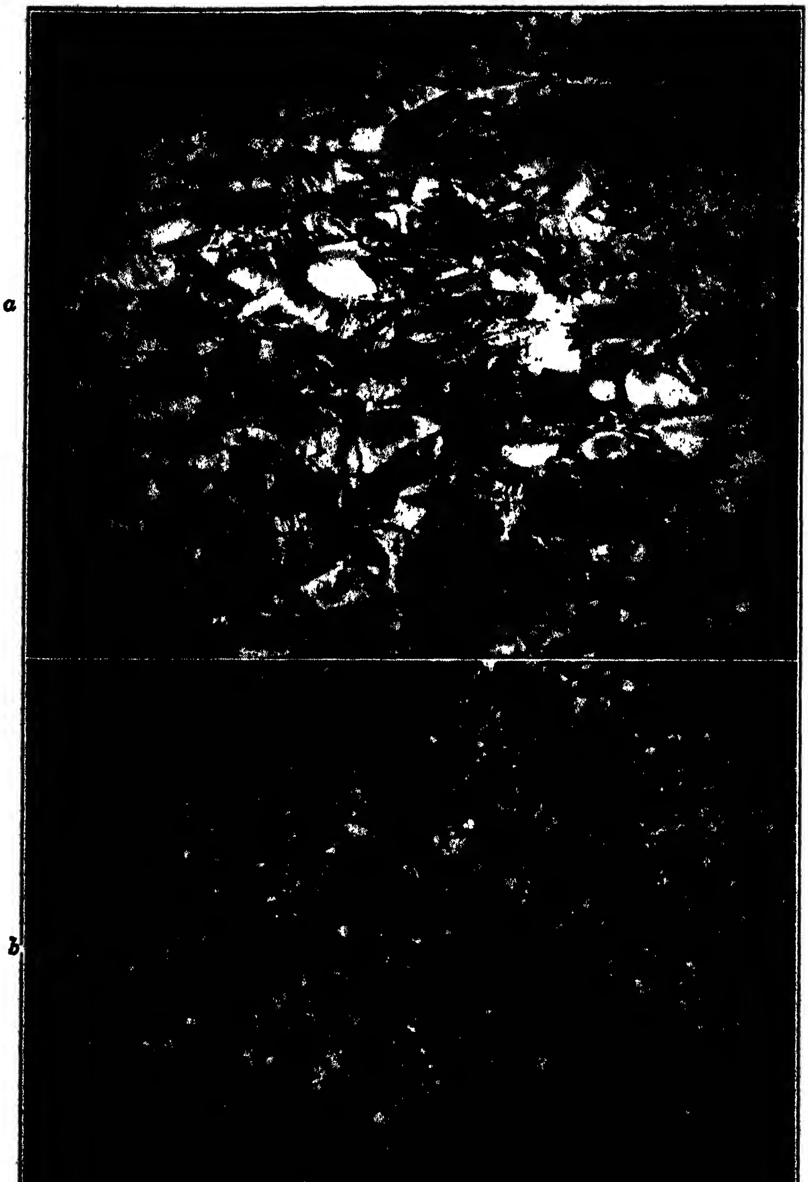
* Jeffries and Archer: The Science of Metals, McGraw-Hill Book Co., 1924, New York. Reprinted by permission.

**Recrystallization.**—If a strain-hardened metal is heated to its recrystallization temperature, the disarranged parts of the original space lattices assemble into new equiaxed crystal grains, and these grains have their smallest possible diameter. If the metal is heated to a still higher temperature, the grains grow larger; and, again as a first approximation, the final size of the grains depends only upon the temperature attained above the recrystallization temperature. Consequently, the best grain size would be obtained if the strained metal were heated to a point just above the recrystallization temperature. Such treatment is called *grain refining.* Cast metals do not show recrystallization or grain growth; these take place only in mechanically worked metals and alloys.

In hot-working, recrystallization and grain growth take place simultaneously with the deformation, and hence hot-working is equivalent to cold-working followed by annealing or grain refining, and in either case equiaxed grain structure results. (Note: annealing is not synonymous with grain refining, but the grain refining process is usually annealing.) The best finishing temperature for hot-working should then be just above the recrystallization temperature. Cold-working increases the hardness of the metal, but it also leaves mechanical strains, and therefore for many purposes cold-worked material is undesirable. Sometimes a metal hardens so rapidly during cold-working that further mechanical work tends to rupture it. It is then necessary to anneal or reheat the metal between the various stages of rolling.

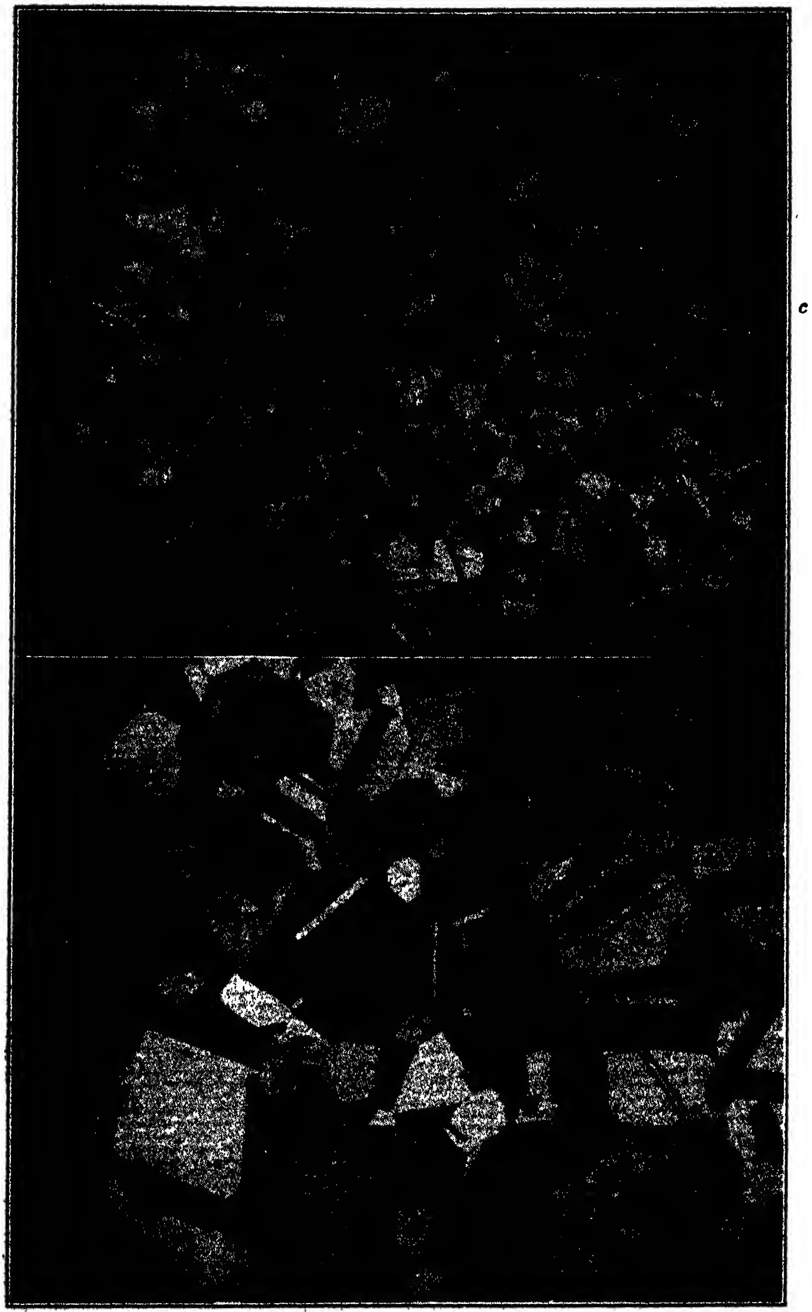
With alloys containing two species of grains, the grain refining process may be complicated by the fact that the recrystallization temperatures of the two types of grains may differ by a large amount, so that it would be impossible to secure the optimum size in both kinds of grains. If a metal passes through an allotropic change on heating, this may entirely mask the effects of grain refining and grain growth. The best example of this is found in steels, where grain refining depends upon such an allotropic change, and not upon the type of grain refining that we have considered here.



*(Courtesy The American Brass Company, Waterbury, Connecticut)*

*a*. Cold rolled. *b*. Annealed ½ hour at 450° C.

FIG. 19.—Illustrating Grain Growth in a Cartridge Brass. (Cu-68%; Zn-32%.)



*(Courtesy The American Brass Company, Waterbury, Connecticut)*

*c.* Annealed ½ hour at 600° C. *d.* Annealed ½ hour at 750° C.

Fig. 19 *cont.*—Illustrating Grain Growth in a Cartridge Brass. (Cu-68%; Zn-32%.)

## SUMMARY

1. Solid metals and alloys are effectively isotropic aggregates composed of allotriomorphic crystals or grains.

2. Between individual grains is found an intergranular cement whose properties differ markedly from the properties of the metal in the grains. This intergranular material has a pronounced effect upon the physical properties of a metallic object.

3. Metal crystals have an atomic space lattice, which permits the existence of free electrons and permits high specific cohesion between metallic atoms. Most of the properties of metals, such as their ductility (plastic deformation), strength, and electrical properties, are the direct consequences of this type of atomic arrangement. Chemical compounds and non-metals are usually associated; their valence electrons are locked in stable shells; they crystallize in molecular or ionic lattices. Such materials have properties which differ sharply from the properties of metals; e.g., they are usually brittle and have little or no electrical conductivity.

4. The individual grain is a mosaic of small crystalline blocks having the same orientation. Grains usually result from growth about a dendritic skeleton.

5. Temporary deformation (elastic deformation) of a metal takes place by the stretching or contraction of atomic bonds. Permanent deformation (plastic deformation) involves motion along slip planes with the rupture of atomic bonds.

6. Any permanent deformation of a metallic object is the result of motion along slip planes. Such deformation may reduce the size of individual grains, but it cannot destroy the essential crystallinity of the metallic object.

7. Cold-working produces strain-hardening, probably because it causes disregistry of slip planes, possibly because it increases the amount of grain-boundary material.

8. Hot-working refines the grain size but does not cause strain-hardening.

9. Grain growth takes place only in strain-hardened crystals. Normal unstrained grains such as those of a cast metal do not show grain growth.

10. Fine grain size is associated with improved strength and hardness.

## EXERCISES

1. Assume that a single grain of copper has a volume equal to 0.1 cu. mm. Calculate the number of copper atoms in this grain. Does it seem reasonable to you that such a large number of atoms should be lined up in a single unbroken lattice, or does it seem more reasonable to assume that the grain is composed of a mosaic of blocks? If the mosaic were assumed to contain blocks 100 atoms to a side, how many blocks would be present in this grain?

2. What reasons can you give to account for the fact that there is a wide variation in the electrical conductivity of different metals?

3. Describe a simple experiment by means of which you could locate the transformation point in a solid metal showing two allotropic modifications.

4. What are meant by the Miller indices of a crystal? How are they used?

5. What is meant by a plane of symmetry in a crystal? A secondary plane of symmetry? Axes of symmetry?

6. Metals have high specific cohesion and high boiling points. Why should there be a connection between the boiling point of a substance and its mechanical strength?

7. Describe the Lewis-Langmuir model of the oxygen atom (from Fig. 4, the sketch of the oxygen molecule).

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# CHAPTER III

## THE STRUCTURE OF ALLOYS

In the previous chapter, the word "alloy" was used several times, although as yet the term has not been formally defined. The reason for so using it was to emphasize the fact that alloys have the same general properties as pure metals—they are crystalline, good electrical conductors, and they have the luster and appearance that are designated as metallic.

A liquid alloy is a homogeneous solution of two or more metals or of metals and certain non-metals. A solid alloy is formed when a liquid alloy freezes. Alloys freeze in a number of ways, and the phenomena which take place on freezing serve as the basis of classification of the alloys.

All alloys melt to form a homogeneous liquid, and the criterion for determining whether or not metals will form an alloy is simply whether or not they are miscible in the liquid state. If two or more metals are miscible in all proportions in the liquid state, they will form a complete, or unbroken, series of alloys. If they are only partially miscible, a broken series of alloys will result. Liquid lead and liquid aluminum are not miscible, but separate into two layers like oil and water; consequently, there are no lead-aluminum alloys.

Alloys of two metals are binary alloys; those containing three metals are ternary alloys; and alloys of four metals are quaternary alloys.

### THERMAL ANALYSIS

Thermal analysis is a method of observing phase changes by the study of cooling curves. A cooling curve is a time-temperature plot which records the temperature of a cooling body over a period of time. The mathematical expression of laws of cooling is usually very complicated, and it is often quite impossible to derive an expression that will satisfactorily define the cooling of a body. However, both theory and experience show that, in cooling, the temperature is a continuous function of time. That is, if time is plotted against temperature, there is obtained a smooth curve free from jogs or inflections, as long as no physical transformation takes place inside the cooling body.

When a substance changes phase, as for example when liquid copper freezes to solid copper, the heat of fusion is given off, and the heat evolved counteracts the cooling loss so that the temperature remains constant for a given time until the metal is completely frozen. After the metal has solidified, cooling again proceeds, and the rest of the cooling curve is continuous. Figure 1 shows simple cooling curves for some common metals, and here the horizontal sections indicate the temperature of the various freezing points. Allotropic changes within a solid metal are accompanied by similar breaks on the cooling curve; the cooling curve of iron (Fig. 2) shows an example of this. The temperatures at which these changes take place in pure metals are called dimorphic points, since at these particular temperatures two phases exist in equilibrium. Any point of discontinuity on a cooling curve is a *critical point.* There is often a dip on the curve, just before the freezing point is reached. This is due to undercooling or surfusion of the liquid (Fig. 3).

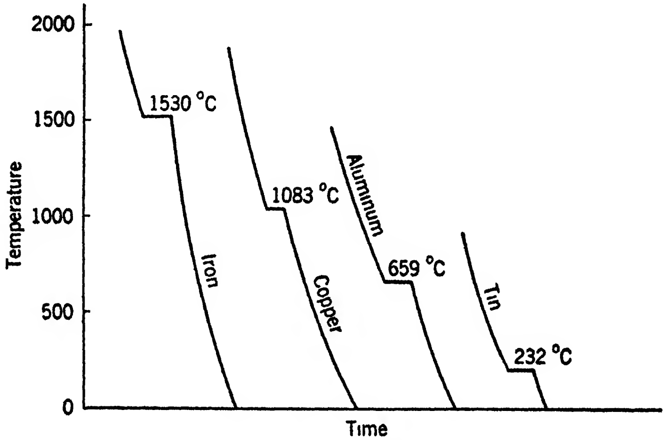

FIG. 1—Cooling Curves of Pure Metals.

If it were required to determine the freezing point of water, the procedure would be quite simple, for it would only be necessary to cool the liquid until crystals of ice began to form, insert a thermometer, and read the temperature. However, when working with opaque materials which freeze at high temperatures, it is physically impossible to observe the phase changes visually; and so they must be determined from the cooling-curve record. Other methods for detect-ing phase changes may be used, such as measurement of electrical resistance, X-ray analysis, microscopic examination, or measurement of changes in density. These methods are usually more accurate than simple thermal analysis and are widely used for research in physical metallurgy.[1]

**Cooling Curves.**—In making a thermal analysis of a metal or alloy, the material is melted and allowed to cool. Generally the melting is done in a clay or graphite crucible, and the most convenient way of heating is by means of a small electric furnace. If the metal oxidizes readily, it must be covered by a reducing agent, such as powdered charcoal, or the melting must be done in an inert or reducing atmosphere. After the metal is completely melted, an instrument for recording temperature (usually a thermocouple) is inserted in the crucible, the heat is turned off, and the metal allowed to cool to room

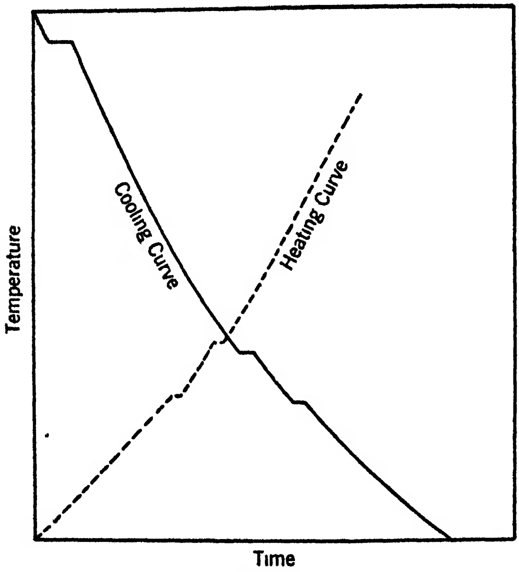

Fig. 2.—Heating and Cooling Curve.

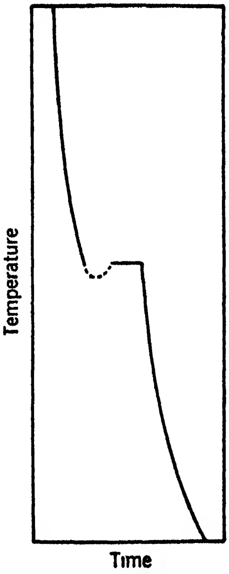

Fig. 3.—Cooling Curve Showing Surfusion.

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[1] Truesdale, E. C., Wilcox, R. L., and Rodda, J. L.: An Investigation of the Zinc-rich Portion of the System Iron-zinc, T. P. 651, 1935, American Institute of Mining and Metallurgical Engineers.

Rowland, Elbert S., and Upthegrove, Clair: Equilibrium Relations in the Copper Corner of the Ternary System Copper-tin-beryllium, T. P. 613, 1935, American Institute of Mining and Metallurgical Engineers.

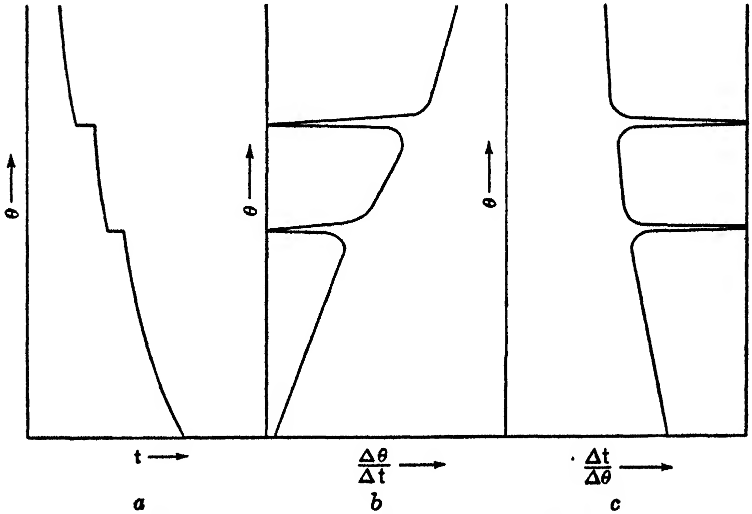
temperature. As soon as the metal begins to cool, temperature readings are taken at regular intervals (30 seconds to 2 minutes) until the metal has cooled as far as necessary. Of course, if it is known that there are no phase changes below a certain temperature, there is no reason for continuing the readings for more than a few degrees below this temperature. Care must be taken that the metal cools slowly, or the temperature will drop so rapidly that the critical points may be missed entirely. The crucible containing the metal should be well insulated or left in the furnace and allowed to cool as the furnace cools.

There are many different ways of conducting a thermal analysis, and in general any method will do which (1) insures that the metal or alloy will be heated well above the highest critical point which is to be located, (2) protects the metal against any chemical reaction such as oxidation, and (3) makes the cooling slow enough so that phase changes are easily recognized on the cooling curve. After all the data have been taken, the cooling curve is obtained by plotting the temperature in degrees (usually vertically) against time in minutes or seconds. Since the phase changes are reversible, they may be detected by means of a heating curve, which is similar to a cooling curve except that the observations are made during the heating cycle. The same critical point will have a slightly different value on a heating curve from its value on a cooling curve; this is due to the hysteresis (molecular or atomic inertia) of the material.

**Special Cooling Curves.**—The cooling curves discussed in the previous section are called temperature-time curves and are obtained by plotting the temperature, $\theta$, as ordinate and the time, $t$, as abscissa. When the thermal changes are small, the temperature-time curve often does not show the critical points very well, and it is necessary to plot the data in another form. Four other types of cooling curves will be presented, all of which are designed to exaggerate the critical points and make it possible to locate them more exactly.

**Temperature-Rate Curve.**—The data for this curve are taken exactly as for the temperature-time curve, but the abscissa is $\frac{\Delta\theta}{\Delta t}$ or the rate of change of temperature per unit of time (cooling velocity). If the time interval is 30 seconds, then the numerical value of $\frac{\Delta\theta}{\Delta t}$ is the change of temperature in degrees for each 30-second interval. The curve would touch the $\theta$-axis at the freezing point since there $\Delta\theta = 0$ and hence $\frac{\Delta\theta}{\Delta t} = 0$.

**Temperature-Inverse Rate Curve.**—As the name indicates, this curve is related to the temperature-rate curve, except that instead of $\frac{\Delta\theta}{\Delta t}$ the abscissa is $\frac{\Delta t}{\Delta\theta}$. In the two previous cases, the independent variable was the time, i.e., uniform time intervals were chosen, and the temperature was read at the end of each interval. To obtain data for an inverse rate curve, the time must be made the dependent variable, and the data recorded are the number of seconds required to cool through unit temperature intervals (0.5° C., for example). The numerical value of $\frac{\Delta t}{\Delta\theta}$ is then the number of seconds required to cool through 0.5° C. The coordinates of this curve are $\theta$ and $\frac{\Delta t}{\Delta\theta}$.



*a.* Temperature-Time. *b.* Temperature-Rate. *c.* Temperature-Inverse Rate.

FIG. 4.—Cooling Curves.

**Differential Curves.**—Fluctuations in furnace conditions often result in small jogs in a cooling curve, which may be mistaken for critical points. To minimize such effects, differential or difference curves are used where high accuracy is desired. This requires the use of two thermocouples, one of which is placed in contact with the substance to be investigated, while the other is embedded in a neutral body—some substance which has no critical points in the temperature range to be investigated. Thus, to obtain difference curves for iron, one thermocouple would be placed in the molten iron, while the other might be embedded in a block of platinum. Both the iron and the platinum are in the same heated chamber; and, as the furnace cools, they cool together. Theoretically, they should have the same temperature, but usually one or the other will lag behind so that there is always a small temperature difference between them at any given time. The neutral body should have about the same heat capacity as the substance to be investigated.

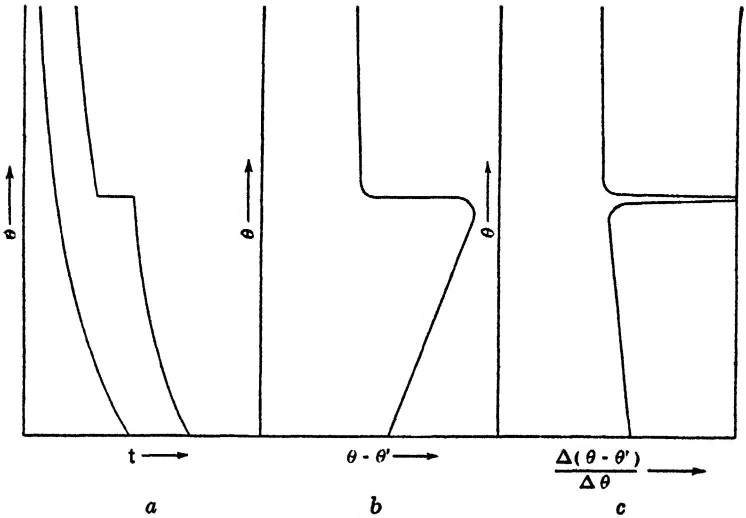
The data recorded are the same as for the temperature-time curve, temperature readings being made at unit time intervals, except that two temperature-time curves are obtained. The cooling curve of the control body will be a smooth curve under normal conditions, and that of the other substance will resemble any other temperature-time curve. The difference between the two temperatures will then be constant, except where a critical point occurs in the second substance. Here the difference will show a large increase. Any fluctuation in the curves due to external effects will affect both curves alike and will not alter the difference. If $\theta =$ the temperature of the material to be investigated at any time $t$, and $\theta' =$ the temperature of the control body at the same time, then the coordinates used in plotting a differential cooling curve are $\theta$ and $\theta - \theta'$, where the numerical value of $\theta - \theta'$ is the difference in degrees of temperature between the bodies at time $t$. Note that here $t$ is the independent variable, although it does not appear on the graph.

Difference curves may also be made by means of a differential thermocouple with one junction placed in the body to be investigated and the other in the neutral body. The readings of the instrument will then give directly the temperature difference between the two bodies.

**Derived Differential Curves.**—These represent the ultimate refinement in accurate cooling curves and are even more effective than the differential curves in diminishing irregularities due to external effects. Here the ordinate is $\theta$ as usual, but the abscissa is $\frac{\Delta(\theta - \theta')}{\Delta\theta}$, or the rate of change of the difference per unit change in temperature. To obtain data for this type of curve, it is necessary to observe $\theta$ and $\theta'$ for each unit (for example, 0.5° C.) of variation in $\theta$, or to make temperature the independent variable.

Another type of derived differential curve has $\frac{\Delta(\theta - \theta')}{\Delta t}$, or the rate of change of the difference per unit time, as the abscissa, and here the time is the independent variable.

These special curves are useful for experimental purposes, but for all subsequent discussion the simple temperature-time curves will be used and the expression "cooling curve" will refer to these only. All the curves which have been discussed up to this point show true dimorphic points or points at which the phase transformation takes place at a single temperature. It soon will be necessary to consider other types of curves in which the transformation takes place over a range of temperature. For these will be given only the temperature-time curves. As a suggested exercise, the student may construct one or more of the special curves to correspond.



*a.* Temperature-Time. *b.* Differential. *c.* Derived Differential.

Fig. 5.—Cooling Curves.

**Freezing of Alloys.**—The properties of metals or alloys depend largely upon their crystalline structure; and in order to understand why alloys have certain properties, it is necessary to investigate the behavior of these alloys on freezing, or in other words to determine how the atoms in the liquid solution assemble as they crystallize.

### THE LEAD-ANTIMONY ALLOYS

Anyone who has used an "anti-freeze" in an automobile radiator is familiar with the fact that a dissolved substance may lower the freezing point of the solvent, and this rule also holds for many liquid solutions of metals. A cooling curve of pure lead shows only one critical point, namely the freezing point of the metal at 327° C., but by making another cooling curve after dissolving a small amount of antimony in the molten lead, it is found that the melt is still liquid below the melting point of pure lead, and that freezing begins at a lower temperature than 327° C. By adding more and more antimony to the lead, the freezing point is lowered progressively, and the curve in Fig. 6 shows the relation between the incipient freezing point and the concentration of antimony in the alloy. In an exactly similar manner, the freezing point of pure antimony may be lowered by the addition of lead. The same sort of curve may be plotted as before (Fig. 6). If the two curves are plotted on the same diagram, they will intersect; and their intersection will represent an alloy having the lowest freezing point of the series. This alloy is called a *eutectic* (in this case an alloy containing 12 per cent antimony, and 88 per cent lead).

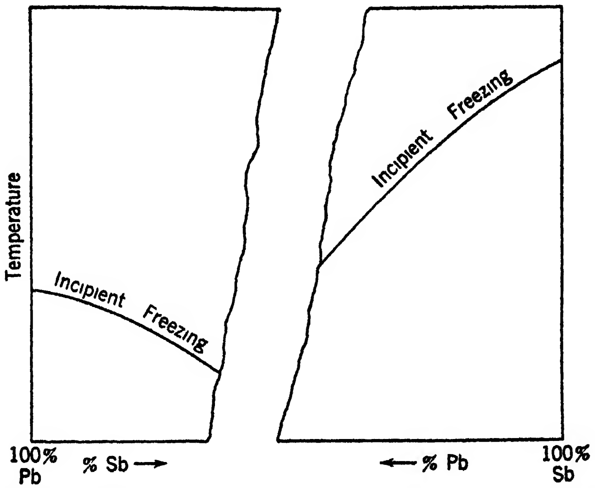


Fig. 6.—Lowering of Freezing Point by Dissolved Impurities.

Examination of the cooling curves in Fig. 7 shows that they differ from the cooling curves of pure metals in that they have two critical points. This type of curve is characteristic of alloys whose components are insoluble in one another in the solid state. By insolubility in the solid state is meant that, on freezing, lead separates as crystals of pure lead and antimony as crystals of pure antimony. Any solid alloy of the series consists of a mechanical mixture of pure lead and antimony grains.

Figure 8 shows the significant portion of curve 2 in Fig. 7 on a larger scale. At the point *A*, the alloy is entirely liquid and consists of a homogeneous solution of 95 per cent lead and 5 per cent antimony. The presence of "foreign" antimony atoms retards the crystallization of lead, and as a result the alloy must be cooled somewhat below the melting point of lead before any solidification takes place. At the point *B*, pure lead begins to solidify, and, as lead crystallizes out, the solution becomes richer in antimony; consequently, it has a lower freezing point than the original solution. As cooling proceeds, lead freezes out continuously, but the temperature does not remain constant, since the freezing point of the remaining liquid becomes progressively lower. Finally, the temperature reaches 247° C.

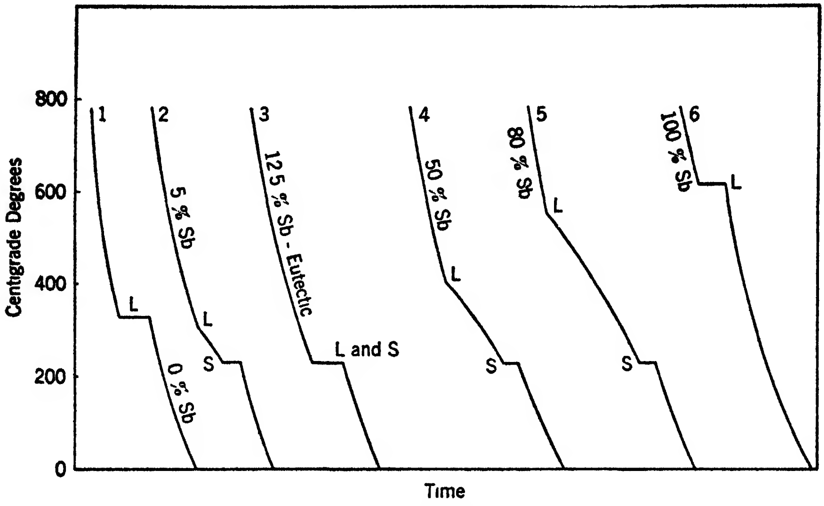


FIG. 7—Cooling Curves of the Lead-Antimony Alloys.

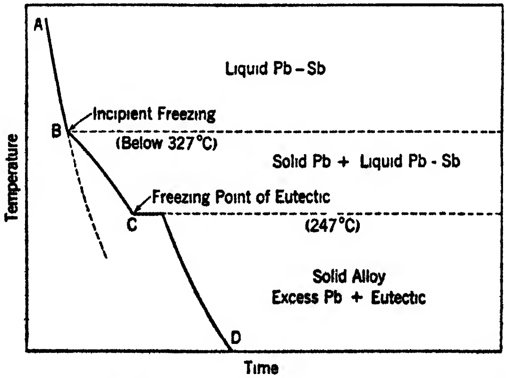


FIG. 8.—Cooling Curve for a Lead-Antimony Alloy Containing 5% Antimony.

as the liquid attains the eutectic composition (88 per cent lead, 12 per cent antimony); this liquid crystallizes at this constant temperature. The deviation of the curve *BC* from the broken line which represents the continuation of *AB* is due to the heat of fusion of the lead which is freezing all along *BC*. If cooling were halted at some point on *BC*, for example at a temperature of 270° C., crystals of lead would be in *equilibrium* with a solution of lead in antimony. The liquid at any point below *B* is a saturated solution in equilibrium with the solute (lead); and, as it cools to lower temperatures, the solubility of lead decreases and more must precipitate out.

Curve 3 in Fig. 7 is the cooling curve of the eutectic alloy—it has only one critical point and freezes at a constant temperature. Curves 4 and 5 are interpreted in exactly the same way as curve 2, except that here pure antimony freezes out, since the alloys contain more than 12 per cent antimony. Curves 1 and 6 are the cooling curves of the pure metals.

**The Lead-Antimony Equilibrium Diagram.**—The information obtained from a set of cooling curves as shown in Fig. 7 may be reproduced on a temperature-composition plot which is called an *equilibrium diagram*, or *constitutional diagram*, and the equilibrium diagram for the lead-antimony series is shown in Fig. 9. The horizontal coordinate is composition expressed in percentage of antimony; since the lead content = 100 per cent − percentage of Sb, the composition can be expressed by a single variable, and each point on the horizontal axis represents an alloy of definite composition. The vertical coordinate is temperature.

Any alloy of the set has either one or two critical points, as shown by the curves in Fig. 7, so that, for any value along the composition axis, there may be located one or two critical temperatures; lines drawn through these points give the diagram in Fig. 9. The upper line or *liquidus* is formed by joining all such points as those marked *L* in Fig. 7; the lower line or *solidus* passes through the points labeled *S*.

The liquidus is the locus of all the incipient freezing points, or the points at which solidification begins; and the solidus is the locus of all points at which solidification is complete. Below the solidus the alloys are all solid; above the liquidus the alloys are wholly liquid. Between the two lines, solid and liquid phases exist in equilibrium. The statements in this paragraph are general and apply to all types of alloy diagrams.

Consider three or four particular alloys in connection with Fig. 9 to make clear the significance of the curves. An alloy of 5 per cent antimony and 95 per cent lead at a temperature of 700° C. is rep sented by the point *a*. The alloy is completely liquid. Now, if this alloy cools, the temperature drops, but the composition remains constant; therefore, the point moves down along the vertical broken line, and no phase changes occur until we reach *c*. Here the cooling line (*ac*) intersects the liquidus, or comes to the point of incipient freezing; and pure lead begins to crystallize out of the melt. As lead is removed, the liquid becomes richer in antimony, and the reference point moves along the liquidus until the point *E* is reached. Here the remainder of the liquid freezes at constant temperature. The liquid at the point *c* is saturated with lead; if the temperature is lowered, lead must crystallize out; and therefore the composition of the liquid must vary automatically with the drop in temperature. This variation is such that the reference point follows the liquidus. Another way of saying the same thing is that the portion of the liquidus *GE* is the solubility curve of solid lead in liquid antimony.

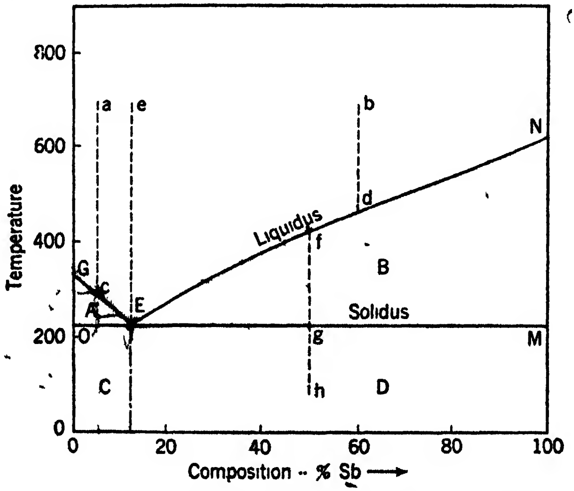


FIG. 9.—The Lead-Antimony Equilibrium Diagram.

At the point *b* is a liquid alloy of 60 per cent antimony and 40 per cent lead. On cooling to *d*, antimony begins to crystallize; and the point of reference again moves down the liquidus until the point *E* is reached; here the remainder of the liquid freezes at a constant temperature. The branch *EN* of the liquidus is the solubility curve of solid antimony in molten lead.

Now, start at point *e* on the diagram with a liquid alloy of the eutectic composition. For points to the left of *e* the tendency is for lead to freeze first; for points to the right of *e*, antimony freezes first.

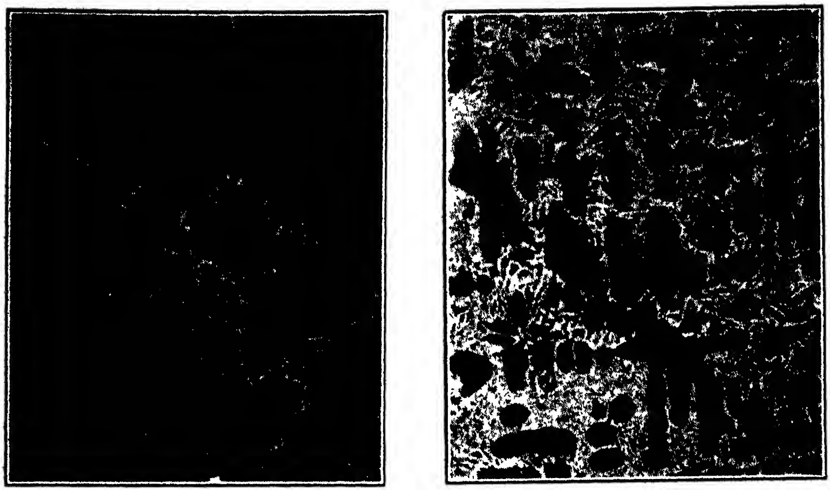
At *e*, therefore, there is no possibility for either to crystallize in preference to the other, and the alloy cools uniformly to *E*, at which point lead and antimony crystallize simultaneously as an extremely intimate mechanical mixture of lead and antimony crystals. In both the previous examples, the eutectic liquid froze in exactly the same way; but, in addition to the eutectic, there was some excess lead in the first case and excess antimony in the second. Figure 10 shows some photomicrographs of lead-antimony alloys. The eutectic has a fine-grained, often lamellar, structure and consists of alternate crystals of lead and antimony. The crystals of excess lead or antimony are relatively large compared with the individual crystals in the eutectic.

Finally, consider what happens when an alloy of this type is melted; here the starting point will be the point *h* on the diagram, which represents a solid alloy of 50 per cent lead and 50 per cent antimony at 50° C. This alloy consists of excess antimony crystals in a matrix of the eutectic. The heating proceeds along the vertical broken line, and when the point *g* (247° C.) is reached, the eutectic ground-mass melts at constant temperature. As soon as the temperature begins to rise above 247° C., there exists a liquid of eutectic composition, in which are floating crystals of antimony. Now, as the temperature continues to rise, the solvent power of the liquid for antimony increases. The antimony crystals do not melt (they could not melt below 630° C.), but dissolve in the liquid. As the temperature rises still higher, more and more antimony dissolves, and the composition of the liquid moves along the liquidus from *E* to *f*. Here the available excess antimony has all been dissolved, the liquid has the same composition as the original solid, and further heating produces only a rise in the temperature of the liquid.

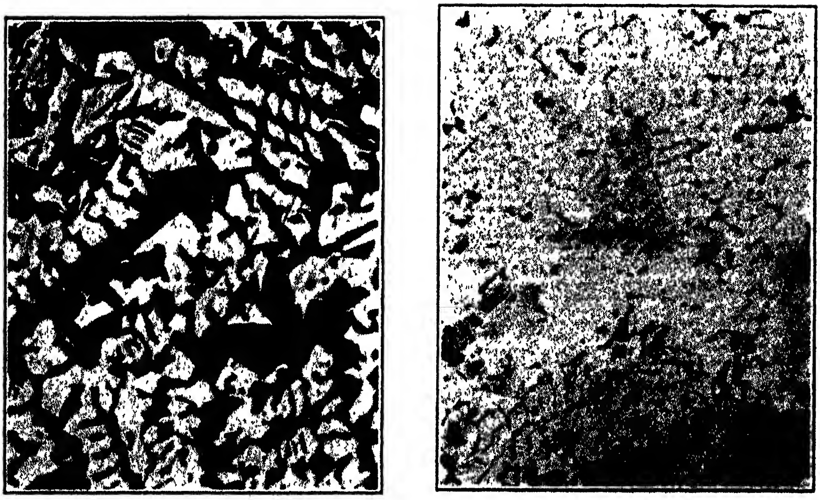
The liquid at the point *c* is saturated with lead, and if it is cooled, lead is thrown out of solution; similarly, the liquid at *d* is saturated with antimony. The fact that these liquids freeze over a range of temperature is due to the change in composition of the liquid caused by the segregation of one of the metals as a solid. The liquid eutectic at its freezing point (*E* on the diagram) is saturated with respect to both lead and antimony; the two metals are thrown out of solution simultaneously; there is no change in the composition of the liquid, and consequently the eutectic freezes at a single definite temperature.

From the preceding discussion, a few of the pertinent facts concerning Fig. 9 may be tabulated:

1. Alloys in the field above the liquidus (above *GEN*) are entirely liquid. In the other four fields, which are lettered, there are: in *A*



*a.*—6% Sb. *b.*—10% Sb.



*c.*—50% Sb. *d.*—90% Sb.

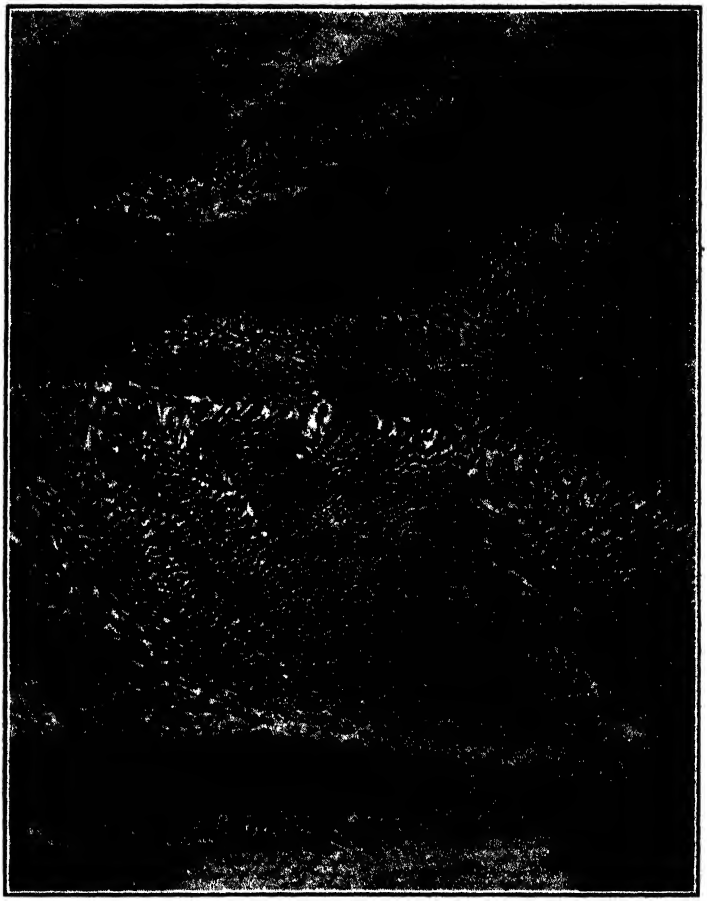
*(Courtesy Robert Butterfield, Case School of Applied Science)*

FIG. 10.—Photomicrographs of Four Lead-Antimony Alloys.

**Sections *a* and *b* contain excess crystals of lead (black) surrounded by a matrix of the eutectic. Sections *c* and *d* contain excess antimony crystals (white). The eutectic structure is shown in *a* and *b* (high magnification) but the eutectic appears uniformly black in *c* and *d* (low magnification).**

a liquid solution + solid lead; in *B* liquid solution + solid antimony; in *C* solid alloys consisting of solid lead in a matrix of the eutectic; and in *D* solid alloys consisting of excess antimony embedded in the eutectic.

2. Any solid alloy in the series (except one of the pure metals) must contain some of the eutectic.



*(Courtesy The American Brass Company, Waterbury, Connecticut)*

Fig. 11.—Eutectic Structure; the Copper-Silicon-Phosphorus Eutectic.

3. Either lead or antimony may be present as the excess constituent (large crystals) but never both.

4. The pure metals and the eutectic alloy are the only three of the series that have definite melting points; all the other alloys freeze or melt over a range of temperature.

5. All the alloys consist of mechanical mixtures of lead and antimony crystals, regardless of whether these crystals are part of the eutectic or not.

6. Liquid lead and liquid antimony are miscible in all proportions; solid lead and solid antimony are immiscible; and the solvent power of liquid antimony for solid lead is given by the branch *GE* on the liquidus, while the solvent power of liquid lead for solid antimony is given by the curve *EN*.

**The General Case.**—The lead-antimony diagram as shown in Fig. 9 is an example of the diagram of a binary alloy whose components are reciprocally soluble in all proportions in the liquid state, and completely insoluble in the solid state. All alloys possessing these characteristics have equilibrium diagrams similar to Fig. 9, and are interpreted in exactly the same manner.

**Eutectics.**—Most of the material presented thus far as applied to the lead-antimony eutectic is perfectly general; for convenience the important general properties of binary eutectics are listed below.

1. Eutectics are mechanical mixtures of two solid phases. They often have a characteristic banded or lamellar structure and are easily recognized under the microscope.

2. Eutectics have constant chemical composition, although they are not chemical compounds.

3. Eutectics freeze and melt at constant temperature.

4. In a series of eutectiferous alloys, the eutectic has the lowest freezing point of any alloy in the series.

5. Because of its fine grain, the eutectic alloy usually displays the best mechanical properties of any alloy of the series.

6. Equilibrium diagrams are not necessarily confined to metallic solutions. Analogous diagrams may be constructed by plotting the solubility curves of salts in water, for instance, and these curves show eutectics which are often called *cryohydrates*.

## THE GOLD-PLATINUM ALLOYS

The gold-platinum alloys illustrate another type of alloy which differs greatly from the lead-antimony alloys. Gold and platinum are reciprocally soluble in all proportions in both the liquid and solid state.

**Solid Solubility.**—If an alloy of 90 per cent gold and 10 per cent platinum is allowed to solidify, there will be only one solid phase present, and this is a solid solution of platinum in gold. This substance has the same crystal pattern as gold and consists essentially of gold crystals in which some of the gold atoms have been replaced by atoms of platinum. In other words, platinum is soluble in gold in the solid state, because it is possible for platinum atoms to fit into the gold space lattice; lead is insoluble in antimony in the solid state, because lead atoms cannot be substituted for antimony atoms in the antimony space lattice.

Gold and platinum both have a face-centered cubic lattice, and they form a complete series of solid solutions. Starting with a crystal of pure gold, it is possible to replace progressively the gold atoms with atoms of platinum, until we have a crystal composed entirely of platinum. In this process there is no "break" in the continuity of the lattice. The lattice dimensions alter slightly in progressing from pure gold to pure platinum, but each one of the solid solutions has the same type of crystal lattice as either the gold or the platinum. Such an unbroken series of crystals is called an *isomorphous series*.

Other pairs of metals form *morphotropic* or broken series, and these metals are partially soluble in the solid state. Zinc atoms normally crystallize in the close-packed hexagonal system, but solid copper dissolves up to about 35 per cent zinc, and the resulting solid solution (alpha brass) has the face-centered cubic crystal pattern characteristic of copper except that the presence of zinc atoms alters the lattice dimensions. Likewise, a small amount of copper dissolves in solid zinc, and this solid solution has a hexagonal close-packed lattice. Two metals such as these could not form an isomorphous series of alloys, since it is not possible to pass from a cubic to a hexagonal system without a break.

The term "mixed-crystals" is sometimes used to denote solid solution; likewise, "solid solution" is used by some writers to designate what we have called an amorphous solid or glass. However, the nomenclature that we have adopted seems to be the one preferred by the majority. "Mixed-crystals" suggest a mechanical mixture, and these solid solutions are not mixtures but are as perfectly homogeneous as any liquid solution.

The constituent whose lattice pattern persists is called the solvent; in alpha brass, for example, the solvent is copper, and this is called a solid solution of zinc in copper. In isomorphous series such as the gold-platinum alloys, there is no criterion by which can be determined which is the solute and which the solvent, except the arbitrary ruling that the metal present in the largest amount shall be called the solvent. In Fig. 13 the alpha solid solution has been denoted as gold in platinum; this might just as well have been platinum in gold.

The solute atoms in a solid solution appear to be uniformly, but randomly, distributed throughout the solvent much as the molecules of salt are dispersed in an aqueous solution. In other words, in a solid solution whose atoms are 50 per cent gold and 50 per cent platinum, gold and platinum atoms are present in equal numbers in all parts of the mass, but all the atoms are not necessarily lined up so that gold atoms alternate with platinum atoms. Before considering the specific case of the gold-platinum alloys, let us summarize a few important facts concerning solid solutions.

1. Pairs of metals may be reciprocally soluble in all proportions, partially soluble, or insoluble, in the solid state.

2. Solid solutions are formed by replacing some of the solvent atoms by solute atoms. The solid solution has the same crystal form as the pure solvent, although the presence of solute atoms alters the dimensions of the lattice. Most solid solutions are of this replacement type, but in some cases the solute atoms appear to fit between the atoms of the solvent.

3. Solid solutions do not have a fixed chemical composition. The alpha solution of gold-platinum may vary from 100 per cent gold to 100 per cent platinum; and although the color, hardness, and other properties of the different alloys of the series change as the composition changes, all these alloys consist of the same solid solution. Similarly, alpha brass may contain any amount of zinc from a few tenths of 1 per cent to 35 per cent. This *variation in composition between limits* is characteristic of all solutions whether liquid or solid.

4. Solid solutions are perfectly homogeneous in the same sense that a liquid solution is homogeneous. In alloys consisting of a single solid solution (such as alpha brass), only one kind of grain is present, and these grains are chemically identical. A photomicrograph of such an alloy resembles that of a pure metal.

5. Solid solutions in general do not have a definite melting point, but melt and freeze over a range of temperature.

**The Cooling Curves.**—Figure 12 shows some representative cooling curves of gold-platinum alloys. Note that they have two critical points (except for the pure metals), freezing takes place over a range of temperature, and there is no horizontal section on the curve corresponding to the freezing of a eutectic. From these curves an equilibrium diagram may be plotted in the same way as for the lead-antimony alloys—this is shown in Fig. 13.

**The Gold-Platinum Equilibrium Diagram.**—The difference between this diagram and the equilibrium diagram of the lead-antimony series will be evident at once. Here there is no minimum point on the liquidus; the solidus is a curve and not a horizontal line, and it joins the liquidus at the extremities. Only one solid phase is present. This diagram is typical of binary alloys which form an isomorphous series.

It might be expected that alloys of this type would freeze at constant temperature; since all possible solid solutions can exist, it might appear that any liquid alloy would freeze without changing composition (and therefore at a constant temperature) to yield a solid solution of the same composition as the original liquid. However, in general, the first solid solution to separate on freezing has a different composition from the liquid solution. A discussion of the freezing of one specific alloy of this series will illustrate the characteristics of this type of alloy.

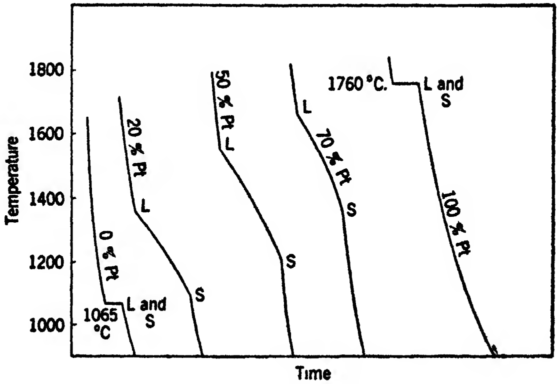


Fig. 12 —Cooling Curves of the Gold-Platinum Alloys.

The point *a* in Fig. 13 represents a liquid alloy containing 70 per cent platinum and 30 per cent gold at a temperature of 1800° C. Cooling proceeds uniformly until the liquidus is intersected at *b* (1660° C.). The composition of the solid which separates at this point is determined by drawing a horizontal line from *b* to intersect the solidus, and this point of intersection gives the composition of the solid phase. The first solid solution to separate from the liquid contains 94 per cent platinum and 6 per cent gold. Separation of this platinum-rich solid phase leaves the liquid richer in gold; and as cooling proceeds, the composition of the liquid changes so that the point of reference moves down the liquidus. In the lead-antimony alloys, the same thing happened to the liquid, but here the composition of the solid phase also changes as the temperature drops, and the reference point moves down along the solidus. As this alloy freezes, the composition of the liquid changes from *b* to *e* (70 per cent platinum to 23 per cent platinum), and at the same time the composition of the solid changes from *c* to *d* (94 per cent platinum to 70 per cent platinum). The last drop of liquid to freeze has a composition of 23 per cent platinum and 77 per cent gold; but by the time this freezes, the composition of the solid has altered until it finally has the same composition as the original liquid, which, of course, is necessary, since the phase changes cannot alter the total amount of gold and platinum in the system.

Figure 13 is an equilibrium diagram, and the solidus and liquidus indicate which phases can exist in equilibrium at any given temperature. A discussion of the subject from this point of view may be of value in connection with the interpretation of this diagram.

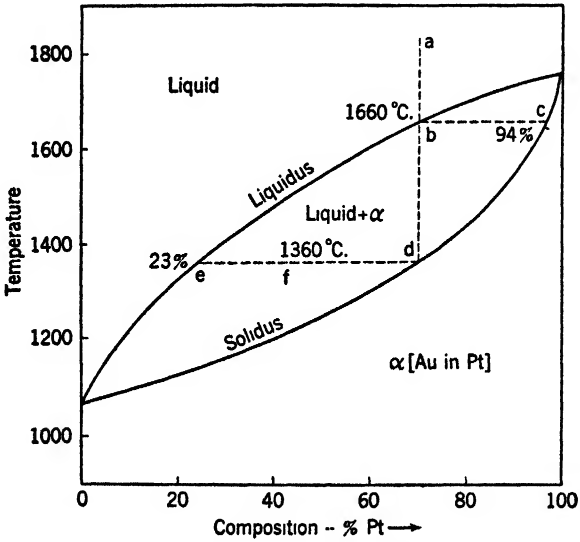


FIG. 13.—The Gold-Platinum Equilibrium Diagram.

In a system containing gold and platinum atoms, two influences determine the phase of the system—thermal agitation which tends to keep the atoms in the liquid state, and the cohesive forces of the atoms which attempt to assemble them into a crystal lattice. When these opposing forces balance, the system is in equilibrium. Now, an alloy of 40 per cent platinum and 60 per cent gold at 1360° C. will be represented by point *f* on the diagram. A horizontal line through this point intersects the liquidus at *e* and the solidus at *d*, and this means that under equilibrium conditions the alloy is present in two phases; part of it is a liquid solution containing 23 per cent platinum and the remainder is a solid solution containing 70 per cent platinum. Since the cohesive forces are inherent in the atoms themselves, and the intensity of thermal agitation is fixed at a given temperature, it follows that the composition of the two phases at 1360° C. must be the same, regardless of the relative proportions of the two kinds of atoms. If to the alloy at point *f* is added pure platinum, the composition of the system will alter, but the composition of the phases will not. After equilibrium is established, there will still be present a liquid containing 23 per cent platinum and a solid containing 70 per cent platinum, but the relative amount of solid will be greater than it was before. Correspondingly, if gold is added to the system, the relative amount of liquid will increase; but the atoms will still be distributed between a 23 per cent platinum liquid phase and a 70 per cent solid phase. If enough gold is added so that the system contains less than 23 per cent platinum, the solid phase will disappear, since the thermal agitation at 1360° C. is great enough to keep the system liquid under this condition: likewise, if platinum is added in excess of 70 per cent (total), the system will consist of a single solid solution, since the cohesive forces now overcome the tendency of thermal agitation to disrupt the lattice.

The intersection of any horizontal line (corresponding to a given temperature) with the liquidus and solidus determines the composition of the liquid and solid phases which can exist at that temperature. If the temperature changes, the composition of both liquid and solid must change in such a way that the equilibrium is maintained. On freezing, this change continues until the liquid phase disappears; on melting, the changes continue until all the solid phase is gone. It will be instructive to apply this mode of reasoning to the lead-antimony alloys (consider the line *GOMN* as the solidus), also to show that a pure substance must have a definite melting point.

Let us now summarize some of the important facts about the gold-platinum diagram.

1. Above the liquidus the liquid phase exists alone, below the solidus a single solid phase (alpha solution) exists, while between the two lines solid and liquid solutions exist in equilibrium.

2. Only one solid solution is formed, although its composition may vary from 100 per cent platinum to 100 per cent gold. After solidification is complete, the solid solution has the same composition as the original liquid solution.

3. None of the alloys except the pure metals has a definite melting point.

4. The solid phase is neither gold nor platinum, but a solu-

tion of one in the other. This solid solution has physical properties which differ widely from those of the constituent metals.

**The General Case.**—The gold-platinum alloy diagram is characteristic of most of the binary systems forming isomorphous series. However, there is a variation of this type as shown in Fig. 14 (copper-manganese diagram). Here we have complete solid solubility, but there is a minimum point on the liquidus. ( Note that the addition of platinum to gold raises the freezing point instead of lowering it. The law which states that a dissolved substance lowers the freezing point of the solvent applies invariably only when the solute is insoluble in the solid state.) The interpretation of this diagram does not require much additional discussion. Cooling from points *a* or *a′* is identical with cooling from point *a* in Fig. 13. There is only one solid solution, but the alloy containing 36 per cent manganese (point *f* on the diagram) has a constant and minimum freezing point.

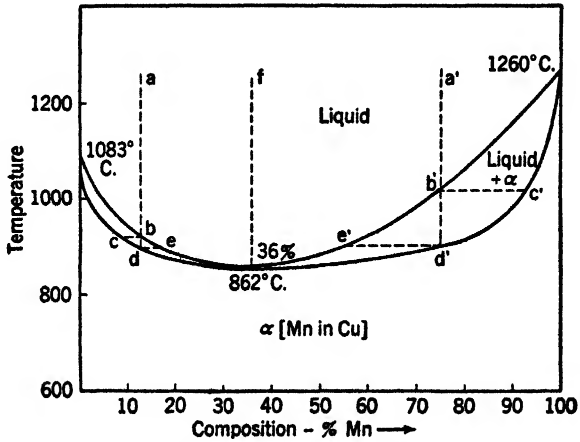
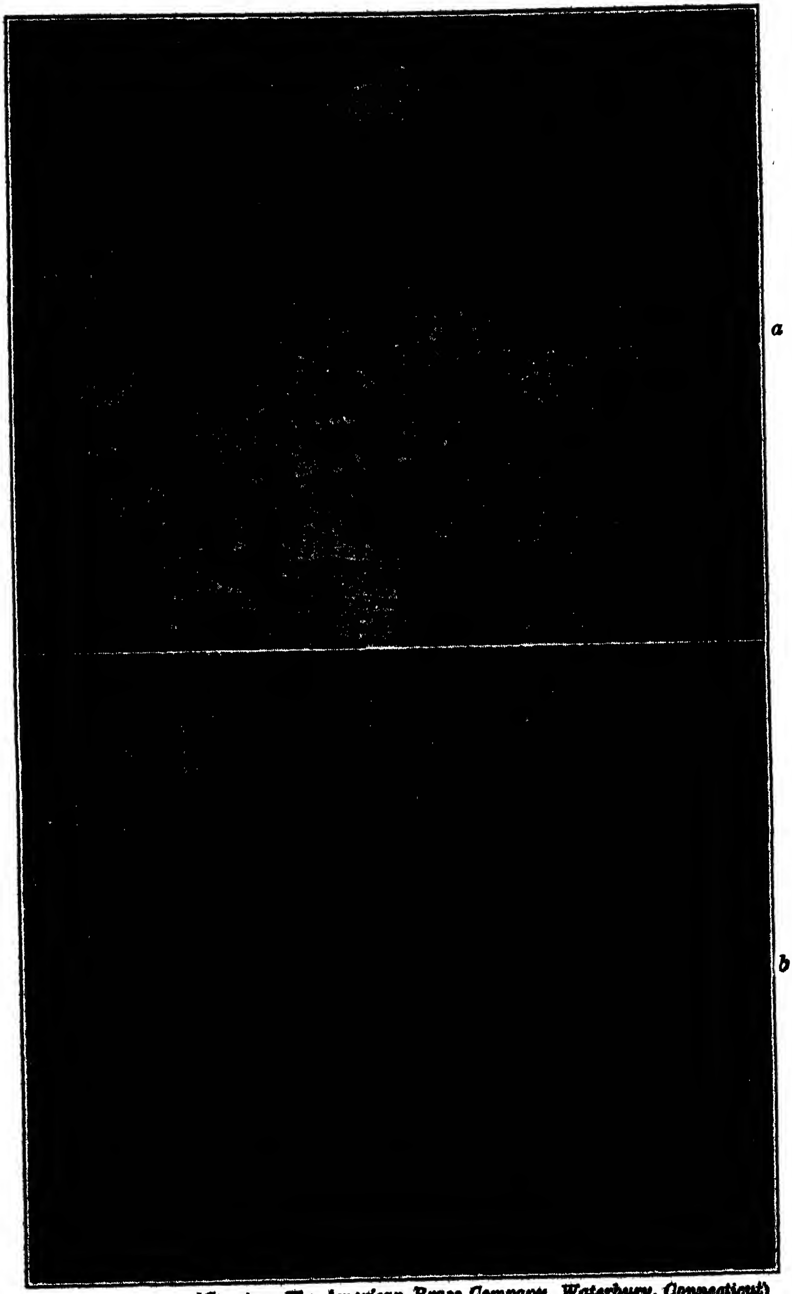


FIG. 14.—The Copper-Manganese Equilibrium Diagram.

**Segregation in Solid Solution Alloys.**—In the discussion of the gold-platinum alloy it was found that, in cooling, the composition of the solid changed as well as the composition of the liquid. Any change in composition must take place through diffusion; and, as has been mentioned in the previous chapter, diffusion in crystalline solids is comparatively slow, even at high temperatures. In order that an alloy should cool in the manner outlined, it would be necessary that cooling take place very slowly—much more slowly than ever occurs in practice. If an alloy of gold and platinum were cooled rapidly, the final grains would not be homogeneous, but they would be com-



(*Courtesy The American Brass Company, Waterbury, Connecticut*)

Fig. 15.—Uniform Solid Solution Alloys.

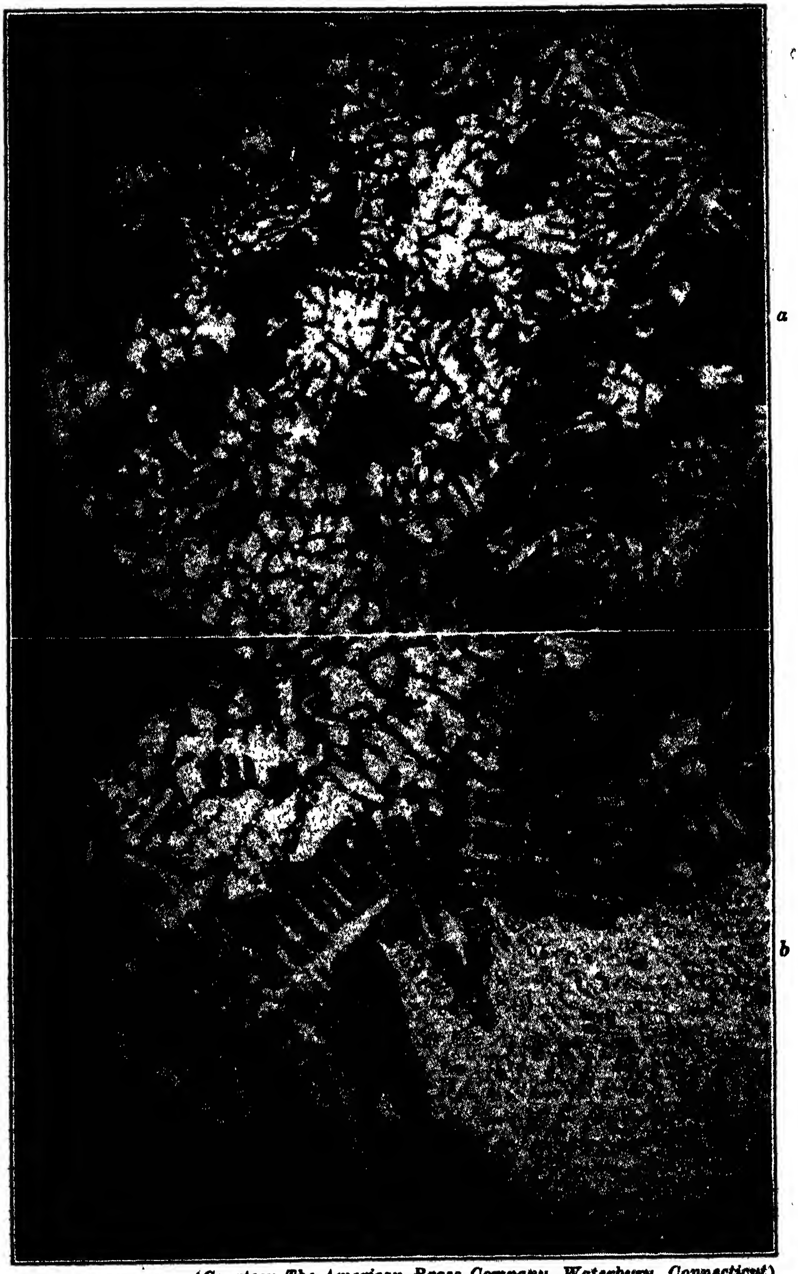
posed of layers of different composition—the inner layer or core would consist of a solution much richer in platinum than the outer layers. *Coring* or *segregation* is noticeable in all cast alloys of the solid

*(Courtesy The American Brass Company, Waterbury, Connecticut)*

Fig. 15. *Cont.*—Uniform Solid Solution Alloys.

*a.*—"Everdur B." Cu, 98.50%; Si, 1.25%; Mn, 0.25%. *b.*—Annealed Nickel Silver. Cu, 65.12%; Zn, 24.10%; Ni, 10.63%. *c.*—Alpha Brass. Cu, 65.00%; Zn, 35.00%. Sections *a* and *b* are ternary solid solutions, but their appearance is the same as that of binary solutions. Note the pronounced grain-contrast etching, and the twinned crystals in *a* and *c*.

solution type, and often the core takes the form of a dendrite, showing that the dendrite is the natural framework about which a crystal grain forms (see Figs. 16 and II-12).



*(Courtesy The American Brass Company, Waterbury, Connecticut)*

FIG. 16.—Cast Solid Solution Alloys Showing Cores and Dendrites.

*a.*—Cast Brass. Cu, 65.04%; Zn, 34.72%; Pb, 0.21%. *b.*—Cast Bronze. Cu, 98.89%; Sn, 1.09%; Si, 0.02%.

In practice, cooling is never sufficiently slow to permit complete diffusion in the solid crystals of cast metal. However, if the cast metal is hot-worked (or cold-worked and annealed), the deformation of the grains and the accompanying mixing of the segregated portions produce homogeneous grains of the solid solution. Homogeneous grains are characteristic of worked solid solution alloys. Cast specimens always show dendritic structure or coring. Prolonged annealing of a cast alloy at a temperature just below the point of incipient fusion will also tend to make the grains homogeneous, since the high temperature promotes diffusion.

### THE LEAD-BISMUTH ALLOYS

Figure 17 is the equilibrium diagram of the lead-bismuth series. These two metals are partially soluble, one in another, in the solid state; and the equilibrium diagram is typical of all such series. Most of the features of the diagram may be deduced from the two simpler diagrams which have already been discussed.

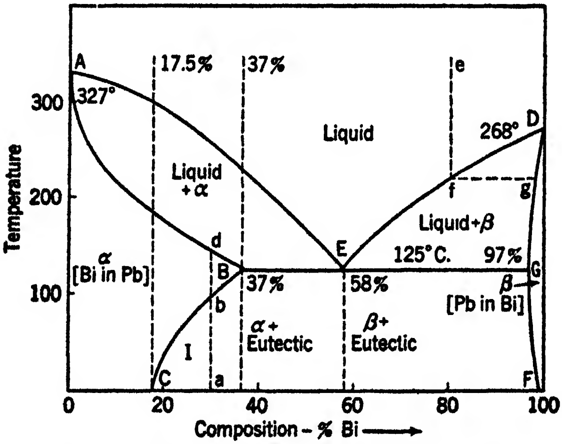


FIG. 17.—The Lead-Bismuth Equilibrium Diagram.

*AED* is the liquidus and *ABGD* is the solidus. Two solid solutions are formed. Alpha is a solution of bismuth in lead and has a face-centered cubic space lattice; beta solution is a solution of lead in bismuth, and its space lattice is rhombohedral, hexagonal like that of pure bismuth. The eutectic is a mechanical mixture of *saturated* alpha and beta solutions. Bismuth is more soluble in lead than lead is in bismuth, and the solid solubility of both metals decreases as the temperature drops, as shown by curves *BC* and *GF*. These curves indicate a transformation in the solid state or precipitation from a solid solution.

A few examples may help to fix some of these facts in mind, and the reasoning back of these statements can be verified by referring to the discussion of the simpler alloy types.

1. Any alloy containing 37 per cent bismuth or less will solidify entirely as alpha solution and will not contain any of the eutectic. Similarly, if the alloy contains more than 97 per cent bismuth, it will freeze as uniform beta solution. Only those alloys containing between 37 per cent and 97 per cent bismuth will contain the eutectic.

2. If the alloy containing 37 per cent bismuth is cooled to 0° C. the solubility of bismuth in solid lead decreases, and some bismuth is thrown out of the alpha solution. This does not come out as pure bismuth, however, but as saturated beta solution; and the beta phase precipitates as small crystallites along the grain boundaries and crystallographic planes of the alpha grains. The field marked *I* contains alloys of this type. There is a field similar to *I*, but smaller, on the bismuth side of the diagram. Any alloy containing less than 17.5 per cent bismuth will solidify as alpha solution and cool to room temperature without decomposition. Note that the lines *BC* and *GF* indicate the equilibrium between two solid phases, just as the solidus and liquidus in Fig. 13 indicate the equilibrium between a solid and a liquid phase.

3. If an alloy represented by the point *e* is cooled, freezing begins at *f*, and the first solid solution to separate has the composition represented by *g*. As cooling continues, the compositions of the liquid and solid move down the liquidus and solidus respectively—when the composition of the liquid is at *E*, the composition of the solid has reached *G;* and the remainder of the liquid freezes at constant temperature as a eutectic. An alloy containing 58 per cent bismuth is the only one of the series which has a definite melting point.

4. If we heat an alloy containing 30 per cent bismuth (starting from point *a* on the diagram) which consists of alpha host crystals and small crystallites of beta solution, the solubility of bismuth in lead increases, and the beta solution is gradually absorbed by the alpha solution. By the time we reach *b* all the beta solution has disappeared, and the alloy is homogeneous alpha solution. Further heating brings us to *d*, and from here the fusion follows in the same way as the fusion of the gold-platinum alloy.

**The General Case.**—All binary alloys which show partial solubility in the solid state have diagrams of the type of the lead-bismuth diagram. The reader will notice that insolubility in the solid state is accompanied by a horizontal line on the solidus. When this horizontal line extends from one side of the diagram to the other, it has complete solid insolubility (Fig. 9); but when the solidus is a uniform curve, the metals are reciprocally soluble in all proportions in the solid state. Figures 9 and 13-14 may be regarded as the two limits of alloys forming morphotropic series (Fig. 17). The minimum point on the liquidus in Fig. 14 seems to be the last vestige of a eutectic, and even this has disappeared in Fig. 13. This association of diagrams may prove helpful in remembering the details of their construction.

In connection with the statement just made, it might be well to mention the fact that no two metals are completely immiscible in the solid state. The lead-antimony series has been used for illustration, because this diagram has become a classic for this purpose, and also because the availability and low melting points of these metals adapt them for convenient laboratory study. As a matter of fact, the solubility of antimony in solid lead is great enough to show on a diagram (see Fig. 34). Theoretically, complete solid insolubility is impossible, and investigation has revealed that there is at least slight solid solubility in practically all cases.

Reference to Fig. 9 shows how the assumption of complete insolubility in the solid state leads to a contradiction. If the lines *GO* and *NM* coincide with the composition ordinates representing 100 per cent lead and 100 per cent antimony respectively (as shown by the diagram), this means that there should be a transformation point at *O* and likewise at *M*. However, there is no such transformation point for either pure lead or pure antimony, and hence the lines *GO* and *NM* cannot exactly coincide with the end composition ordinates of the diagram. In other words, the lines *GO* and *NM* must lie *within* the boundaries of the diagram, and such a fact indicates solid solubility (however slight), and the diagram is actually of the same type as the lead-bismuth diagram (Fig. 17).

## INTERMETALLIC COMPOUNDS—THE CALCIUM-MAGNESIUM ALLOYS

Certain pairs of metals combine to form one or more *intermetallic compounds*, and the presence of such a compound is usually indicated by a maximum point on the liquidus as shown in Fig. 18. These have many of the properties of ordinary chemical compounds; they obey the law of definite proportions, have a definite melting point, and have a definite heat of formation. However, they differ from the compounds formed between metals and non-metals in several important respects, among which are the following:

1. The heat of formation of intermetallic compounds is low compared to the heats of formation of such compounds as PbS or $NaCO_3$ (metals and non-metals). A low heat of formation means that the compound is easily decomposed.

2. It appears that the "molecules" break down when the compound is melted; and molecules of the compound do not exist in the liquid state.

3. The molecular composition of these compounds cannot be accounted for by the ordinary valence rules.

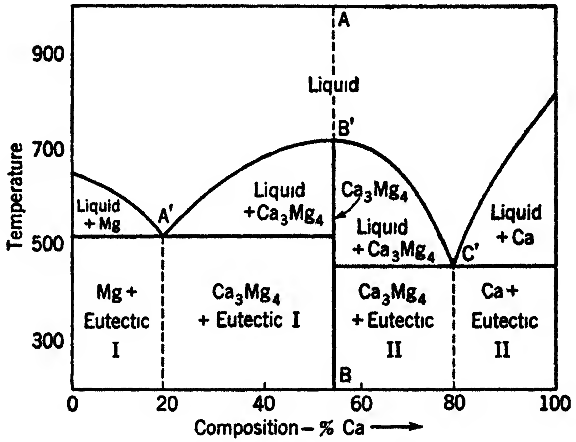


FIG. 18.—The Calcium-Magnesium Equilibrium Diagram.

4. These compounds have a "metallic" appearance and are fair conductors of electricity. This implies that they are not formed by the sharing or interchanging of all available valence electrons.

Considerations such as these, together with the fact that intermetallic compounds usually have a complicated lattice structure, lead to the conclusion that intermetallic compounds are largely due to secondary valence forces; these compounds are the result of an ability to form a unique and complicated lattice pattern, rather than of chemical combination in the ordinary sense with which is associated the assembling of valence electrons into stable shells (primary valence).

**The Calcium-Magnesium Alloy Diagram.**—The diagram in Fig. 18 shows the composition of the calcium-magnesium alloys. The diagram is interpreted very easily, if the line *AB* is drawn dividing the figure into two parts. The portion to the left of *AB* is the equilibrium diagram of Mg and the compound, and is exactly the same as the lead-antimony diagram; the right-hand portion represents the $Ca_3Mg_4$-Ca alloys.

Note that: (1) all the alloys contain some of the compound; (2) two eutectics are formed; (3) the pure compound and the eutectics are the only alloys having definite freezing points; (4) any alloy must contain some of one of the eutectics, but both eutectics cannot be present in the same alloy; and (5) the freezing point of the compound is considerably higher than that of either of the eutectics and is even higher than the freezing point of pure magnesium.

**The General Case.**—A set of binary alloys may contain one or several intermetallic compounds, and each has a definite freezing point and a separate branch on the liquidus (*A'B'C'* in Fig. 18). The interpretation of alloy diagrams showing the presence of compounds is best done by resolving the diagram into simpler ones, as was done in the case of the calcium-magnesium alloys. Here it was found that each of the individual parts represented complete insolubility in the solid state; generally, either or both of these sections might have shown partial or complete solid solubility.

**The Lever Principle.**—It is often necessary to calculate the amount (weight) of each phase in a two-phase alloy. In all the equilibrium diagrams illustrated in this chapter, the various fields or regions on the diagram represent either two-phase or single-phase alloys. To find the amount of each phase present in a two-phase alloy, locate the point which corresponds to the composition and temperature, and draw a horizontal line through it, intersecting the boundaries of the region; the points of intersection give the composition of the two phases present. If the original point (*b* in Fig. 19) is thought of as the fulcrum of a lever, and the lines *ab* and *bc* as the lever arms, then the percentage of solid phase is:

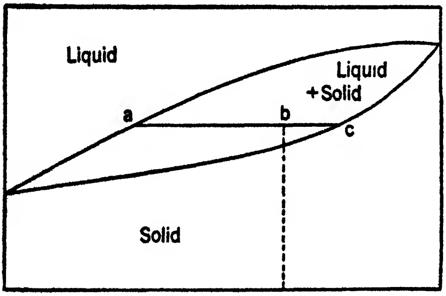


Fig. 19.—Diagram to Illustrate the Lever Principle.

$$100 \times \frac{ab}{ac}$$

and the percentage of liquid phase is:

$$100 \times \frac{bc}{ac}$$

Although this illustration applies to equilibrium conditions between a liquid phase and a solid phase, the same method can be applied to equilibrium between two solid phases or two liquid phases.

## THE PERITECTIC REACTION

Let us return for a moment to consider the eutectic shown in Fig. 17 of the lead-bismuth diagram. We have seen that when the eutectic liquid freezes, it yields two phases—saturated alpha solution containing 37 per cent Bi and saturated beta solution containing 97 per cent Bi—which appear as finely disseminated particles in the characteristic eutectic structure. When the solid eutectic is heated, it melts to form a homogeneous liquid of eutectic composition, and both the freezing and melting of the eutectic take place at constant temperature. We may regard this change as a reaction taking place at a constant temperature; upon cooling, a single phase (liquid of eutectic composition) reacts to form two solid phases (saturated alpha and beta solutions); and upon heating, the two solid phases react to form a single (liquid) phase.

$$\text{Liquid (eutectic)} \underset{\text{heating}}{\overset{\text{cooling}}{\rightleftarrows}} \text{Saturated } \alpha \text{ solution} + \text{Saturated } \beta \text{ solution}$$

In a number of alloys there occurs a *peritectic reaction* which we may regard as being the reverse of the eutectic reaction, since, upon cooling through the transformation temperature, two phases react to form a single phase, and upon heating a single phase "reacts" or decomposes to yield two phases. The single phase concerned in peritectic reactions which appears on cooling and decomposes on heating may be either (1) a solid solution or (2) an intermetallic compound. The peritectic reaction takes place at a constant temperature, just as the eutectic reaction does. We shall illustrate the two aspects of peritectic reactions by means of simple hypothetical diagrams.

Figure 20 illustrates the equilibrium diagram of two metals $A$ and $B$ which undergo a peritectic reaction at temperature $T$. The single phase which undergoes a decomposition on heating is the alpha solid solution; the phases formed are a liquid solution having the composition given by the point $D$ and saturated beta solid solution whose composition is given by the point $F$. Let us consider the heating and cooling of two particular alloys to illustrate the meaning of the diagram.

At the point $a$ we have a uniform liquid solution. As this alloy is cooled, we reach the liquidus at $x$, and beta solution of composition $y$ begins to precipitate. Upon further cooling, the composition of the liquid moves down the liquidus *ED*, and the composition of the solid moves down the solidus *EF*. When the composition of the liquid has reached *x'*, the solid has the composition *y'*; and finally we reach the temperature *T* and have a liquid of composition *D* and saturated beta solid solution of composition *F*. The stage is now set for the peritectic reaction. The saturated beta solution (composition *F*) reacts with the liquid solution (composition *D*) to yield solid alpha solution having the composition given by the point *G*. The reaction takes place at constant temperature, and it continues until one of the reagents runs out. In our case, the beta solution will disappear first, so that, at the completion of the peritectic reaction, we shall have alpha solid solution of composition *G* + excess liquid of composition *D*. If our initial point had been to the right of *G*, the liquid would disappear first; and at the end of the peritectic reaction we would have alpha solution of composition *G* + excess beta solid solution (composition *F*).

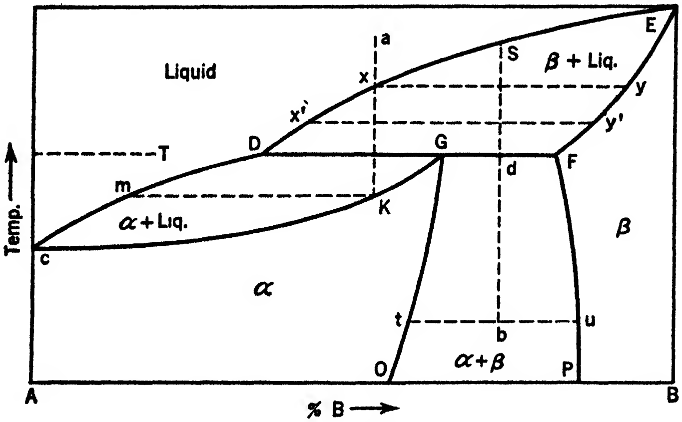


FIG. 20.—Hypothetical Diagram to Illustrate the Peritectic Decomposition of a Solid Solution.

As cooling continues after completion of the peritectic reaction, the composition of the liquid moves down *DC* to *m*, while the composition of the solid changes from *G* to *K*, and our alloy eventually solidifies as uniform alpha solid solution.

Let us consider what happens when an alloy represented by the point *b* is melted. This alloy consists of a mixture of saturated alpha and beta solid solutions, and the composition of each of these phases is given by the points *t* and *u* respectively. As the alloy is heated, the solid phases undergo slight changes of composition, as shown by the lines *GO* and *FP*. When we reach *d*, the composition of alpha is given by *G*, and that of beta is given by *F*. Now the reverse peritectic reaction begins. The alpha solution begins to decompose into liquid of composition *D* and additional beta solid solution of composition *F*. At the end of the isothermal reaction we have two phases—liquid of composition *D* and solid beta solution of composition *F*. Further heating causes the composition of the solid beta phase to move up along *FE*, while the composition of the liquid moves up along *DE*. At point *S* the solid beta phase disappears, and we have a uniform liquid solution.

A second peritectic reaction involving an intermetallic compound is illustrated in Fig. 21. Assume that the two metals involved are *A* and *B*, and that the intermetallic compound *AB* is formed. The vertical line *HP* gives the composition of the compound *AB* which undergoes a peritectic reaction at temperature *T*. In other words, the compound is too unstable to melt, but decomposes before it can be melted. Let us again take two illustrative examples.

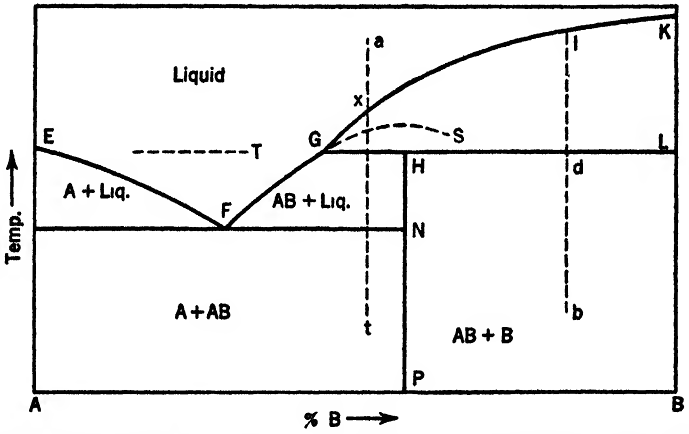


Fig. 21.—Hypothetical Diagram to Illustrate the Peritectic Decomposition of a Compound.

At point *a* we have a homogeneous liquid alloy. Upon cooling to *x*, metal *B* begins to separate, and precipitation of *B* continues as the composition of the liquid moves from *x* to *G*. Now at temperature *T* we have solid metal *B* + liquid of composition *G*. The peritectic reaction begins with solid *B* reacting with liquid *G* to form the compound *AB* with a composition given by *H*. When the peritectic reaction is complete, we have compound *AB* + excess liquid of composition *G*. (If our point had been to the right of *H*, we would have compound $AB$ + excess solid $B$ at the end of the reaction.) As cooling continues, the composition of the liquid moves down from $G$ to $F$ as more $AB$ precipitates; and at $F$ the remaining liquid crystallizes as a eutectic between $A$ and $AB$. Our final solid alloy (point $t$), therefore, would be a mechanical mixture of $A$ crystals + $AB$ crystals; some of the crystals of $AB$ would be large "excess" crystals, and the rest of the $AB$ crystals would be in the eutectic. All the $A$ crystals would be in the eutectic.

On heating the alloy at point $b$, we pass from $b$ to $d$ without change in our alloy which consists of crystals of $B$ + crystals of $AB$. At $d$ the compound $AB$ (composition $H$) decomposes at constant temperature to give solid $B$ and liquid of composition $G$. After the reaction is complete, further heating causes the composition of the liquid to move from $G$ to $l$; here all the $B$ crystals have dissolved, and we have a uniform liquid.

We may draw the line $GS$, which is a prolongation of $FG$, to show the form we would expect the liquidus to have if the compound $AB$ had a true melting point. Whenever a compound has a true melting point (*vide* the Ca-Mg diagram, Fig. 18), the ordinate representing the composition of the compound is at a maximum point on the liquidus. The case of a compound which decomposes peritectically is therefore called the case of a "hidden" or "suppressed" maximum.

It will be evident to the student that peritectic reactions will seldom reach equilibrium conditions, unless the cooling and heating are done very slowly, because the reaction of a liquid and a solid to form another solid requires considerable time for the necessary diffusion to take place. When the peritectic reaction between a liquid and a solid phase does not go to completion, it leads to the formation of the "peritectic wall" structure.

## TRANSFORMATIONS IN THE SOLID STATE—THE IRON-CARBON ALLOYS

The changes which may take place upon cooling an alloy are not confined to freezing. After an alloy has become completely solid, phase changes may occur on further cooling, and these changes are often of great importance. Solid-solid phase transformations are governed by the same laws of equilibrium as liquid-solid changes, and no new principles are involved. Allotropic changes in pure metals and the partial decomposition of the lead-bismuth solid solution have been mentioned already. Another example of transformation in the solid state is illustrated by a portion of that most important of all alloy diagrams, the equilibrium diagram of the iron-carbon alloys.

**The Iron-Carbon Diagram.**—Figure 22 is really an equilibrium diagram of iron and iron carbide, $Fe_3C$ (*cementite*) rather than of iron and carbon (compare with the left-hand portion of Fig. 18), and the diagram does not even extend to 100 per cent $Fe_3C$. However, the portion shown contains all that is of importance, and for present purposes only those alloys containing less than 1.7 per cent carbon will be considered. The line *ABD* is the liquidus and *AEC* the solidus. From the characteristics of these curves it is seen that carbon (or $Fe_3C$) is partially soluble in iron, and that any alloy containing less than 1.7 per cent carbon solidifies as a uniform solid solution. To this solution the name *austenite* is given. It might seem that the solute should be $Fe_3C$, but there is no exact information as to the state of the carbon in solid solution. Austenite is usually regarded as a solid solution of carbon in gamma iron (the form stable above 900° C.).

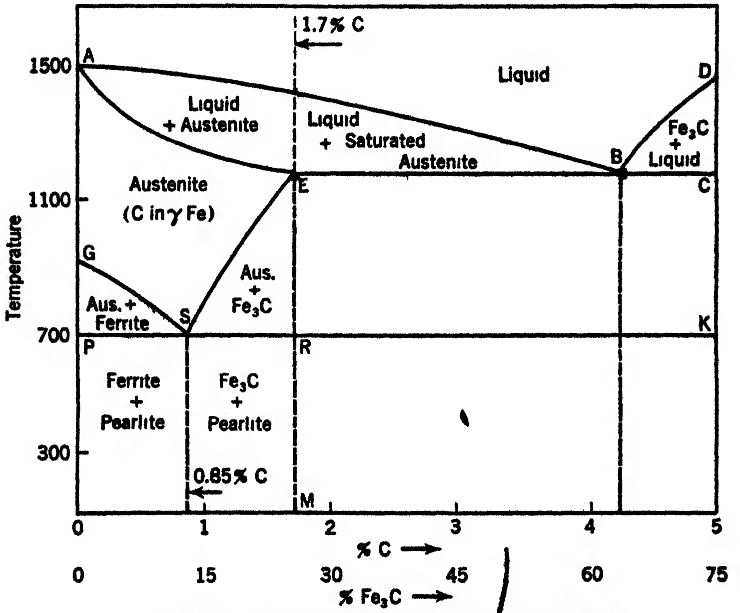


FIG. 22—The Iron-Carbon Equilibrium Diagram.

The portion of the diagram bounded by the line *AEMO* bears a striking resemblance to the lead-antimony diagram, except that, instead of a liquid in the upper field, there is a solid solution. When the lead-antimony solution is cooled, it freezes in a characteristic manner to give lead and antimony crystals. When this solid solution of carbon in iron is cooled, it undergoes a transformation in exactly the same way to give crystals of iron and crystals of cementite. These iron-carbon alloys which freeze as a homogeneous solid solution (alloys with less than 1.7 per cent carbon) are the ordinary *carbon steels;* and by a comparison of this diagram with that of the lead-antimony series, the following conclusions concerning the steels may be drawn:

1. Steel containing 0.85 per cent carbon has a structure exactly like that of a eutectic, being composed of alternate narrow bands of pure iron (ferrite) and $Fe_3C$ (cementite). This aggregate is called a *eutectoid;* and the difference between a eutectic and a eutectoid is simply that the former separates from a liquid solution, whereas the latter is formed from a solid solution. The name *pearlite* is given to the Fe-$Fe_3C$ eutectoid.
2. All steels must contain some pearlite. Steels with less than 0.85 per cent carbon (hypoeutectoid) contain excess ferrite, and steels with more that 0.85 per cent carbon (hypereutectoid) contain excess cementite.
3. All carbon steels are mechanical mixtures of ferrite and cementite.

*(Courtesy Joseph T. Ryerson and Son, Inc., Chicago)*

FIG. 23a.—Hypoeutectoid Steel (× 100) Containing About 0.40% C. Shows Ferrite (White) and Pearlite (Dark).

4. A eutectoid steel has the lowest transformation point of all, and is the only one in which transformation takes place at a constant

temperature. The eutectoid steels have the best mechanical properties of any of the carbon steels, although the hypereutectoid steels are harder owing to the intrinsic hardness of the cementite.

*(Courtesy Joseph T. Ryerson and Son, Inc., Chicago)*

FIG. 23*b*.—Hypoeutectoid Steel (× 1000). Shows Structure of Lamellar Pearlite.

*(Courtesy Joseph T. Ryerson and Son, Inc., Chicago)*

FIG. 23*c*.—Hypereutectoid Steel (× 100). Shows Cementite (White) and Pearlite. The Cementite Network Outlines the Original Austenite Grains.

## THE PHASE RULE

The alloy diagrams which we have been studying up to this point represent examples of heterogeneous equilibria, or the equilibria that exist between two or more phases. The thermodynamic law which governs all cases of heterogeneous equilibrium is known as Gibbs' phase rule, which we may state as follows:

$$F = C - P' + 2$$

where $C$ is the number of *components* in the system, $P'$ is the number of *phases* present, and $F$ is the number of *degrees of freedom* of the system. Let us first consider the meaning of this law, and then some of its applications to the binary alloy systems.

The phase rule tells us how many phases $P'$ may exist in equilibrium in a system of $C$ components under given conditions of pressure, temperature, and volume.

The number of degrees of freedom ($F$) of any system is defined as the least number of variables of the system which must be fixed in order to define the system completely. Suppose, for example, that we consider a very simple system such as one mol of oxygen gas. Obviously, such a system is not completely defined—it may exist at high or low temperatures, it may be under high or low pressures, it may have a large volume or a small volume. If we are to define this system in such a way as to leave no doubt as to its physical condition, we must arbitrarily fix a certain number of variables. In the case of a pure gas, pressure, temperature, and volume are functionally related, i.e.:

$$V = f(P,T)$$

where the nature of the function $f$ depends upon the gas concerned. For an ideal gas this functional relation (equation of state) becomes

$$PV = RT$$

Whatever the relation, however, the fact remains that $V$ is uniquely determined whenever we assign definite values to $P$ and $T$, and therefore it is necessary to fix only two variables in order to determine unambiguously the physical state of a pure gas. If we say, for example, that we have one mol of oxygen gas under a pressure of 76 mm. of mercury and at a temperature of 0° C. we have a system which is completely defined; and all its physical properties, such as its heat content, internal energy, entropy, and volume have definite and unique values. This system, therefore, has two degrees of freedom, since it is possible arbitrarily to change two independent variables (temperature and pressure) within certain limits without the appearance of a new phase in the system.

If we consider a system consisting of a mixture of two gases (gaseous solution) such as oxygen and nitrogen, for example, we find that there are three degrees of freedom, for it is possible to vary arbitrarily three independent variables (temperature, pressure, and composition) without causing a new phase to appear.

Liquid water, ice, and water vapor can exist together in equilibrium at only one combination of temperature and pressure, which is called the triple point (+ 0.0075° C. and 4.579 mm.) If either the pressure or the temperature is changed, one of the phases disappears, and therefore this system is invariant or has no degrees of freedom.

If we consider the two-phase system of a liquid in equilibrium with its vapor, we find that the pressure of the vapor (which is the same as the total pressure on the system) is a function of temperature. This constitutes a univariant system having one degree of freedom, since only one variable can be varied arbitrarily—if a given temperature is assigned, the pressure is automatically fixed, or if we decide on a definite pressure, there is only one temperature which will permit the existence of such a pressure.

The number of components ($C$) of any system may be defined as the minimum number of independently variable constituents by means of which the composition of all the phases present can be represented. Suppose, for example, that we have the system represented by the equilibrium

$$\underset{\text{solid}}{FeCO_3} \rightleftarrows \underset{\text{solid}}{FeO} + \underset{\text{gas}}{CO_2}$$

This is a two-component system, since we can express the composition of each phase in terms of any two of the three substances, $FeCO_3$, $FeO$, $CO_2$. Suppose that we take $FeO$ and $CO_2$, as the two components; then $FeCO_3$ is not a component since it can be regarded as being made up of $FeO$ and $CO_2$ according to the equation

$$FeO + CO_2 \rightarrow FeCO_3$$

If, however, we had a gaseous solution of $O_2$, $N_2$, and $CO_2$ this would be a three-component system, since the chemical composition of any one gas could not be derived from any combination of the other two.

A phase ($P$ = number of phases in a given system) is a physically and chemically homogeneous mass, and it is separated from the other phases by a surface. Since all gases are miscible one with another, there can be only one gaseous phase in any system. Any substance is usually capable of existing in more than one phase provided that the conditions (temperature, pressure, composition, etc.) are suitable. The phase rule defines the conditions under which various phases can exist together in equilibrium.

Let us now consider the application of the phase rule to the equilibria which we find in the binary alloy systems. By confining ourselves to these particular systems, we can simplify the general equation of the phase rule as follows:

1. $C = 2$ in all cases, since we are to deal with binary (two-component) systems.

2. In any of these systems one vapor phase will be present, and only one, as we have noted. Ordinarily we are not interested in the vapor phase as much as in the solid and liquid phases. Let us let $P =$ the number of phases present which are either solid or liquid. Then we have the relation

$$P + 1 = P'$$

3. Our equilibrium diagrams are constructed at constant (standard) pressure, and in none of them has the variation of pressure been considered. For our purposes, the pressure is constant, and only two quantities are subject to arbitrary change—temperature and composition. Since the composition of a binary system is defined by a single variable, it follows that the maximum number of degrees of freedom is two, corresponding to variation of the two independent variables temperature and composition. Therefore we may have only three possible values for $F$; 2, 1, or 0.

Adopting these simplifications, we may rewrite the phase rule for our special case as:

$$F = 2 - (P + 1) + 2;\ F \leq 2 \qquad (1)$$

or

$$F = 3 - P;\ F \leq 2 \qquad (2)$$

From equation (2) we see immediately that the maximum value for $P$ is 3 and that, if $P = 3$, $F = 0$. Consequently, we cannot have more than three (solid or liquid) phases in equilibrium; and if we do have a three-phase system, it has no degrees of freedom. If we change the temperature of any three-phase system, one of the phases must disappear. Let us consider one such system as an illustration.

A three-phase system which may be used as an example is the lead-antimony eutectic alloy at its melting point. Here we can have three phases in equilibrium—the liquid lead-antimony alloy of eutectic composition, and the two solid phases, lead and antimony. The eutectic, of course, is not a separate phase, since it consists of a mixture of lead and antimony. If we lower the temperature of such a system, the liquid freezes, and the liquid phase disappears. If we raise the temperature, the solids melt, and only the liquid phase remains.

Now the phase rule does not take cognizance of the amount of each phase present. We might have 1 gram of eutectic liquid and a ton of the solid mixture in equilibrium, or vice versa. Suppose now we try to cause a phase change by altering the composition of our system. If composition is a variable and if we change this variable in our invariant system, we should, according to the phase rule, cause one of the phases to disappear, but actually nothing of the sort happens. If we keep the temperature constant and add pure solid antimony, we have that much more solid antimony present, but we still have solid lead and liquid solution (three phases). In the same way, we can add solid lead without disturbing the equilibrium. The liquid is saturated with both metals, so that we cannot add anything to it. This apparent dilemma leads to the statement that composition cannot be regarded as a variable (degree of freedom) *unless the system contains an unsaturated solution* (solid or liquid) such that its composition may be altered by the addition of one of the components. This leads us to a related discussion of the one- and two-phase fields in binary alloy diagrams.

We have already had occasion to mention the "one-phase" and "two-phase" fields which are found in all the diagrams we have studied. We have seen that no phase changes occur in any alloy unless we cross the boundary between two fields—i.e., when we cool a liquid alloy, there is no phase change until we reach the liquidus. Since apparently we can change both the temperature and composition within certain limits in these fields, the systems represented by points within fields might be expected to have two degrees of freedom. However, the phase rule states that, if we have two phases, we can have but one degree of freedom, and two degrees of freedom can exist only in single-phase systems.

Let us consider briefly some of the characteristics of the alloys found in single-phase fields. In Figs. 24–29 are reproduced several simple diagrams in which the two-phase regions are shaded. If we start from a point such as *a* (Fig. 24), we can move in two directions without altering the phase relations as long as we stay within the field. We can raise or lower the temperature by moving along a vertical line, or we can change the composition by moving along a horizontal line, and always have a single homogeneous liquid solution. The same statements apply to the point *d* which represents a solid solution in a single phase field. In each of these cases we have the two degrees of freedom as required by the phase rule. If we are to have a single phase with two degrees of freedom, i.e., a phase which can suffer changes in both temperature and composition without the appearance of another phase, there is only one type of phase which fits the requirements—a solution. Hence, all single-phase fields in binary diagrams must contain a single solution, either a liquid or solid solution; or, in other words, no single-phase field can contain a pure metal, compound, or saturated solution, since these substances have a definite chemical composition and permit of no variation of composition.

The term "two-phase region" or "field" is too useful to be abandoned, and it would be awkward to describe a substitute for it.

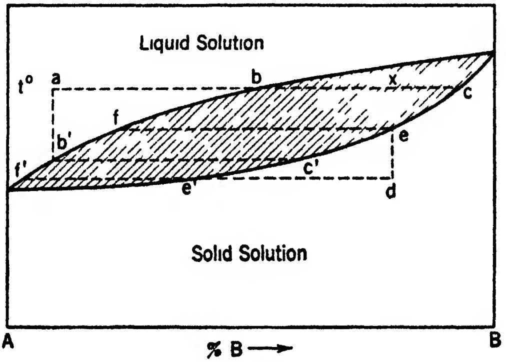


FIG. 24.

Actually, however, the phase rule makes this a contradiction in terms, because the word "field" connotes two degrees of freedom (two dimensions), and this is impossible when we have two phases in equilibrium. For the sake of gaining a better insight into the meaning of these diagrams, let us make the assumption that two-phase fields (the shaded portions in Figs. 24–29) are *gaps* in the equilibrium diagram which do not form part of the diagram proper. Consider now only the one-phase fields and the boundaries as part of the diagram, since it is only in these regions that the phase rule applies.

If we start from a point such as *a* in Fig. 24 and add metal *B* to the melt, we may think of our point as moving along the line *ab*. No phase changes occur until we reach the point *b*, and, as far as our liquid solution is concerned, this is the end of the line. It is saturated with metal *B*, and no further change can take place in it. We may think of the liquidus as a barrier which prevents our imaginary moving point from entering the cross-hatched field. If we add more metal $B$ to our saturated liquid solution of composition $b$, a new phase appears—the saturated solid solution having the composition given by $c$. As long as these two solutions exist together in equilibrium, they must both be saturated. No unsaturated solution can exist together in equilibrium with any other phase, because if an unsaturated solution is in contact with another phase, it will tend to saturate itself at the expense of the second phase.

When an alloy is at temperature $t$ (Fig. 24), it consists of a mixture of saturated liquid and solid solutions of composition $b$ and $c$ respectively for all alloys whose total composition lies between $b$ and $c$. We may think of the point $x$ (or any point inside a two-phase field) as *exterior to* the equilibrium diagram proper, and the location of such a point simply determines the amount of each phase present (by the lever principle). *The composition of each phase is determined by a point on the boundary of the field.*

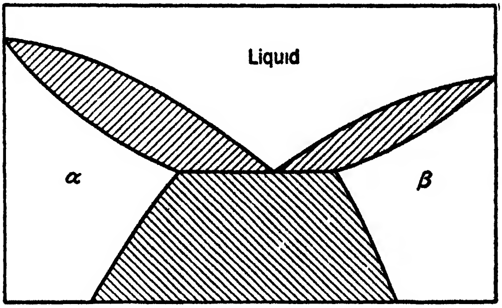


FIG. 25.

Two principal types of phases occur in binary alloys, which we may designate as:

1. *Invariant phases*, which have a constant chemical composition at any definite temperature and which include pure metals, compounds, and saturated solutions (solid or liquid). The composition of these may or may not change as the temperature changes.

2. *Unsaturated solutions* (solid or liquid), which are characterized by the fact that their composition can be varied within certain limits.

Let us now summarize some of the facts about equilibrium diagrams which we have deduced from the phase rule:

1. All single-phase fields must contain unsaturated solutions.

2. All "two-phase" fields represent the equilibrium of two invariant phases whose compositions are given by points on the boundary of the field. Such fields may be regarded as "blocked out" of the

diagram, since, if we consider them as "fields," we are contradicting the phase rule.

3. Any unsaturated solution is defined by a two-dimensional area; it has two degrees of freedom; and if it is to exist in a binary system in equilibrium, it must be the only phase present. If a binary system has two degrees of freedom, the phase rule permits the existence of only one phase (Equation 2).

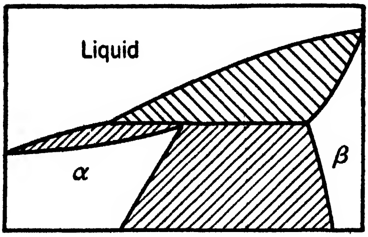


FIG. 26.

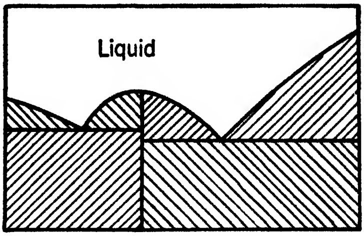


FIG. 27.

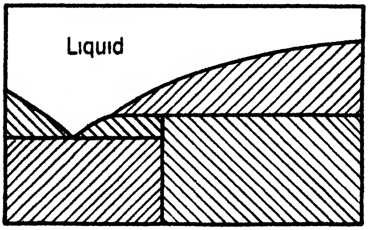


FIG. 28.

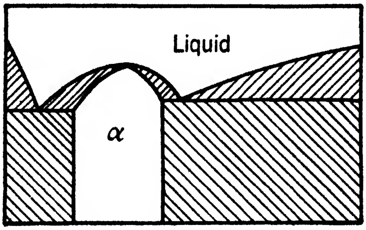


FIG. 29.

4. Any invariant phase is defined by a line on the diagram, and all the lines which form the field boundaries on our diagrams define some one invariant phase, except the horizontal lines. A vertical boundary locates an invariant phase which does not change composition with temperature changes (pure metals, compounds, and some saturated solutions); any curved boundary locates an invariant phase which changes its composition as the temperature changes (saturated solutions). At any given temperature an invariant phase can have only one composition, and this is determined by the intersection of the temperature abscissa with the boundary line which defines the phase. A horizontal boundary would intersect one temperature abscissa at an infinite number of points, so that it would be meaningless to say that such a boundary defined a phase.

5. In any system containing an invariant phase the composition of the phase is a function of the temperature, since the composition of the phase is given by a definite line on the temperature-composi-

tion plot. This means that, when a value is arbitrarily assigned to the temperature, the composition of the phase is fixed, or that we have only one degree of freedom. Now, with one degree of freedom, we must have two phases present, so that in any system containing invariant phases we always have two such phases, except in the limiting case where the composition of the system happens to be exactly the same as the composition of some one invariant phase.

6. In a binary system in which one phase alters to another of exactly the same composition, the phase rule must be applied as if the system had only one component. For example, if we have a liquid alloy of exactly the same composition as a compound which forms on freezing, the system freezes at a definite temperature to give a single solid phase exactly as a pure metal (one-component system) would. This is a corollary to a statement which we made before, that a liquid alloy freezes at a definite temperature, if, and only if, the composition of the separating phase or phases is exactly the same as the composition of the liquid, so that the composition of the liquid is not changed by the separation of the solid phase (or phases). If only one phase separates (e.g., the compound cited above), we have an apparent violation of the phase rule, unless we regard our system as a one-component system. If two phases separate (eutectic), the phase rule for two-component systems applies, but the total composition of the two solid phases is still the same as the composition of the liquid.

7. Horizontal lines on the diagram always indicate the presence of an isothermal reaction between three phases—either a eutectic or a peritectic reaction. Such a line always intersects other boundaries at three (and only three) points, and these points give the composition of the interacting phases. The only exception to this rule is when two of the points are so close together that they coincide—the transition between a eutectic reaction and a peritectic reaction. In this special case we must again assume that our system behaves as a one-component system, in order to make it fit the restrictions of the phase rule.

An unlimited amount of similar discussion could be given, relating to the interpretation of equilibrium diagrams in the light of the phase rule; but the material given here should be sufficient to indicate how this is done. It is suggested that the reader practice on various diagrams until their interpretation is perfectly clear, always keeping in mind that the phases involved are defined by one-phase fields and by the boundaries of two-phase fields. In diagrams such as Figs. 27–28, all the diagram below the liquidus should be considered as a "skeleton," because no single-phase fields are present, and all the phases concerned have their compositions given by lines.

## TERNARY ALLOYS

All the alloys considered up to this time have been alloys of two metals, or binary alloys. Many important alloys contain three or more metals, and an outline of the construction of the equilibrium diagram for one hypothetical ternary alloy is given here in order to illustrate the manner in which the phase changes may be represented.

Assume that there are three metals, *K*, *L*, and *M*, which are miscible in all proportions in the liquid state and completely insoluble in the solid state. This represents a system of ternary alloys which is analogous to the lead-antimony binary series. As the composition of a binary alloy can be represented by a single variable, so the composition of a ternary alloy can be represented by two variables. Since temperature is a third variable, the equilibrium diagram of a ternary alloy must be a three-dimensional solid. The framework of the binary alloy diagram is a rectangle—the framework of a ternary alloy diagram is a right triangular prism with an equilateral base. Points in the horizontal base represent composition, and the distance along the vertical represents temperature.

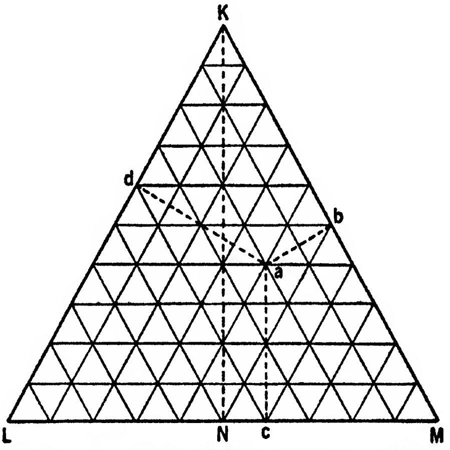


Fig. 30—Base of a Ternary Equilibrium Diagram.

Figure 30 is a sketch of a triangular coordinate system that is used to represent the composition of ternary alloys. Any point on the diagram represents a single ternary alloy of definite composition.

Each apex of the triangle represents pure metal—the point at the upper apex represents pure metal *K*, and the two lower corners represent pure metals *L* and *M* respectively. The percentage of any metal in a given alloy is determined by the perpendicular distance from the reference point to the side opposite the metal in question. This means that the percentage of metal *L* in an alloy whose composition is given by the point *a* is *ab*; this alloy also contains *ad* per cent of *M* and *ac* per cent of *K*. Applying this rule to the point *K*, the percentage of *K* in this alloy equals *KN*; but since this point represents pure metal *K*, the line *KN*, or any altitude of the triangle, equals 100 per cent. Perpendiculars such as *ab*, *ac*, and *ad* drawn from any interior point of an equilateral triangle must be such that $ad + ab + ac$ shall equal the altitude of the triangle. Therefore, the total composition of any alloy must always add to 100 per cent. If the lines such as *ab* are measured in units such that the length of *KN* equals 100, then their lengths are numerically equal to the respective percentages. Since the units of the ruling in Fig. 30 divide *KN* into ten equal parts (each unit equal 10 per cent), the alloy represented by the point *a* contains 20 per cent *L*, 40 per cent *K*, and 40 per cent *M*. Any point on the boundaries of the triangle represents a binary alloy; the alloy given by the point *d*, for instance, contains 60 per cent *K*, 40 per cent *L*, and 0 per cent *M*.

It is evident that if this horizontal triangle represents composition, and a vertical coordinate represents temperature, the equilibrium diagram will be contained in a solid (triangular prism) and the liquidus and solidus will be *surfaces*. Consequently, a true equilibrium diagram of a ternary alloy cannot be shown in two dimensions, but must consist of a solid model.

Along the sides of the equilateral triangle, construct the binary diagrams formed by the three possible combinations of *K*, *L*, and *M* (Fig. 31). Now imagine that these diagrams are bent upright so that the temperature coordinate is normal to the plane of the triangle, and the points *A*-*A*, *B*-*B*, and *C*-*C* are brought to coincidence. This will give the shell of the ternary diagram, and the line $AE_1BE_2CE_3A$ represents the intersection of the liquidus surface with the boundary planes of the diagram. The shape of the liquidus surface on the interior must be determined by experiment (thermal analysis), and when enough points have been located, the entire diagram can be constructed. Figure 32 shows how the solid diagram, or model, would appear.

Points $E_1$, $E_2$, and $E_3$ are on the liquidus surface and represent the three possible binary eutectics. Point *E* is the lowest point on the liquidus surface and represents a *ternary eutectic.* Such a eutectic consists of an intimate mechanical mixture of three metals, and has a constant melting point which is lower than that of any of the binary eutectics. Point $E$ lies in the horizontal plane $KLM$, and this plane is the solidus surface; the warped surface representing the "top" of the diagram is the liquidus surface.

The freezing of one particular alloy will illustrate the properties of this diagram. Assume a liquid alloy whose composition is given by the point $x$. As this alloy cools, the reference point strikes the liquidus surface at $y$ in the field $E_1EE_2B$, and this indicates that the solution is now saturated with metal $L$. Further cooling causes precipitation of $L$, and the composition of the liquid moves down the liquidus surface along the line $yz$. Since only $L$ is precipitating, the ratio of $K$ to $M$ in the liquid must remain constant. Reference to Fig. 30 shows that, if this is the case, the composition must change along a right line through $L$ and x. Therefore, the line $yz$ is the intersection with the liquidus surface of a plane passing through $B$, $L$, and $x$. As the point $z$ is reached, the liquid is saturated with both metals $L$ and $M$, and the eutectic $E_2$ begins to precipitate, the composition of the liquid moving down the "valley" $E_2E$. Finally, the composition of the liquid reaches $E$, the melt is now saturated with all three metals, the remaining liquid solidifies as a ternary eutectic. After freezing, this alloy would consist of crystals of metal $L$, some binary eutectic $E_2$, and the ternary eutectic $E$.

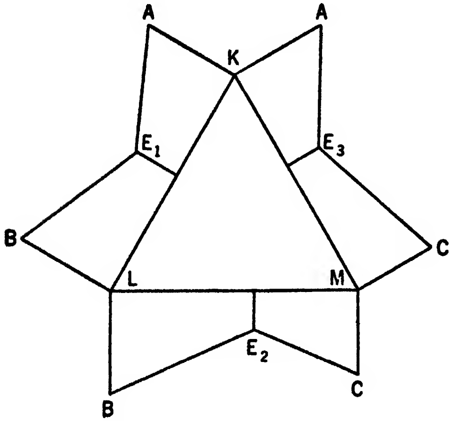


Fig. 31.—Ternary Equilibrium Diagram; First Stage of Construction.

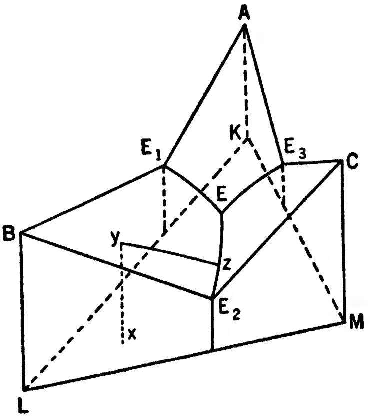


Fig. 32.—Ternary Equilibrium Diagram Completed.

No alloy could contain more than one of the binary eutectics, nor more than one pure metal in excess. The ternary eutectic is the only one of the series with a constant melting point. It is possible that the binary eutectic, or the excess metal, or both might be absent in certain cases (explain).

The extension of this analysis to other types of ternary alloys is obvious but not necessarily simple, and the straightforward analysis of quaternary or higher alloys by this method is impossible, since our geometry is limited to three dimensions.

By the use of contour maps, mountains and valleys may be represented on a flat sheet of paper, and in the same way the "topography" of a liquidus surface may be represented by the use of isothermal contours. Figure 33 illustrates a set of contour lines which correspond to the liquidus surface shown in Fig. 32. In order to give this picture more meaning, hypothetical "actual" temperatures have been indicated (contour interval equals 20° C.) If the solidus plane is warped (when there is solid solubility) it also may be shown by its contours.

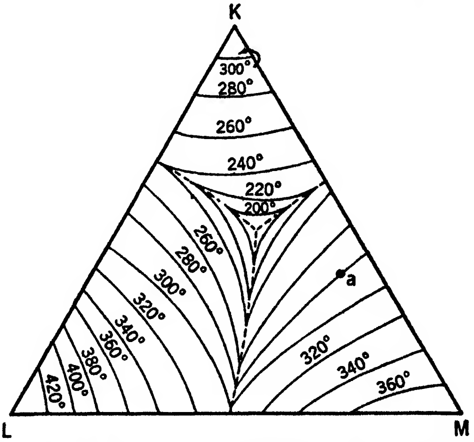


Fig. 33.—Contours of Liquidus Surface of Ternary Diagram.

## SUMMARY

1. Alloys are crystalline substances having a characteristic metallic appearance, and are formed by the solidification of homogeneous metallic solutions. The metalloids C, Si, and B (also non-metals such as P and N) enter into some alloys.

2. The physical properties of alloys depend upon the form in which the atoms crystallize. In the next chapter the relation between structure and physical properties will be considered.

3. The type of crystals present in any alloy may be learned from

a study of the equilibrium diagram of the series concerned. The equilibrium diagram is a temperature-composition plot and indicates

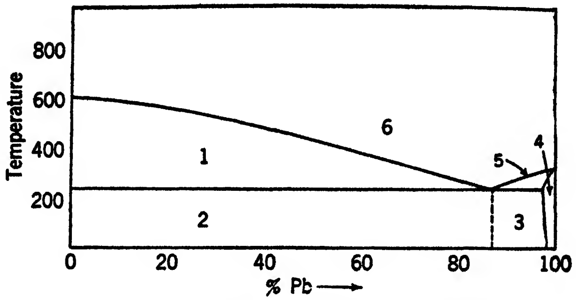


FIG. 34.—The Lead-Antimony Diagram.

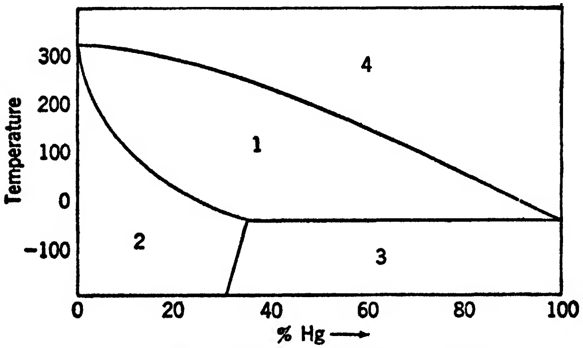


FIG. 35.—The Lead-Mercury Diagram.

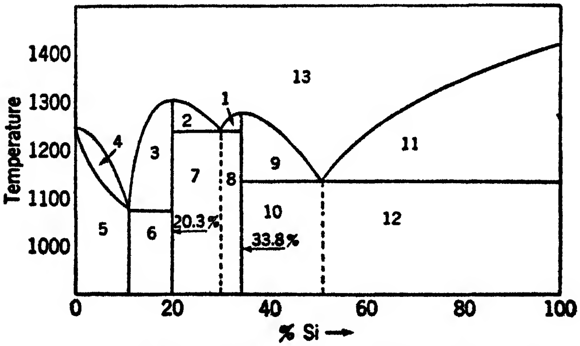


FIG. 36.—The Manganese-Silicon Diagram.

the composition of the phases which can exist in equilibrium at any given temperature.

4. Most alloys have no definite melting or freezing point, and solidification or liquefaction takes place over a range of temperature.

5. In simple binary alloys one or more of the following substances may be identified microscopically:

(1) Pure metals.
(2) Solid solutions.
(3) Eutectics.
(4) Eutectoids.
(5) Compounds.

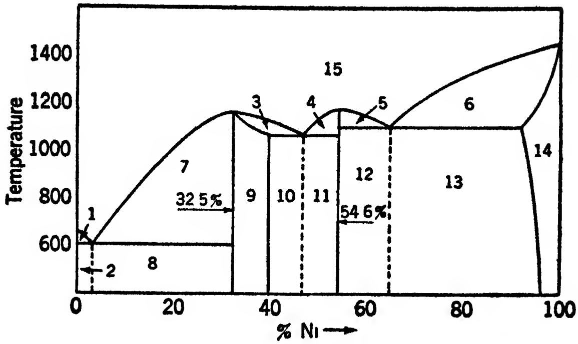


Fig. 37.—The Nickel-Antimony Diagram.

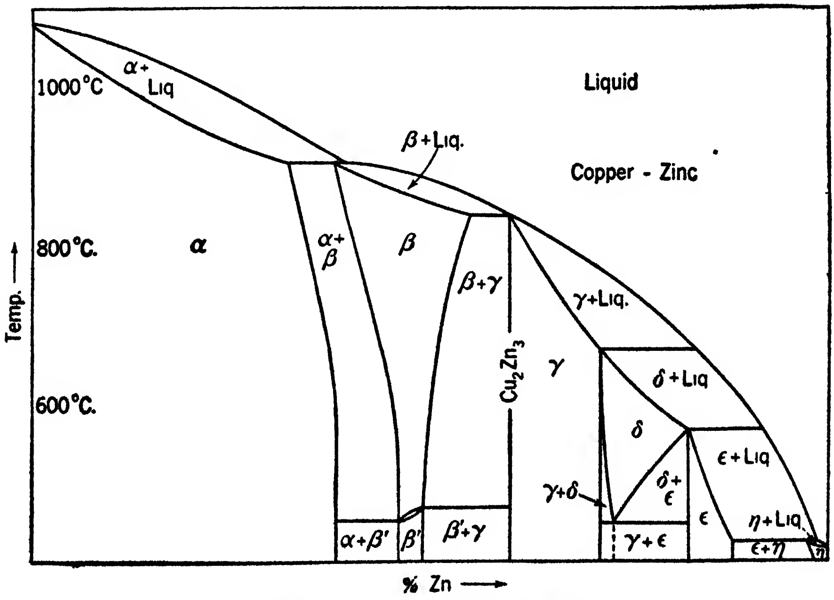


Fig. 38.—The Copper-Zinc Diagram.

In the binary alloys, in equilibrium, no other structural types are possible. If an alloy is not in true equilibrium, we may find other substances such as cored solid solution crystals, or the "peritectic wall."

6. The location of the critical points in any single alloy may be obtained by thermal analysis. The lines on an equilibrium diagram represent the loci of all possible critical points in an entire series of alloys.

## EXERCISES

1. In the Pb-Bi diagram (Fig. 17) the saturated alpha solution contains 37 per cent Bi and the saturated beta solution contains 97 per cent Bi at 125° C. At 0° C. the alpha solution contains 17.5 per cent Bi and the beta solution contains 99 per cent Bi. Calculate the percentage of alpha and beta solutions in an alloy of eutectic composition at 125° C. and at 0° C., assuming that the transformation is slow enough to establish equilibrium conditions.

2. Aluminum (m.p. 660° C.) and silicon (m.p. 1420° C.) may be assumed to form a complete series of alloys showing complete insolubility in the solid state. The eutectic melts at 578° and contains 13 per cent Si. Assume that the liquidus consists of two straight lines.

(1) Sketch the Al-Si diagram, labeling all fields.

(2) Give a brief history of the cooling, sketch the cooling curve indicating the numerical values of the temperatures of incipient and final crystallization, and sketch the microstructure of:

(*a*) An alloy containing 10 per cent Si.
(*b*) An alloy containing 13 per cent Si.
(*c*) An alloy containing 50 per cent Si.

(3) Calculate the percentage of solid and liquid present when the alloys in (*a*) and (*c*) have cooled through half of their crystallization range.

3. Copper (m.p. 1083°) and silver (m.p. 961° C.) form a morphotropic series of alloys. The eutectic contains 72 per cent silver and melts at 778° C. At 778° the solid solubility of silver in copper is 7 per cent and the solid solubility of copper in silver is 5 per cent. At 0° the solid solubility is 1 per cent in both cases.

(1) Sketch the Cu-Ag equilibrium diagram, labeling all fields.

(2) Sketch the same diagram on a scale of atomic percentages rather than weight percentages.

(3) Trace the cooling history, sketch the cooling curve, and sketch the microstructure of:

(*a*) An alloy containing 2 per cent Ag.
(*b*) An alloy containing 50 per cent Ag.
(*c*) An alloy containing 72 per cent Ag.

4. Magnesium (m.p. 650° C) and lead (m.p. 327° C) form the compound $Mg_2Pb$ which melts at 550°. One eutectic contains 67 per cent Pb and melts at 455°; the other eutectic contains 97 per cent Pb and melts at 275°. The series shows complete solid insolubility.

(1) Sketch the Mg-Pb diagram, labeling all fields.

(2) Sketch the same diagram on an atomic percentage scale.

5. Discuss the four alloy diagrams in Figs. 34, 35, 36, and 37. Identify the constituents in the various fields and pick out all alloys which have a constant freez-

ing point. Calculate the simplest molecular formula of each of the compounds formed.

6. Assume that we have an alloy represented by the point *a* in Fig. 33. As it freezes, which pure metal will separate? Which binary eutectic? What will be the range of temperature over which the alloy freezes?

7. The binary eutectics which are found in ternary alloys of the type that we have discussed are called "pseudo-eutectics"; they differ from true binary eutectics in one important respect—they have no definite freezing point. Explain why a eutectic which freezes at constant temperature from a binary melt should freeze over a range of temperature when it separates from a ternary melt.

8. From Fig. 17 sketch time-temperature cooling curves for the following Pb-Bi alloys: (1) pure Pb; (2) 10 per cent Bi; (3) 25 per cent Bi; (4) 37 per cent Bi; (5) 45 per cent Bi; (6) 58 per cent Bi; (7) 80 per cent Bi; (8) 99 per cent Bi; (9) pure Bi.

9. Cooling curves such as those of the lead-antimony alloys or those of the gold-platinum alloys may be said to have an infinite number of dimorphic points, Explain.

10. Prove that the sum of three perpendiculars drawn to the sides of an equilateral triangle from any interior point is equal to the altitude of the triangle.

11. Discuss in detail the diagram shown in Fig. 38. Account for the fact that the compound $Cu_2Zn_3$ is the same as the copper-saturated gamma solution.

## LITERATURE

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# CHAPTER IV

# THE PHYSICAL PROPERTIES OF METALS AND ALLOYS

In the two previous chapters we have considered the atomic structure of metals, and we found that metals and alloys have certain definite characteristics which set them apart from the non-metallic elements and from most chemical compounds. Both the physical and chemical properties of metals depend upon the nature of their atomic structure. We shall try to correlate these properties with what we have learned about atomic structures.

In the last analysis, all metallurgical processes depend upon the variation in physical and chemical properties of the metals. The differences in physical properties account for the fact that adaptive metallurgy is concerned with a wide variety of metals and alloys; some are lighter than others, some are better conductors of electricity, others are relatively strong, etc. When we consider extractive metallurgy, we shall see that all the processes depend upon the fact that different metals have different chemical properties; therefore, each metal requires a certain definite treatment to extract it from its ores, and metals which are alloyed may be separated by virtue of the differences in their chemical properties. In the early days of science, metals were said to be characterized by such properties as high specific gravity, metallic luster, good conductivity of heat and electricity, and malleability. As knowledge of chemistry increased, it was found that these properties were not sufficient to define this group of elements; the metals sodium, potassium, aluminum, and magnesium have low specific gravities; iodine, tellurium, and graphite have "metallic" luster; tellurium is a good conductor of heat; and graphite and selenium conduct electricity. When zinc and bismuth were first discovered, they were called semi-metals, and mercury was not recognized as a metal until after it had been solidified. No matter what properties are selected as defining metals as a class, it will be found that these properties vary between wide limits; and although arsenic and antimony, for example, are called metals, they are decidedly less "metallic" than iron and copper. From the standpoint of the chemist, sodium and potassium are the most metallic of the common metals.

It is evident that the term "metal" is somewhat arbitrary. Many elements lie on the borderline between the true metallic elements and those which are definitely non-metallic. Carbon, silicon, and boron resemble metals in some of their physical properties, i.e., they conduct heat and electricity, they have a metallic luster, and they alloy with some of the metals. Although their chemical properties class them as non-metals, they are often called *metalloids*, because of their physical resemblance to the metals and their ability to form alloys. The term "metalloid" is sometimes used to refer to all the elements (Mn, P, C, Si, S) other than iron found in the ferrous alloys—cast iron, steel, wrought iron, etc.

Before beginning a study of the specific physical properties of metals and alloys, let us summarize a few points relating to their physical properties in general:

1. Solid metals and alloys are crystalline, have a high specific cohesion due to the strong secondary valence bonds, and have atomic lattice patterns. Consequently, both metals and alloys in general have:

    *a*. Strength.
    *b*. Malleability.
    *c*. Ductility.
    *d*. High boiling points.

2. Metallic space lattices are characterized by the presence of free electrons, and therefore have:

    *a*. Good heat conductivity.
    *b*. Good electrical conductivity.
    *c*. Thermoelectric properties.

3. Metals have a characteristic "metallic" luster.
4. Most metals have high specific gravity.
5. Many metals display strong adsorption of gases.
6. Metals are usually monatomic in the liquid and vapor states.

## GENERAL PROPERTIES

**Color.**—Copper and gold are the only two metals that have a true distinguishing color. Ag is usually called white; Al, Pt, Sn, Ni, Hg, and Cd, silvery; Sb, Zn, and Pb, bluish; Bi, reddish; Au, yellow; and Cu, red. Fe and As have a grayish color. These colors are seen only in relatively large pieces of solid metal—finely divided metals are usually gray, brown, or black; colloidal gold may be red or purple, and colloidal copper is green. A molten metal may differ in color from the solid metal; molten copper, for example, is pale green. Gold is yellow by reflected light but green by transmitted light (light passing through a thin sheet of gold).

Alloys, such as brass or bronze, show definite color only when they contain one of the colored metals, gold or copper. The American five-cent coin has a silvery color, although it contains 75 per cent copper and only 25 per cent nickel.

**Luster.**—The luster which is characteristic of metals and alloys is due to the manner in which light is reflected from the surface, and metallic luster is observed on polished surfaces, on crystal facets, and on the surface of molten metals. Finely divided metals have no luster. This property is not of great importance, but it seems to have a fundamental connection with metallic properties because a truly metallic luster ordinarily cannot be produced on non-metallic material.

**Density.**—The density of a metal is its weight per unit volume. The specific gravity is the ratio of the weight of the metal to the weight of an equal volume of water. In the metric system, density and specific gravity are numerically equal, since the unit volume (1 cc.) is the volume of a unit weight of water (1 gram). Specific gravity depends on two factors—the mass of the individual atoms (atomic weight), and the spacing of the atoms (atomic volume). The atomic weights are invariant, and any change in the specific gravity of a given substance must be due to a change in the spacing of the constituent atoms. When solid or liquid material is heated, the increased agitation of the molecules or atoms causes them to spread farther apart so that the specific gravity decreases as the temperature rises. Cast metals usually have a lower density than forged metals, because of the presence of pores or cavities.

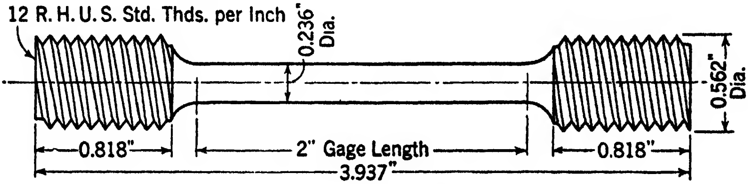
Phase changes involve a rearrangement of atoms and are usually accompanied by a sudden change in density. Most metals contract on freezing. The atoms are packed more closely in the space lattice than in the liquid at the freezing point, and therefore the density of the solid is greater than the density of the liquid. Water expands on freezing, however, because the molecules are more closely packed in the liquid state than in the crystal lattice. Bismuth is the only common metal which expands on freezing, and for this reason it is often used in type-metal alloys because the expansion insures that the type will faithfully reproduce all the details of the mold in which it is cast.

**Transparency.**—All metals are densely opaque to visible light, although silver, for example, is quite transparent to the ultra-violet. The most malleable metals may be beaten into sheets so thin as to be transparent to visible light; gold becomes transparent when its thickness has been reduced to about 1/300,000 inch.

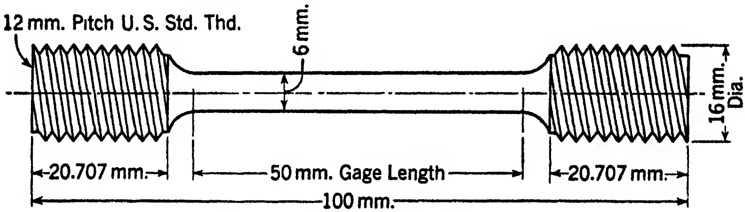
## MECHANICAL PROPERTIES

In the previous chapters we discussed the mechanism by which metals are deformed, and we found that there are two fundamental types of deformation: elastic or temporary deformation, and plastic or permanent deformation. The mechanical properties of metals and alloys are concerned exclusively with the deformation produced by the action of external forces.

**Tensile Strength and Related Properties.**—The most useful test for the determination of mechanical properties is the tensile or pulling test, by which several important physical properties may be measured. The metal or alloy to be tested is cast or machined into a standard test bar (Fig. 1), such that the ends of the bar may be grasped by the jaws of the testing machine; the test bar must have a uniform cross-section throughout part of the length, and usually two marks are made on the bar and the distance between them carefully measured. The distance between the marks before loading begins is the original length $l_0$, and the original cross-sectional area of the bar is $a_0$. The testing machine is made so that the tensile load may be applied gradually, and the total tensile force acting on the specimen



TENSILE TEST SPECIMEN (English)

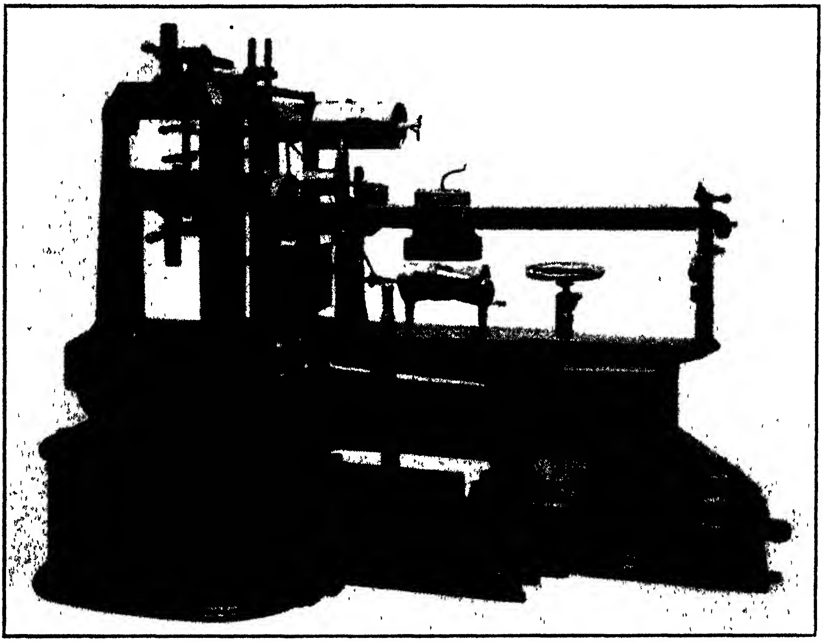


TENSILE TEST SPECIMEN (Metric)

*(Courtesy Tinius Olsen Testing Machine Company, Philadelphia)*

Fig. 1.—Tensile Test Specimens.

may be determined at any time. The test is made by applying larger and larger loads until the specimen breaks; as the load increases, the bar stretches and the cross-sectional area contracts, so that it becomes necessary to measure the distance between the reference marks each time that the load is increased (by means of a strain gauge). From the data obtained in this manner a stress-strain diagram may be plotted; and because of the importance of this diagram, it will be discussed in some detail.



*(Courtesy Tinius Olsen Testing Machine Company, Philadelphia)*

FIG. 2.—Machine for Tensile Tests.

The total force in pounds acting at any time is $P$, and the stress corresponding to the force $P$ is $S = \frac{P}{a_0}$ in pounds per square inch (psi.). As the force increases, the cross-sectional area of the bar decreases; but the stress at any time is calculated as pounds per square inch of original area, and is not figured on the actual cross-section of the bar at the time the force $P$ is acting. As the bar stretches, the distance between the reference marks becomes greater. Let $l$ be the distance between the marks at the time the force $P$ is acting. The increment of length is $\Delta l = l - l_0$, and the per cent elongation is

El. $= \frac{\Delta l}{l_0} \cdot 100$. A simple diagram of this type is shown in Fig. 3. As $S$ increases from zero, the curve is a straight line until the point $A$ is reached, and this is the region of elastic deformation; the stress acting at $A$ is the elastic limit of the material. *Hooke's law* which applies to elastic deformation states that stress is proportional to strain, or that $S = k \frac{\Delta l}{l_0}$. The constant $k$ is Young's modulus in tension, and since $\frac{\Delta l}{l_0}$ is a pure number, the dimensions of $k$ are the same as those of $S$; in other words, Young's modulus is measured in pounds per square inch. The value of Young's modulus for this specimen is the slope of the line $OA$ multiplied by 100.

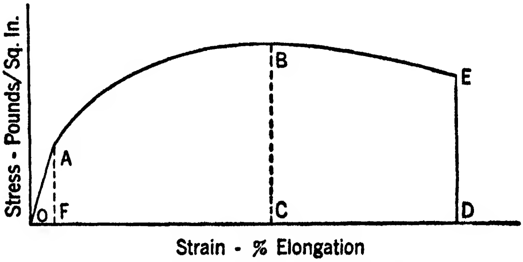


Fig. 3.—Stress-Strain Diagram.

After the elastic limit is exceeded, plastic deformation begins; and the strain (El) increases more rapidly than Hooke's law permits. The portion of the curve $ABE$ shows the stress-strain relations which obtain during plastic flow. It might be expected that, after the elastic limit has been reached, the metal would begin to yield and finally fracture without any increase in stress; but the diagram shows that the stress continues to increase after the elastic limit has been passed. This fact is due to the strain-hardening of the metal. The pulling of a bar of metal at room temperature represents the severest kind of cold-working, and the more the specimen is deformed, the harder and stronger it becomes because of increased resistance to slip. The shape of the curve $ABE$ is due to two factors, the constantly increasing intrinsic strength of the metal due to strain-hardening, and the decrease in cross-sectional area of the specimen caused by the elongation. The bar increases uniformly in strength and diminishes uniformly in cross-section until the point $B$ is reached. Here the strain becomes so great that the contraction begins to concentrate at some one point on the bar, the piece begins to "neck down," and the reduction of area takes place at this point so rapidly that the stress actually drops as shown by *BE*. Rupture finally takes place at the local constriction or neck. In Fig. 3, the curve is almost flat near the point *B*, and this is due to the fact that the stress $S$ is calculated on the original area of the bar $\left(S = \frac{P}{a_0}\right)$ and the stress plotted does not represent the actual stress acting on the specimen. By measuring or computing the area, $a$, each time the load is increased and plotting $S = \frac{P}{a}$, the curve shown in Fig. 4 is obtained. This emphasizes the fact that the intrinsic strength of the metal increases regularly as the cold-working continues. The slope of the upper curve is an approximate measure of the work-hardenability of the metal.

The curve in Fig. 3 represents an ideally simple case of a stress-strain diagram—actually most diagrams differ considerably from the form shown here. However, before discussing the complications which may arise, it will be profitable to consider the interpretation of the simplest case (Fig. 3).

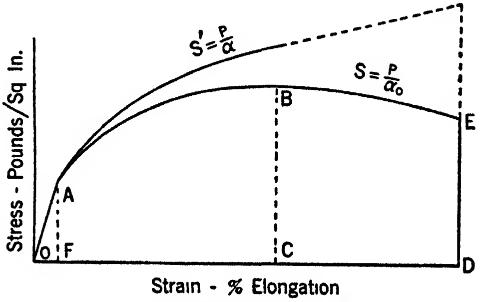


FIG. 4—Stress-Strain Diagram.

1. The *tensile strength* or *ultimate strength* is defined as the greatest tensile stress that a metal can bear without rupture—in Fig. 3 the tensile strength is represented by *BC*, the maximum ordinate on the curve. In making a determination of tensile strength, it is not necessary to plot a complete stress-strain diagram, since all that is required is the maximum total load, $P_m$, and the original cross-sectional area of the test piece, $a_0$. The tensile strength, T. S. $= \frac{P_m}{a_0}$ is measured in pounds per square inch.

2. The elastic limit in tension is a stress measured in pounds per square inch or equivalent units. It may be defined as the greatest tensile stress that a substance can withstand without permanent deformation. The line *AF* represents the magnitude of the elastic limit.

3. The elongation or per cent elongation is El. $= \frac{\Delta l}{l_0} \cdot 100$, but the per cent elongation of a metal usually means the total elongation before rupture as represented by the line *OD* in Fig. 3. This value of El. is a measure of the ductility or formability of the metal.

4. The reduction of area, R. A., is likewise a measure of the ductility of a metal and is given in percentage; R. A. $= \frac{a_0 - a}{a_0} \cdot 100$. As in the case of El., R. A. usually refers to the total reduction of area before failure, and if a neck or constriction is formed, the value for $a$ is determined by measuring the cross-sectional area at the point where the break occurs.

5. The area *OFA* is a measure of the resilience of the metal, and the area *OAED* measures its toughness. These properties will be discussed in more detail in another section.

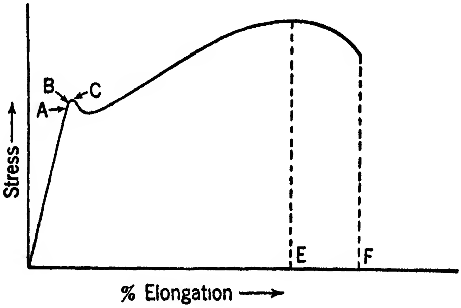


Fig. 5.—Stress-Strain Diagram.

When a metal is stressed beyond its elastic limit, the plastic deformation often begins so suddenly that the loading or stress cannot keep up with the strain, and as a result the measured stress may drop slightly before it begins to increase again (Fig. 5). To the operator of the testing machine this appears as if the metal had suddenly yielded to the tensile stress, and the point at which the drop takes place is called the *yield point* (*C* in Fig. 5). Point *B* is called the *proportional limit* and indicates the point at which the stress-strain curve first deviates from a straight line. *A* is the *elastic limit* as defined before. The reason for the introduction of these new quantities is simply that they are much easier to determine than the true elastic limit, and for most practical purposes serve just as well. Both the yield point (Yd. Pt.) and the proportional limit are stresses and are always slightly higher than the elastic limit. If a yield point exists, it can be located without plotting a stress-strain diagram, but the proportional limit must be determined from the stress-strain curve. Some of the curves (Figs. 6 and 8) show no yield point. In cases such as this, the yield point may be fixed arbitrarily; for example, the yield point may be defined as that stress at which the stress-strain curve shows a deviation of 0.2 per cent from the modulus line produced (the modulus line is the initial straight portion of the curve).

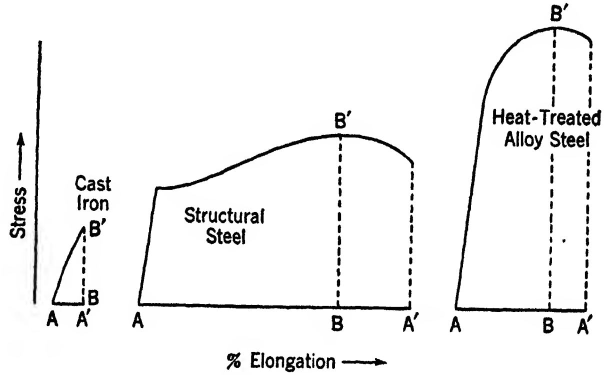


FIG. 6.—Stress-Strain Diagrams.

For most purposes the yield point, proportional limit, and elastic limit may be regarded as practically the same; they indicate that stress at which plastic deformation begins. In Fig. 3 the point *A* should properly be called the proportional limit, since the diagram alone does not indicate that it is the true elastic limit. In some metals and alloys such as cast iron (Fig. 6) and for soft ductile metals such as annealed copper (Fig. 8) plastic deformation begins with the first loading, and there is no elastic limit or yield point. The stress-strain curve for such substances is a uniform curve which contains no straight portion.

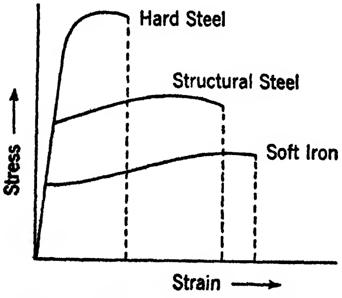


FIG. 7.—Stress-Strain Diagrams.

**Tensile hardness** is the same as tensile strength. Other methods of measuring hardness yield values which correspond closely to the tensile hardness.

**Plasticity.**—The plasticity of a metal is the property of having large permanent deformation without rupture; it is also called formability, since it determines the amount of mechanical working that the specimen will stand. The total elongation El. is a measure of the plasticity (*OD* in Fig. 3; *AA′* in Figs. 6 and 8).

*Malleability* is the property which permits great extension in all directions (hammering) without rupture; it is a special aspect of plasticity. The order of malleability[1] for common metals is: Au, Ag, Cu, Al, Sn, Pt, Pb, Zn, Fe, Ni. (Au is most malleable.)

A metal which is not malleable when cold is said to be "cold short"; if it is non-malleable when hot, it is "red short."

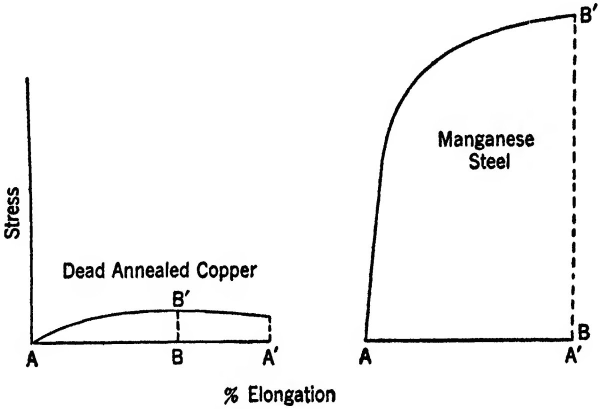


FIG. 8.—Stress-Strain Diagrams.

*Ductility* is that property which allows a metal or alloy to be drawn into wire. The term is often used in a broader sense as the equivalent of plasticity. Ductility and malleability are not quite the same, as is shown by the order of ductility[1] of the metals (Au is most ductile): Au, Ag, Pt, Fe, Ni, Cu, Al, Zn, Sn, Pb, Sb.

**Elasticity.**—The elasticity of a substance is measured by its elastic limit (*AF* in Fig. 3). Some of the hard steels are highly elastic and ivory is the most elastic substance known.

**Resilience** is defined as the work done by an elastic body in returning to its original shape. In a stress-strain diagram the stress (vertical coordinate) is a force, and the elongation represents the distance through which that force acts. The product of a force by a distance represents work done or energy, and consequently the resilience of a metal or other substance is measured by the area under the elastic portion of the stress-strain diagram (*OFA* in Fig. 3). Steel is more highly elastic than soft rubber, because the force required to cause elastic deformation is much greater. However, the resilience of the rubber may be greater than that of steel, because of the much

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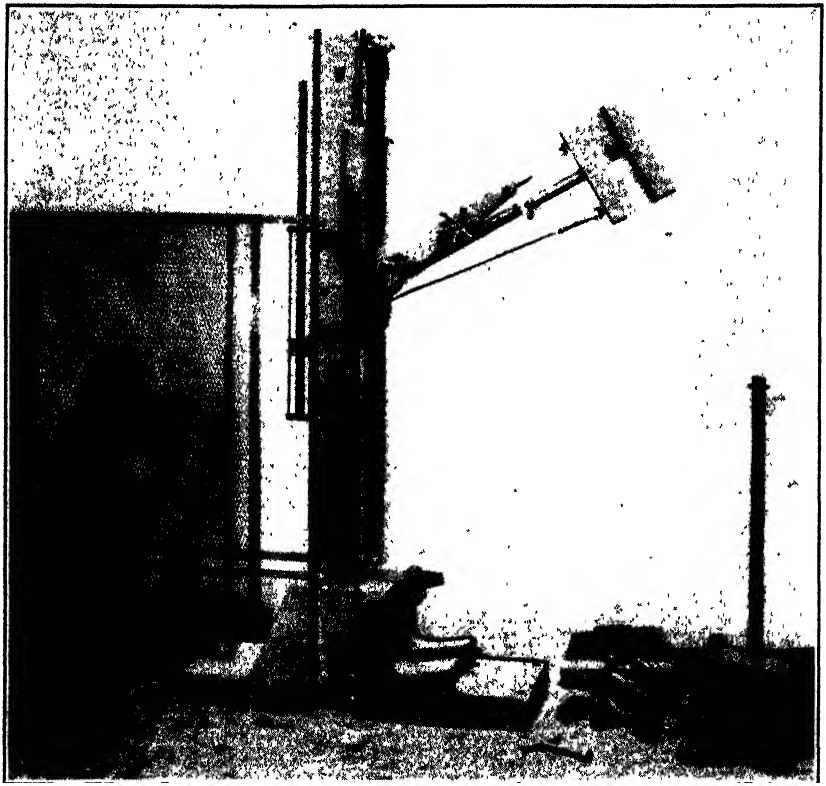
[1] **Hofman, General Metallurgy, McGraw-Hill Book Co., New York, 1913.**

larger "elastic stretch" in the rubber specimen. Elasticity is measured by a force; resilience is a product of the average force acting by the length of the elastic deformation.

**Toughness.**—The tensile strength and the elastic limit are measured by a single stress or force. Toughness is the resistance of a metal to plastic deformation and depends upon two factors: the magnitude of the force acting, and the magnitude of the plastic deformation. Toughness is measured in energy units, and from a stress-strain diagram the toughness is determined by the total area under the stress-strain curve. The numerical value of this area in foot-pounds per cubic inch (or equivalent units)[1] is often called the *work factor*. The toughness of a metal or the energy required to cause



*(Courtesy Tinius Olsen Testing Machine Company, Philadelphia)*

FIG. 9.—Combination Charpy-Izod Impact Tester.

The hammer or "tup" on the machine is used for the Charpy impact test. The Izod hammer is shown removed from the machine.

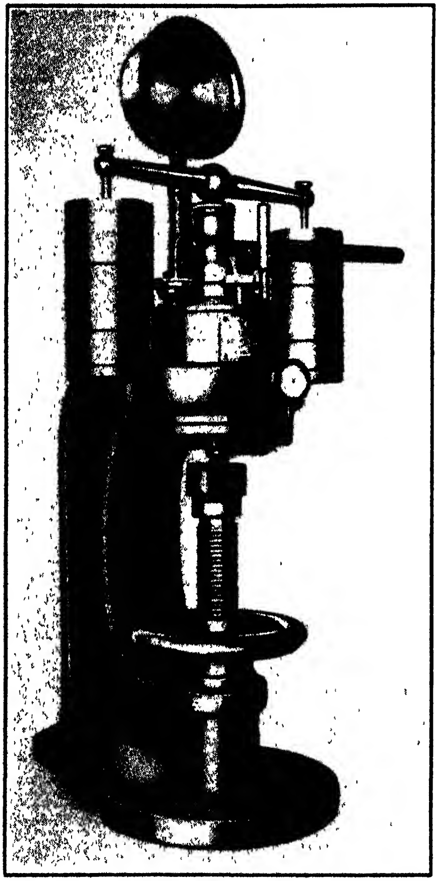
fracture is sometimes measured by a notched bar test in a machine such as the Charpy-Izod impact machine (Fig. 9). In tests of this nature the notched bar is broken by a single blow of a heavy pendulum. The height to which the pendulum swings after the blow has been struck measures the portion of the original energy that was not absorbed in fracturing the specimen, and the difference between this value and the original energy of the pendulum is the energy absorbed by the fracture. Values obtained from impact tests are not always comparable with the work factor shown by a tensile test. Two reasons for the discrepancy are (1) the test bar is notched for the impact test, and this introduces complications which do not permit direct comparison with tests made on bars of uniform cross-section; and (2) the impact test measures the effect of a sudden blow whereas the tensile test measures the effect of a slowly applied force.

**Brittleness.**—A body which breaks after a sudden shock or which breaks after slight mechanical deformation is said to be brittle. There is no exact definition of brittleness, except that it means a lack of ductility and toughness.

**Interpretation of Stress-Strain Diagrams.**—Before considering some of the other mechanical properties of metals, it will be instructive to consider the meaning of the stress-strain diagrams shown in Figs. 6, 7, and 8. In Fig. 6 it is seen that structural steel is more ductile than cast iron or the alloy steel (*AA′* on diagrams) and is also the toughest of the three materials. Cast iron is the weakest (lowest T. S.) and the alloy steel is the strongest; cast iron is the most brittle. In Fig. 7 three diagrams have been superposed; note that the "hard steel" is the strongest, soft iron is the most ductile (plastic), and structural steel is the toughest. Figure 8 shows diagrams for annealed copper and for manganese steel. The copper is soft (low tensile hardness), but because of its ductility it is fairly tough. The manganese steel is the toughest of all the metals considered because of its unusually high ductility combined with great strength. It will be noted that there is no drop in the manganese steel curve before fracture; specimens of manganese steel generally show uniform reduction in area and do not neck down at the point of fracture. The elasticity and resilience of soft copper and cast iron are practically zero.

**Hardness.**—The hardness of a body may be defined as the resistance that its atoms or molecules offer to penetration by another body. The tensile hardness which we have mentioned before is the resistance offered to separation of the atoms by pulling. Hardness may be measured in several different ways. Though there is some connection between the different methods, they are not all strictly equivalent.

**Scratch Hardness.**—The scratch hardness is the resistance offered to scratching by another body. This method is used for the determination of the hardness of minerals, and the hardness is reported as a number in Moh's scale. Scratch hardness of metals is determined by scratching the metal with a hard needle or diamond point. If a standard weight is used on the needle, the hardness is proportional to the depth or width of the scratch. If a scratch of standard depth is produced, the hardness is proportional to the load required on the needle. Scratch hardness is commonly used to compare the hardness of two or more metals, and one of the most useful applications of this method is in the determination of the relative hardness of the various microconstituents of alloys.



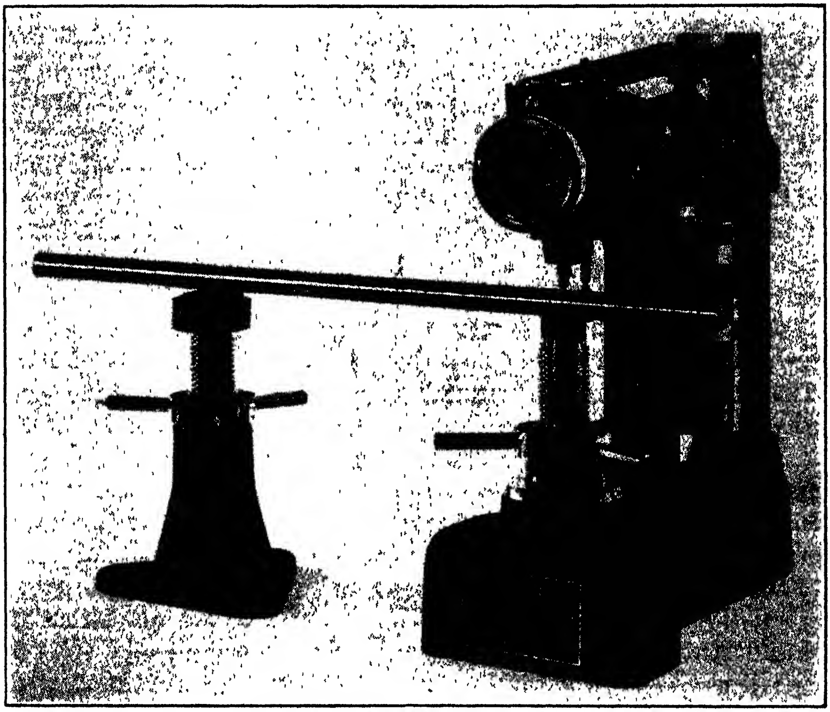
*(Courtesy Pittsburg Instrument and Machine Company, Pittsburgh)*

FIG. 10.—Hand Operated Brinell Machine.

**Indentation Hardness.** — The *Brinell hardness number*, which is often taken as the standard measure of the hardness of a metal, measures the resistance of a metal to permanent indentation by another body. The Brinell machine is a device whereby a hardened-steel ball (usually 10 mm. in diameter) is forced into a flat surface of the metal under a certain definite pressure. The size of the indentation produced is a measure of the hardness of the metal. Figure 10 indicates the general appearance of the Brinell machine. In a test the pressure is maintained on the ball for 15 seconds when testing iron and steel; 30 seconds for softer metals. The load used may vary, but the common loads are 500 kg. for soft metals. and 3000 kg. for iron and steel. The hardness is given by the Brinell number; and the greater the number, the harder the specimen. The Brinell number, $N$, is defined:

$$N = \frac{\text{Load in kilograms}}{\text{Spherical area of indentation in square millimeters}}$$

Brinell numbers of some common metals and alloys are: Pb 5, Sn 14, Al 40, Zn 46, Sb 55, Ag 59, Cu 89, gray cast iron 180, white cast iron 460.



*(Courtesy Wilson Mechanical Instrument Company, New York)*

FIG. 11.—The Rockwell Hardness Tester.

The *Rockwell* hardness test is similar to the Brinell test in that it produces a permanent indentation, but it differs from the latter in many details. In the Rockwell "C" test, the penetrating point is a diamond cone with an apex angle of 120°. With an initial load of 10 kg. on the point, the depth gauge which measures the depth of indentation is set to read zero. Then, the load is increased to 150 kg., and the hardness is read directly from the "C" scale on the dial of the depth gauge which is graduated in arbitrary hardness numbers. The Rockwell "B" test is made in a similar way, except that a

$\frac{1}{16}$-inch steel ball is used in place of the diamond point, and the load is 100 kg. The "B" hardness numbers are read from the "B" scale on the depth gauge. The Rockwell "B" test is used for soft metals.

The Rockwell Superficial Hardness Tester is similar to the standard Rockwell machine, except that it uses a smaller load and makes a shallower indentation. It is used in determining the hardness of thin sheets of metal and the surface hardness of such material as case-hardened steel.

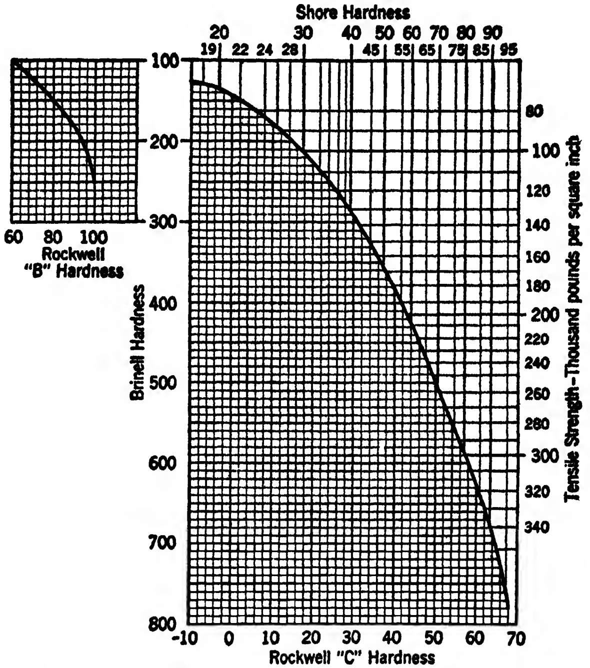
**Rebounding Hardness.**—The *Shore scleroscope* determines hardness by measuring the height of rebound of a diamond-pointed weight from a flat surface of the metal in question. The higher the rebound, the harder the metal; and the scleroscope hardness number is determined by the height of the rebound measured on an arbitrary scale.

**Cutting Hardness.**—In determining the cutting hardness of a metal, a hole of standard depth is bored, using a standard drill operating at a fixed speed under standard pressure. The number of revolutions required gives a measure of the cutting hardness, which in turn indicates the machinability of the material.

**Abrasive Hardness.**—Tests to determine the resistance of a metal surface to abrasion may be made by grinding the metal with an abrasive according to standard procedure. The loss of weight of the specimen is an indication of the abrasive hardness of the metal surface.

**Comparison of Hardness Values.**—Figure 12 shows certain approximate relations between the three principal hardness scales and the tensile strength. Figure 12 is based on data obtained from the testing of structural alloy steels. The application of these conversion tables to other metals and alloys may lead to erroneous results in certain cases; the fact that such relationships exist does not mean that the tensile strength of any alloy can be determined directly from its Brinell or Rockwell hardness number. What is meant is that, if the relation between hardness number and tensile strength is known for a given type of alloy, the Brinell or Rockwell test may be used in routine testing as a check on the tensile strength. The hardness tests are much simpler and more rapid than tensile tests; they do not require a standard size and shape for the test piece; and they can often be used without destroying the usefulness of the part tested. Tensile-strength tests require a specimen of definite size and shape, and the object is tested to destruction.

**Compressive Strength.**—Compressive strength is defined as the greatest compressive stress that a metal will bear without rupture. Ductile metals have no "compressive strength," since they do not fail under compression but simply shrink their axial dimension and increase their cross-section. Actual compressive tests are seldom made except on brittle alloys such as cast iron. Corresponding to ultimate tensile and compressive strengths there are shearing strength, bending strength, and torsional strength. These are of importance in certain special cases to determine the suitability of a metal or alloy for some specific purpose.



(*Courtesy The International Nickel Company, Inc., New York*)

FIG. 12.—Approximate Relations Between Brinell, Rockwell and Shore Hardness and the Tensile Strengths of Structural Alloy Steels.

Conversions from one hardness scale to another or to tensile strengths are made at the intercepts with the curve crossing the main part of the chart. For example, follow the horizontal line representing 200 Brinell hardness to its intersection with the conversion curve. From this point follow vertically upward for equivalent Shore hardness values (28), vertically downward for Rockwell C values (14+), and horizontally to the right for the tensile strength (96,000).

**Other Mechanical Tests.**—Many other tests have been devised to measure certain special properties of metals and alloys. One example is the bend test, in which the specimen is bent cold about a mandrel until it shows a crack on the tension side. The angle of bend is the quantity measured. Another test determines the suitability of sheet for deep drawing or flanging. A specimen of the metal is "cupped" by forcing it through a die by means of a plunger, the depth of the depression when the first crack appears being a measure of that property which determines the formability of the sheet.

**Creep.**—Up to this point two types of deformation have been discussed: plastic deformation or slip, and temporary or elastic deformation. Creep in metals and alloys cannot be classified as either of these, for it produces permanent deformation, and yet it does not appear to be due to slip as we have considered it. All the physical tests described so far have been short-time tests. Importance of the time that the deforming force acts has not been mentioned.

The property of solids in resisting all change of form is called rigidity. All crystalline substances possess a certain degree of rigidity by virtue of the tendency of the atoms or molecules to maintain their positions in the crystal lattice. However, the units of a crystal lattice are continually vibrating back and forth, and the average amplitude of the vibration increases as the temperature rises. As the atoms or molecules absorb more and more thermal energy, the probability that they will remain in one fixed position decreases, and the result is a loss of rigidity of the crystal. All metals and alloys become quite soft at temperatures just below the melting point because of this weakening effect of temperature on the atomic bonds in the crystal lattice. Tensile strength and elastic limit decrease as the temperature rises, this being the principal reason why the mechanical working of metals is commonly done at high temperatures.

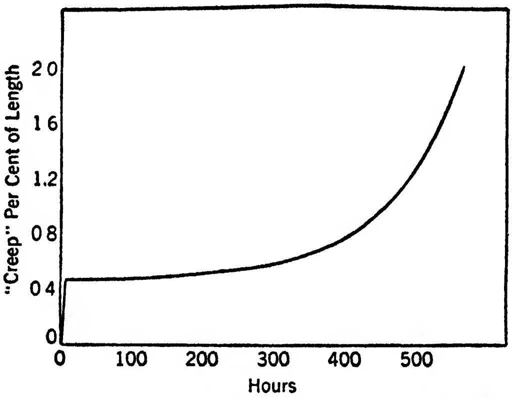


FIG. 13.—One of a Series of Curves Used in Determining the Creep Limit.

*Creep* is the permanent deformation produced by a relatively small, steady force acting for a long period of time, the stress being so small that it would not cause any measurable plastic deformation if applied for a short time. Most metals do not show creep at room temperature.

Metals under steady load at high temperatures give the most concern. The total amount of plastic deformation caused by creep depends on three factors: the magnitude of the stress, the time that the force is acting, and the temperature of the object (lead, tin, and zinc show appreciable creep at room temperature). The determination of the amount of creep is carried out in a manner similar to a tensile test. The specimen is subjected to a steady pull for a long period of time, and the elongation of the test piece is measured at intervals. For determining creep at high temperatures the specimen must be inclosed in a heating chamber. The *creep limit* or the maximum stress at which creep is not dangerous is, of course, an arbitrary value and depends upon the purpose for which the metal is intended. For iron and steel the creep limit is commonly defined as the steady stress which will cause a creep (elongation) of 1 per cent in 100,000 hours. The creep limit decreases rapidly as the temperature rises (Fig. 14)—a fact of considerable importance. Probably the greatest obstacle to the further development of heat engines is that more efficient engines require higher operating temperatures, and none of the known metals or alloys possesses sufficient strength at high temperatures to permit their construction.

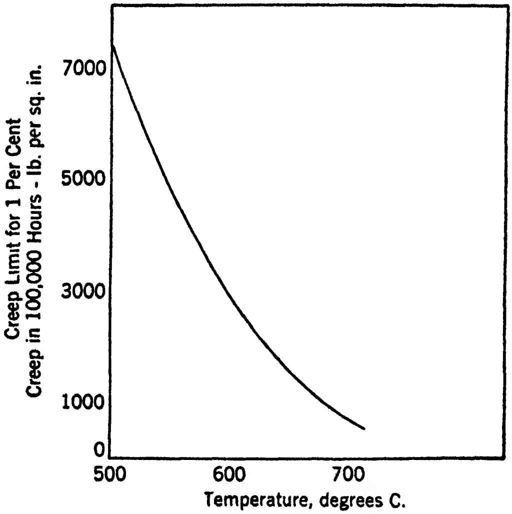


Fig. 14.—Variation of Creep Limit with Temperature.

It remains to mention the important and fundamental difference between slip and creep. Slip is essentially a discontinuous process and is to a certain extent self-stopping. A metal may be deformed by slip under the action of a given stress, but it will usually work-harden to such an extent that no further deformation is produced unless the force is increased. Creep, on the other hand, differs from slip in that it has no hardening effect. If a metal begins to creep, the creep will continue (usually the rate of creep will increase with time; see Fig. 13) as long as the force is acting, and it is this continuous effect that makes creep so dangerous.

**"Fatigue" or Progressive Fracture.**—Machine and structural parts are usually so designed that the maximum load on any section will never exceed the elastic limit of the material, and therefore the piece will not be plastically deformed and theoretically should never fail in service. However, it has been known for a long time that metal parts such as shafts, axles, springs, and piston rods which are subjected to repeated stresses often fail, even though the maximum stress on the part has never exceeded the elastic limit of the metal. Such failure is characterized by an absence of plastic deformation, and even in ductile material the fracture resembles that of a brittle substance. It was formerly thought that the vibrations or repeated stresses caused a rearrangement of the metallic atoms. The metal was said to have "crystallized" and become "fatigued," so that it could no longer withstand the load. The term "fatigue failure" is still used, although it is now known that the trouble is not due to crystallization or to any fatigue or weakening of the mass of metal. Fatigue failure is caused by the formation of a small localized crack which spreads under the influence of repeated stresses until it becomes large enough to cause failure of the section. Just why the action of repeated stresses should cause a minute crack to increase in size is not known with certainty, but the fact that fatigue failure is always due to such progressive fracture has been firmly established.

The ordinary calculations of stresses yield the total stress on a given member, and it is assumed that this stress is uniformly distributed so that the stress at any point in the section will be the same as the stress at any other point. If this assumption were uniformly true, there would be no fatigue failures. It is known that certain structural discontinuities in metals cause a concentration of stress so that the stress at some particular point may be several times the average stress on the section. Slag inclusions, tool marks, sharp corners on keyways or fillets, rivet holes, etc., are typical "stress raisers," and the beginning of a fatigue fracture can usually be traced to some such flaw or groove on or in the piece of metal. The area in which the stress is concentrated is so small that the increased stress has very little effect under steady load; under repeated loading, however, fracture may start at one or more such points and spread throughout a large part of the section.

No metallic specimen is so free of flaws that it will not show fatigue failure. To determine the *endurance limit* of a specimen, the piece is placed in a testing machine which repeatedly stresses it at a certain amount until it eventually fails. One complete period of loading and unloading is called a cycle, and the specimen often undergoes several million stress cycles before failure. The machine may be designed to produce tensile, compressive, shearing, or torsional stresses. If determinations are made at several different stresses and the stress is plotted against the number of reversals necessary to cause fracture (Fig. 15), it will usually be found that the curve approaches asymptotically a certain minimum stress below which the metal will not fail after any number of reversals. This minimum stress is the endurance limit. Often the endurance limit is defined as the maximum stress which will permit one hundred million ($10^8$) reversals without failure.

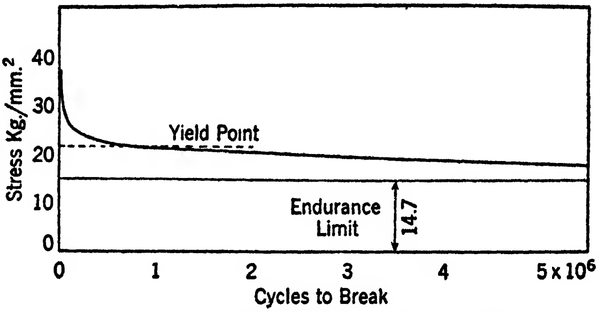
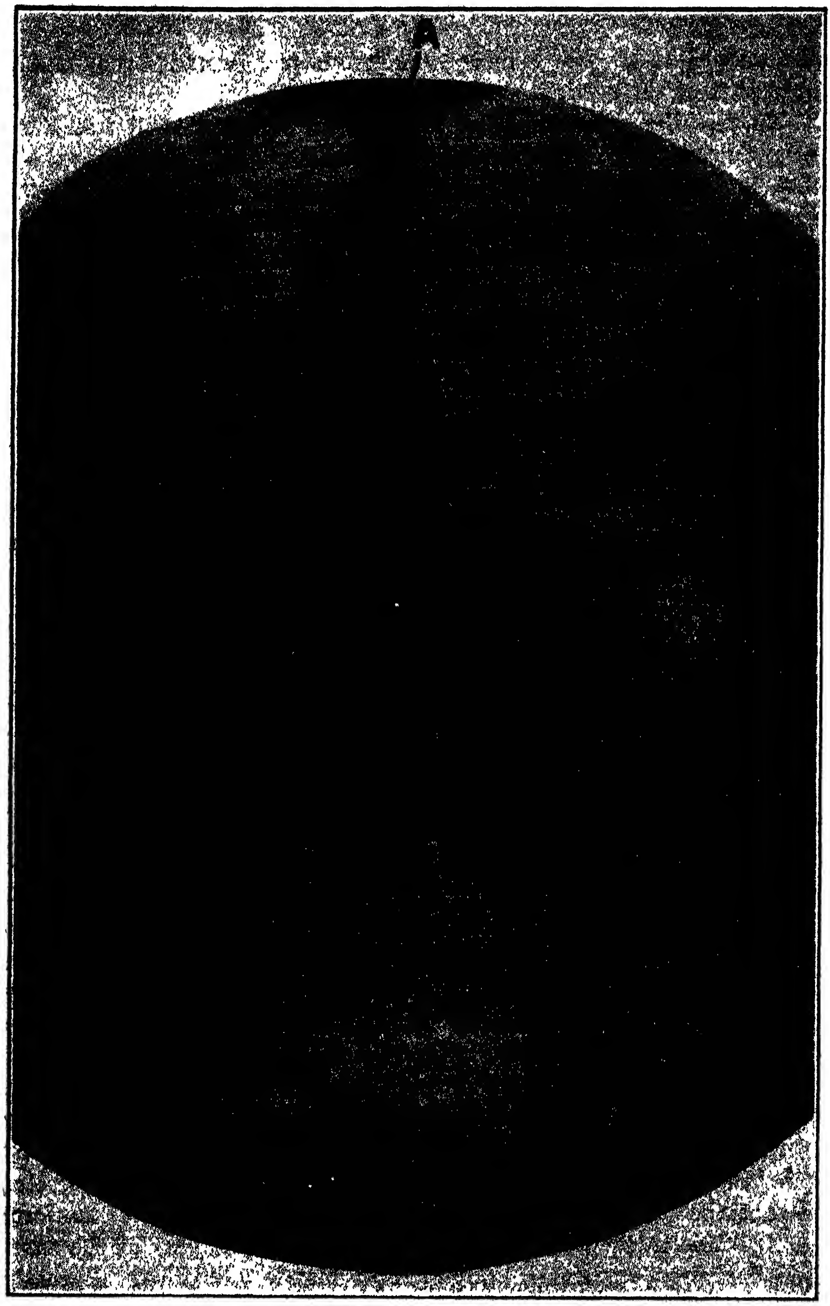


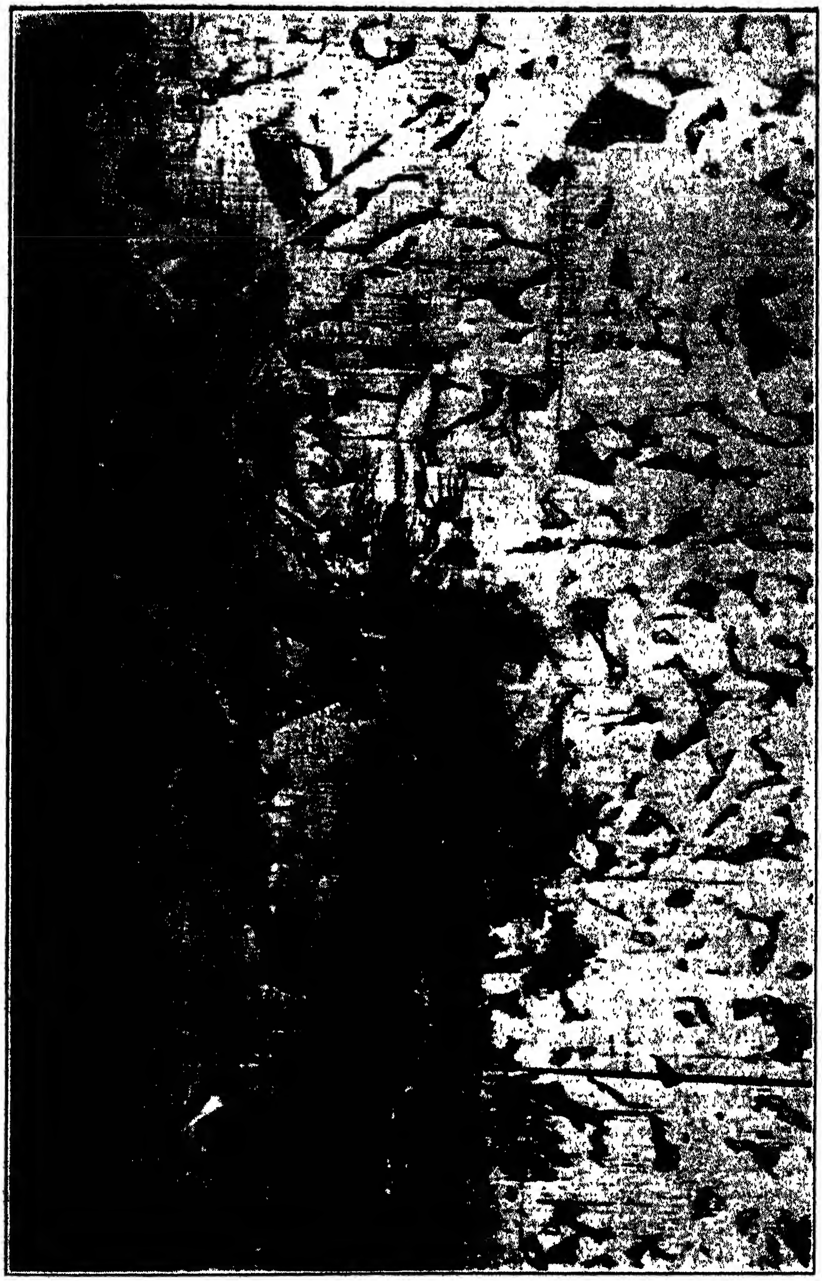
FIG. 15.—Plot of a Test to Determine Endurance Limit.

The endurance limit seems to be more closely related to the tensile strength of a metal than to any other property. The ratio of endurance limit to tensile strength is the *endurance ratio*. For most steels, the endurance ratio is about 50 per cent, for cast iron about 33 per cent, and for some non-ferrous metals it may fall as low as 25 per cent. It must be remembered that the endurance limit is lowered by the presence of sharp corners, abrupt changes of cross-section, etc., so that the endurance limit as determined on a sample of uniform cross-section might not apply to a finished machine part of the same material. The endurance limit of most metals and alloys is greatly lowered if the metal is in contact with a corrosive liquid, for the pits caused by corrosion serve as starting points for fatigue cracks.



*(Photograph by R. E. Cramer, University of Illinois)*

**FIG. 16.—Fatigue Crack in Boiler Plate (× 35), Unetched. Crack Started at the Small Hole at A.**



*(Photograph by R. E. Cramer, University of Illinois)*

**Fig. 17.—End of Fatigue Crack (× 200) in Boiler Plate (Etched).**

Note the slip bands "ahead" of the crack.

## EFFECT OF COLD-WORK AND ANNEALING ON MECHANICAL PROPERTIES

The general effect of cold-working is well illustrated by the repeated bending of a soft metal such as a piece of copper or iron wire. As the bending proceeds the wire becomes harder at the bend, and finally breaks. The cold-working increases the tensile strength of the wire, and at the same time makes it less ductile (more brittle). Figure 18 shows the general effect of cold-working and annealing. Note that the tensile strength increases and that the ductility, as measured by R. A. and El., decreases. The use of "reduction" in two places may be confusing—the "per cent reduction," which is the horizontal coordinate in the left-hand portion of the diagram refers to the reduction in thickness of the sheet, and is a measure of the amount of cold-working done. The "reduction of area" which is plotted vertically refers to the reduction of cross-sectional area in the separate tensile tests, and is a measure of the ductility of the specimen tested.

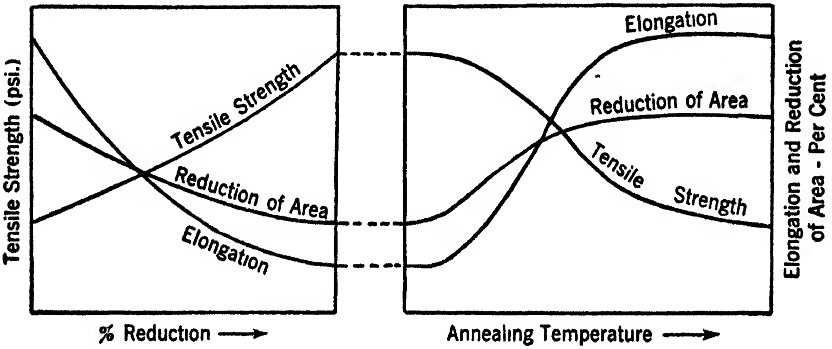


FIG. 18.—Curves Showing the General Effect of Cold Working and Annealing on the Strength and Ductility of a Metal.

*Annealing* (heating followed by slow cooling) removes the effect of cold-working; the right-hand portion of the diagram illustrates this. Cold-working and annealing affect the elastic limit and Brinell hardness in much the same way as they affect the tensile strength. Cold-rolled copper, for instance, will show definite elastic properties, whereas annealed copper is almost non-elastic. The steel used in watch springs is cold-drawn, because cold-drawing raises the elastic limit and hence increases the resilience.

## THERMAL PROPERTIES

The thermal properties of metals have to do with the manner in which heat is stored in and conducted by metals, with the effect of heat on phase changes, and with the effect of heat on other physical properties. Heat is the energy of thermal agitation and is usually measured in calories or B.t.u.

**Thermal Conductivity.**—The thermal conductivity of a metal or alloy is a definite constant characteristic of the metal; it measures the rate at which heat will flow through it. If we have a layer of material with parallel plane faces, one face being maintained at $T_1$ degrees Centigrade and the other face at $T_2$ degrees; and if the area of the plate in square centimeters equals $A$, and its thickness in centimeters equals $l$, the number of calories of heat, $q$, that will flow through the plate in $t$ seconds is:

$$q = k_1 At \frac{(T_1 - T_2)}{l}$$

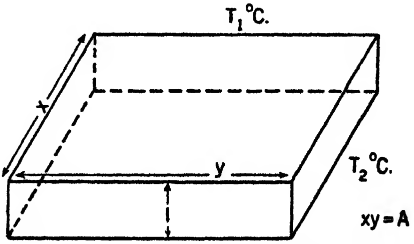


FIG. 19.—Diagram to Illustrate Heat Flow.

and the proportionality constant $k_1$ is the thermal conductivity of the material and is measured in calories per square centimeter per second per centimeter thickness per degree Centigrade. In the English system, another value is often given to the thermal conductivity which we will designate as $k_2$; $k_2$ is measured in B.t.u. per square foot per hour per inch thickness per degree Fahrenheit. Both the above constants represent the thermal conductivity of the substance in question. The thermal resistivity is the reciprocal of the conductivity, and if the thermal resistivity equals $r$, the equation becomes:

$$q = \left(\frac{1}{r}\right) \cdot At \frac{(T_1 - T_2)}{l} \qquad (1)$$

The expression $\frac{(T_1 - T_2)}{l}$ is the *thermal gradient* or the number of degrees (Centigrade) drop in temperature per centimeter of thickness, and may be designated as $g$. Rewriting equation (1) we have:

$$\frac{q}{t} = \frac{Ag}{r} \qquad (2)$$

and $q/t$ is the rate of transfer of energy, or power. If $q/t = w$, where $w$ is power measured in watts,

$$w = \frac{Ag}{r} \tag{3}$$

and the thermal resistivity is that resistance which will permit 1 watt to flow through unit area under a unit thermal gradient. This unit for $r$ is the *thermal ohm.* The thermal ohm is so called because of the analogy with the unit of electrical resistivity, and its use is becoming more common since it is less awkward than the units of thermal conductivity ($k_1$ and $k_2$). If $A$ and $l$ are measured in centimeters, $r$ is the thermal ohm per centimeter cube. The thermal ohm per centimeter cube is 2.54 times the thermal ohm per inch cube. If the value of $w$ in watts is obtained from equation (3), it may be converted to common heat units by the relation: 1 watt = 0.239 calorie per second.

Most metals and alloys have high thermal conductivities (low resistivity) and feel cold to the touch because they rapidly conduct heat away from the body. Recent investigation seems to indicate that the free electrons in metals play a large part in the transfer of heat. This accounts for the facts that (1) metals are much better conductors of heat than those substances which have no free electrons (heat insulators), and (2) those metals which are the best conductors of electricity usually show the highest thermal conductivity. The thermal conductivity of metals and alloys varies somewhat with temperature, but there is no definite rule governing this variation. For most metals and alloys the thermal conductivity decreases at high temperatures, and for most non-metallic solids it increases. Values for $k_1$ at ordinary temperatures for some common metals are given in Table 1. Note that aluminum has almost five times the thermal conductivity of cast iron. This is one of the principal reasons for the use of aluminum alloys to replace cast iron for engine heads and pistons in internal-combustion motors.

TABLE 1

THERMAL CONDUCTIVITY OF METALS AND ALLOYS

| Metal | $k_1$ in cal./cm./cm.$^2$/sec./deg. C. | Metal | $k_1$ in cal./cm./cm.$^2$/sec./deg. C. |
|---|---|---|---|
| Ag | 1.006 | Steel | 0.113 |
| Cu | 1.000 | Cast iron | 0.109 |
| Al | 0.504 | Pb | 0.083 |
| Ni | 0.142 | | |

**Thermal Expansion.**—The application of heat tends to increase the average atomic volume of the atoms in a liquid or solid. In a crystal the spacing of the atoms in the lattice widens as the thermal vibrations increase in amplitude. The external effect of the addition of heat to a body takes the form of an expansion (or contraction on cooling). If a body has a length $l_0$ at 0° C., its length at any temperature $t$ will be given by

$$l = l_0\,(1 + \alpha t) \tag{4}$$

where $\alpha$ is the coefficient of linear expansion of the material in question. If the coefficient is not constant, $\alpha$ in equation (4) must represent the average value of the coefficient between 0° C. and $t$ degrees Centigrade. For extended ranges of temperature a more accurate formula should be used, of the form

$$l = l_0(1 + at + bt^2 + ct^3) \tag{5}$$

For most problems only the first constant need be considered, and to a first approximation $a$ and $\alpha$ are identical.

The volume expansion of a body is given by

$$V = V_0(1 + \beta) \quad \text{where } \beta = 3\alpha \tag{6}$$

In other words, the volume coefficient of expansion of a given substance is three times the linear coefficient as a first approximation.

In order to indicate the order of magnitude of these various constants, a few values of $\alpha$ for some common metals and alloys are given in Table 2. The first four constants for copper in the range $-100°$ to 400° C. are:

$a = 16.2 \times 10^{-6}$ $\quad c = -20 \times 10^{-10}$

$b = 4.5 \times 10^{-9}$ $\quad d = 23 \times 10^{-15}$

TABLE 2

COEFFICIENTS OF LINEAR EXPANSION

| Metal | $\alpha$ | Metal | $\alpha$ |
|---|---|---|---|
| Invar | $0.25 \times 10^{-6}$ | Aluminum | $25 \times 10^{-6}$ |
| Nickel | $10.00 \times 10^{-6}$ | Magnesium | $26 \times 10^{-6}$ |
| Steel | $13.00 \times 10^{-6}$ | Lead | $27 \times 10^{-6}$ |
| Silver | $17.00 \times 10^{-6}$ | Mercury | $41 \times 10^{-6}$ |

Invar, which contains 36.1 per cent Ni and 63.9 per cent Fe, is widely used for surveyors' tapes, pendulums, etc., because of its low coefficient of thermal expansion.

**Fusibility and Volatility.**—(1) The heat of fusion of a substance is the number of calories of heat required to convert 1 gram of the substance from solid at the melting point to liquid at the same temperature. For the common metals, the following approximate formula may be used to calculate the heat of fusion:

$$\text{H. F.} = 2.4 \times \frac{Tm}{\text{At. Wt.}} \tag{7}$$

H. F. = heat of fusion.
$Tm$ = absolute melting point.
At. Wt. = atomic weight.

(2) The boiling point is the temperature at which the vapor pressure of the liquid equals the total pressure of the gas above it. The normal boiling point is the boiling point under 760 mm. external pressure.

(3) The heat of vaporization is the number of calories required to convert 1 gram of liquid at the boiling point to vapor at the same temperature. The heat of vaporization of a metal can be calculated approximately from *Trouton's rule*:

$$\frac{ML_v}{T} = 17 + 0.011T \tag{8}$$

where $M$ = atomic weight.
$L_v$ = heat of vaporization.
$T$ = absolute boiling point.

(4) The heat of transformation is the number of calories absorbed or liberated when 1 gram of a substance passes through an allotropic change.

**Specific Heat.**—The specific heat of a metal is the number of calories required to raise 1 gram of metal 1° C. without change of phase. The specific heat usually varies with the temperature and is expressed:

$$\text{S. H.} = a + bt \tag{9}$$

or more accurately

$$\text{S. H.} = a + bt + ct^2 \ldots\ldots \tag{10}$$

The constants $a$, $b$, $c$, etc., depend upon the material concerned. Usually $a$ represents the specific heat at 0° C.; $t$ is the temperature in degrees Centigrade. For temperatures near room temperature the specific heat is nearly constant, and if exact information is not available, the specific heat of pure metals may be approximated from the formula of Dulong and Petit:

$$\text{S. H.} = \frac{6.4}{\text{At. Wt.}} \tag{11}$$

The total heat content in a body at $t$ degrees Centigrade (provided that no phase changes occur between 0° and $t$ degrees) is obtained by multiplying the mass in grams by the temperature and by the *mean* specific heat between 0° and $t$ degrees. In using values from tables, care must be taken to observe whether the values given are true specific heats or mean specific heats. The mean specific heat between 0 and $t$ degrees is found by the general rule for finding an average with respect to $t$. Thus if $a + bt$ represents the actual specific heat at $t$ degrees, the mean specific heat between 0° and $t$ degrees is

$$\text{S.H.}_{\cdot m} = \frac{a + (a + bt)}{2} = a + \tfrac{1}{2}bt \tag{12}$$

If the expression for the actual specific heat contains more than two terms, we must use a more general formula, viz.:

$$\text{S. H.}_{\cdot m(0-t)} = \frac{\int_0^t (a + bt + ct^2 \cdots)dt}{\int_0^t dt} = \frac{at + \frac{bt^2}{2} + \frac{ct^3}{3} \cdots}{t}$$

$$\text{S. H.}_{\cdot m(0-t)} = a + \frac{bt}{2} + \frac{ct^2}{3} + \frac{dt^3}{4} \cdots \tag{13}$$

Of course if the specific heat is constant, then the actual and mean specific heats are the same.

The *sensible heat* of a body at temperature $t$ is defined as the total amount of heat necessary to raise a body to $t$ degrees Centigrade from room temperature. "Room temperature" is usually about 18 to 20° C., but for most calculations 0° C. may be used, since the error is not large and work is simpler. The meaning of the term "sensible heat" may be most easily seen from the following example:

### Example 1

Calculate the sensible heat of 4 kg. of copper at 2000° C.
Solution:

$$
\begin{aligned}
&S_{m_{(0-t)}} = 0.092 + 0.0000125t.\\
&\text{S. H. liquid} = 0.112.\\
&\text{Heat of fusion} = 41.8 \text{ calories.}\\
&\text{Melting point} = 1083^\circ \text{ C.}\\
&\text{Heat } (0^\circ\text{–}1083^\circ) && = 4000(0.092 + 0.0000125 \cdot 1083)1083.\\
& && = 4000(0.1055)1083.\\
& && = 457{,}000 \text{ calories.}\\
&\text{Heat of fusion} && = 4000 \cdot 41.8.\\
& && = 167{,}200 \text{ calories.}\\
&\text{Heat } (1083^\circ\text{–}2000^\circ) && = 4000 \cdot 0.112 \cdot 917.\\
& && = 410{,}800.\\
&\qquad\text{Total calories} && = 1{,}035{,}000.
\end{aligned}
$$

Hence the sensible heat of 4 kg. of copper at 2000° C. is 1,035,000 gram calories (cal.) or 1035 kilogram calories (Cal.).

## MISCELLANEOUS PROPERTIES

**Electrical Conductivity and Resistivity.**—The unit of resistivity is the ohm, which is the resistance offered by a unit cube to the passage of 1 ampere under pressure of 1 volt. The conductivity is numerically equal to the reciprocal of the resistivity, and the unit of conductivity is the *reciprocal ohm* (written *mho*).

An electric current is a drift of the cloud of free electrons under electrical pressure. The motion or mean free path of any electron is determined by the number of obstructions in its path, and in a crystal these obstructions are the atoms vibrating about the lattice corners. As the thermal vibrations become greater, the stopping power of the atoms increases, and as a consequence the electrical resistance of any solid metal increases rapidly as the temperature rises. On the other hand, at extremely low temperatures some metals display "superconductivity," i.e., their electrical resistance becomes practically zero. In certain non-metallic conductors of the first class (magnesite, boron, carbon, and silicon) the electrical resistance decreases as the temperature rises; and it would seem that in these cases the thermal agitation releases more free electrons to carry the current. This increase in the number of free electrons available overshadows the resistance offered by the increased agitation of the atoms. The resistance of all second-class or electrolytic conductors also decreases as the temperature rises, but for an entirely different reason.

The variation of electrical resistivity with temperature is approximately linear at ordinary temperatures. Thermal conductivity and electrical conductivity are related, as we have mentioned before; the best electrical conductors have the highest thermal conductivities. The relation between electrical and thermal conductivities is given by the Wiedemann-Franz law:

$$\frac{K}{\sigma} = aT \tag{14}$$

where $K$ is the thermal conductivity, $\sigma$ is the electrical conductivity, $T$ is the absolute temperature, and $a$ is a proportionality constant. The law holds fairly well for most metals within restricted temperature ranges. Note that if the thermal conductivity is approximately constant in a given range of temperature, we may write $\rho = AT$, $\left(A = \frac{a}{K}\right)$, where $\rho$ = electrical resistivity $= \frac{1}{\sigma}$, and the resistivity varies linearly with the temperature.

Any treatment that tends to disorganize the internal structure of a metal increases its electrical resistance. Cold-working increases the resistance and annealing restores the original conductivity.

**Magnetism.**—The three metals which display pronounced magnetic properties are iron, cobalt, and nickel; and they are called ferromagnetic. Any substance whose magnetic susceptibility is greater than that of air is paramagnetic; other substances are diamagnetic. Iron, cobalt, and nickel are paramagnetic, but their magnetic properties are so much more pronounced than those of the other paramagnetic substances that they are placed in a separate classification. Alloys containing these metals may or may not be magnetic (high-nickel, "austenitic" steels are non-magnetic). Heussler's alloys are examples of magnetic alloys which contain none of the three ferromagnetic metals.

All these three metals lose their ferromagnetism at high temperatures (iron at 769° C., cobalt at 1100° C., and nickel at 350° C.) because of allotropic changes. Most chemical compounds containing these metals are non-magnetic. The important exceptions are the compounds of iron: FeO, $Fe_3O_4$, FeS, $Fe_3P$, and $Fe_3C$.

In explaining the behavior of magnets, it is assumed that each atom of iron (iron and steel are used almost exclusively in the manufacture of permanent and temporary magnets) is a tiny dipole or magnet. Ordinarily these are oriented at random in a bar so that the bar as a whole has no magnetic effect but under the influence of a magnetic field these small magnets are lined up so that they all point in one direction. The result is a bar magnet (Fig. 20.) In iron and soft steel these atoms lose their orientation as soon as the magnetizing field is removed. To make a permanent magnet a hardened alloy steel must be used, and here there is a certain "braking action" which holds the atoms of alpha iron in position after they have been lined up by the magnetic field. In permanent magnets some other substance must be present besides alpha iron (usually the solid solution of gamma iron or one of its decomposition products). If the steel consists entirely of the gamma solution (austentite), it will have no ferromagnetism.

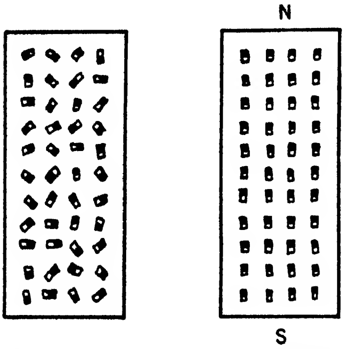


FIG. 20.—Illustrating the Magnetizing of an Iron Bar.

**Diffusion.**—In discussing the atomic structure of metals, it was mentioned that diffusion in solids, liquids, and gases is due to the thermal energy of the atoms or molecules; high temperature always promotes diffusion. Following are a few technical processes in which diffusion plays an important part.

Hot galvanizing, tinning, and similar operations depend upon the diffusion of a liquid metal into solid metal. The reverse operation, or the diffusion of solid into liquid, is important in alloying where a solid metal is to be dissolved in a liquid metal or alloy. Interdiffusion between two solid metals is the basis of most pressure welding operations. The diffusion of a gas into a solid metal is technically important in processes such as the nitriding of steel—ammonia gas diffuses into the solid metal and reacts to form extremely hard nitrides of iron; and the rate of diffusion regulates the depth of the case.

**Occlusion of Gases.**—Many metals have the property of absorbing or occluding large quantities of gas at their surfaces. Finely divided platinum will adsorb great volumes of oxygen or ammonia. Of more interest to the metallurgist, however, is the fact that molten metals and alloys will dissolve gases (especially oxygen and nitrogen) much as water does. The solubility of gases is greater in cold water than in hot, but the reverse is true of gases dissolved in liquid metals. When these metallic liquids cool and freeze, the solubility of the gas is lowered and large numbers of gas bubbles are liberated throughout the body of the metal, producing a weak and porous structure; dissolved oxygen may combine with iron in steels, and the oxides which are formed have a very bad effect on the strength of the alloy. Gases are removed from molten metals by allowing the liquid to stand in a mold until most of the gas has risen to the surface (*killing*) and/or by adding a *scavenger* which combines with the gas to form a light non-gaseous compound which will rise to the surface. Metallic aluminum is often used for degasifying steel. It combines with both oxygen and nitrogen, and the resulting oxides and nitrides rise to the surface of the molten metal.

## PROPERTIES AS RELATED TO STRUCTURE

Most of the "metals" used in engineering and the arts are alloys and not pure metals. Chemically pure metals are rarely found except in the laboratory. The reason for the almost universal use of alloys is that alloys have properties which differ from the properties of their constituent metals, and by suitable alloying it is possible to accentuate certain desirable properties, or to "build" an alloy to specifications. Hundreds of different alloys are used because they have certain characteristics which are not found in any of the pure metals. The properties of alloys are often quite surprising since, for example, nickel can be alloyed with a softer metal (copper) to produce an alloy which is harder and stronger than nickel. In this section the properties of the simpler binary alloys will be correlated with the properties of the constituent metals.

Before dealing with the specific question of the properties of alloys, let us briefly sum up some of the important facts about the constituents of alloys, since it is the properties of the individual grains that determine the properties of the aggregate. We have seen that binary alloys fall into certain definite types, and for our purposes we may make the following rough classification.

Group I. *Eutectic Alloys.* The metals are completely insoluble in the solid state, and any alloy of the series consists of a mechanical mixture of the two pure metals. Any atom of either metal is held in its own normal space lattice; i.e., there is no solid solubility.

Group II. *Isomorphous Series of Alloys.* The two metals form a complete series of solid solutions. In any normal alloy (where there is no coring), only one type of grain is present, and its crystal form is identical with that of either of the constituent metals, but the lattice parameters of the solid solutions lie between those of the constituent metals. In these alloys no single atom is contained in its normal crystal lattice, since foreign atoms are always present; and as a result the space lattices of solid solutions are always distorted by a certain amount, since they must accommodate atoms which are too large or too small for the normal lattice of the pure metal. The maximum distortion occurs in the alloy containing 50 atomic per cent of each of the constituents.

Group III. *Morphotropic Series of Alloys.* The two metals are partially soluble in the solid state. Alloys of the series may consist entirely of one solid solution or the other, or of a mechanical mixture of both saturated solutions. One solid metal will not dissolve an unlimited quantity of the other, and the limit of solid solubility corresponds to the maximum possible distortion of the space lattice of the solvent. In alloys of this type no atom is present in its normal crystal lattice, unless one metal is totally insoluble in the other (lead-antimony series, Fig. III-34).

Group IV. *Alloys Containing Compounds.* The intermetallic compounds are best considered as if they were separate metals which alloy with other metals (or other compounds), as we have seen in Chapter III. Intermetallic compounds invariably owe their existence to the formation of a complex crystal structure. They are hard and brittle, and have low electrical conductivity. These properties are the natural result of a complex crystal pattern. Intermetallic compounds may alloy with neighboring metals, or compounds, to form alloys of Groups I, II, or III.

**Hardness.**—The Brinell hardness is a measure of the resistance of a metal or alloy to plastic deformation, and anything that is said about the hardness may be considered to apply also to the tensile strength. The effects of cold-working and annealing are such that, if hardness is gained, ductility is sacrificed. The same thing is true in alloying—an increase in hardness is usually accompanied by a decrease in the plasticity or ductility of the alloy.

*Group I.* Since these alloys consist of a mechanical mixture of two metals, the fact that the hardness of any alloy is the average of the hardness of the two constituent metals is to be expected. In plotting hardness against composition (Fig. 21), a straight-line relationship is found. Sometimes the tensile strength shows a maximum at the eutectic point because of the fine-grained structure of the eutectic alloy.

*Group II.* Hardness and tensile strength depend upon the resistance to slip offered by the constituent grains of a metal or alloy. In a solid solution the crystal lattices are distorted to a certain extent; the "slip planes" are warped surfaces rather than planes, and as a result slip takes place less readily in a solid solution than in the normal crystals of the solvent metal. No two metals have crystal patterns of exactly the same shape and dimensions. Each kind of atom has a "normal atomic volume" which it "occupies" in its normal lattice; and when an atom is held in a foreign lattice, it is always too large or too small for the space allotted. The effect of this is to distort the lattice in its neighborhood as shown by the schematic

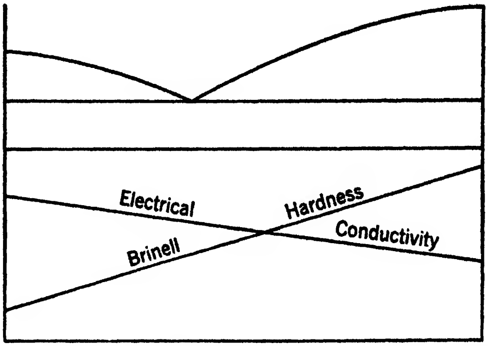


Fig. 21.—Hardness and Conductivity of Group I Alloys.

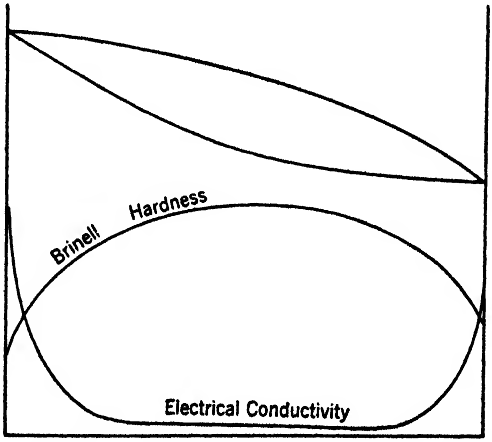


Fig. 22.—Hardness and Conductivity of Group II Alloys.

representation in Fig. 25. Actually, of course, it is not a question of the atom being too large or too small, but rather that the force field of the stranger atom is not the same as that of its neighbors, so that it attracts or repels them more than a native atom would. However we explain the actual mechanism, the fact remains that solid solution lattices show considerable deformation or distortion; and as a result slip is made more difficult, and the hardness and strength are increased. When nickel is hardened by adding copper, the effect is not due to any intrinsic hardness of either copper or nickel atoms, but to the fact that the dissolved copper atoms roughen or distort the slip planes of the nickel lattice and increase the resistance to slip.

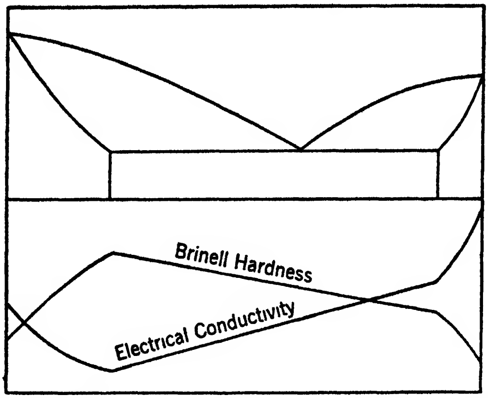


FIG. 23.—Hardness and Conductivity of Group III Alloys.

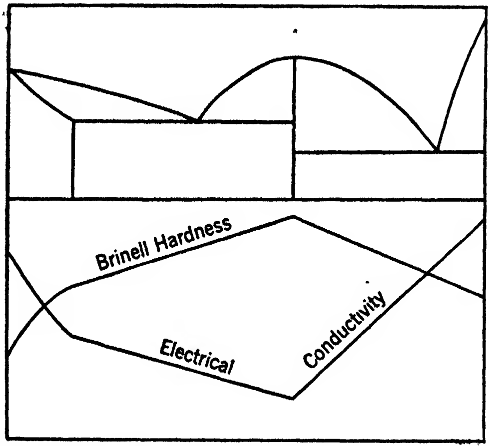


FIG. 24.—Hardness and Conductivity of Group IV Alloys.

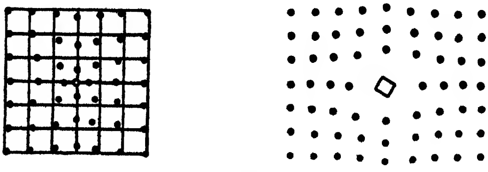


FIG. 25.—Illustrating the Distortion of a Metallic Space Lattice, (*a*) by the Presence of a "Foreign" Atom, and (*b*) by the Presence of a Submicroscopic Particle.

Figure 22 shows the relation between hardness and composition of an alloy of Group II. Note that the hardness rises to a maximum value, which corresponds to a composition of 50 atomic per cent of each metal. From the explanation given, this would be expected, since the space lattice of this particular alloy shows the maximum distortion.

*Group III.* The relation of hardness to composition in alloys of Group III is shown in Fig. 23. In the regions of solid solubility, the hardness increases rapidly up to the limit of solubility. Between the two points of maximum solubility, the hardness follows a straight line, as would be expected, since the alloys in this region are mechanical mixtures of the two saturated solutions. In some instances the tensile strength increases to a maximum at the eutectic point, as in Group I alloys.

The limit of solid solubility of a given metal for another depends upon the amount of distortion that the solvent lattice can undergo. This accounts for the profound changes in physical properties which are caused by small amounts of certain impurities in metals (phosphorus in copper, for example), since a small amount of a sparingly soluble metal may have the same distorting effect as a much larger amount of a highly soluble metal.

*Group IV.* It has been seen that intermetallic compounds are relatively hard and brittle. The cause of this is that the space lattices of compounds are usually so complicated that considerable resistance is offered to slip, and that the ruptured space lattice does not "heal" readily after slip-displacement. Figure 24, showing the hardness-composition plot of an alloy series containing a compound, is self-explanatory.

Following is a list of a few of the most important intermetallic compounds found in commercial alloys:

(1) $Fe_3C$, iron carbide or cementite. All the carbon in ordinary steels and in white cast iron is in the form of this hard, but brittle, compound. The strength of steel is due to the fact that this hard material is intimately associated with tough, ductile iron (ferrite).

(2) $Cu_3Sn$—a hard compound found in certain bronzes. In bronze bearings it is the $Cu_3Sn$ which serves as the wear-resisting constituent.

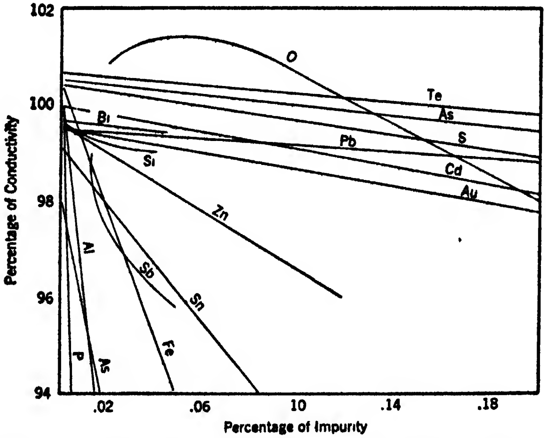
(3) $Cu_2O$—this is a hard and brittle compound and is a normal constituent of commercially "pure" copper. The regulation of the amount of $Cu_2O$ is of great importance in the fire refining of copper.

(4) SnSb—this compound is the wear-resisting constituent in the babbitts and white metal bearings.

(5) $CuAl_2$; $Mg_3Al_2$; $Mg_2Si$—these compounds lend much of the hardness and strength to the light metal (aluminum- and magnesium-

base) alloys, and their functions may be compared to the function of $Fe_3C$ in steels.

**Electrical Conductivity.**—The electrical conductivity of any metallic grain depends upon the ease with which the cloud of free electrons can pass through the body of the crystal. Anything which tends to distort the space lattice lowers the electrical conductivity, and it is not surprising that solid solutions and compounds should have low electrical conductivity, since the distortion of the space lattice hinders the passage of the free electrons. In alloys of Group I, each metal grain has its normal conductivity, and the conductivity of any alloy is an average of the conductivities of the constituent metals (Fig. 21). A small amount of metal dissolved in the space lattice of another metal greatly lowers its electrical conductivity, as shown by Fig. 22. The more sparingly soluble the foreign metal, the greater is its effect.



*(Addicks in Metallurgy of Copper by Hofman and Hayward, McGraw-Hill Book Co., New York, 1924)*

FIG. 26.—Effect of Impurities on the Conductivity of Copper.

Figure 26 shows the effect of various impurities on the electrical conductivity of copper, and it is those substances which are very slightly soluble in copper that have the greatest effect on the conductivity. Examination of this diagram shows quite clearly why copper for electrical use must not contain more than traces of these harmful substances.

No known alloy of any type has a higher electrical conductivity than both of its constituent metals; for electrical conductance pure metals are the best. When, however, a high resistance is desired in order to produce electrical heat, solid solution alloys are employed. Nichrome, Chromel, Alumel, and other alloys used in heating coils are all of the solid solution type. These alloys also have a high melting point and are resistant to oxidation.

The electrical conductivity of alloys of all four types is shown in Figs. 21, 22, 23, and 24; and the interpretation of these curves is quite easy. There is a marked parallelism between the hardness and electrical resistivity. This is to be expected, since the changes in both properties are due to the same cause—the distortion of metallic space lattices.

In general, the thermal conductivity of alloys obeys the same laws as the electrical conductivity (the Wiedemann-Franz law).

**Specific Volume of Alloys.**—The specific gravity in the metric system is the weight in grams of 1 cc. of a substance. The specific volume is the volume in cubic centimeters occupied by 1 gram of a substance and is numerically equal to the reciprocal of the specific gravity. If a metal has a specific gravity of 10, 1 cc. of the metal weighs 10 grams. The specific volume is one-tenth or 0.1, and this means that 1 gram of the metal occupies 0.1 cc.

The specific volume of any mechanical mixture is the weighted average of the specific volumes of the constituents, as may be shown by the following example.

### EXAMPLE 2

Given an eutectic alloy (mechanical mixture) of two metals $A$ and $B$ containing 30 per cent $A$ and 70 per cent $B$. If the specific gravity of $A$ is 10, and of $B$ is 4, find the specific gravity of the alloy.

Solution: It might be assumed that the result would be found as follows:

$$\begin{aligned} 10 \times 0.3 &= 3.00 \\ 4 \times 0.7 &= \underline{2.80} \\ & \phantom{=} 5.80 = \text{specific gravity of the alloy.} \end{aligned}$$

A more complete analysis shows that this is incorrect. Assume that there is 1 gram of the alloy; this will contain 0.3 gram of $A$ and 0.7 gram of $B$. The specific volume of $A$ is 0.1; hence, 0.3 gram of $A$ will occupy $0.1 \times 0.3 = 0.03$ cc., and the 0.7 gram of $B$ will occupy $0.25 \times 0.7 = 0.175$ cc. The total volume of 1 gram of the alloy, or its specific volume, is $0.030 + 0.175 = 0.205$ cc., and the specific gravity of the alloy is $\frac{1}{0.205} = 4.87$.

Let us consider a mechanical mixture of $A$ and $B$ containing $100x$ per cent of $B$ ($x$ the fraction of the alloy which is $B$), and designate the specific volume of any alloy of the series by $y$. Following the reasoning as outlined above, we have:

$$y = 0.1\,(1 - x) + 0.25x$$

$$y = 0.1 - 0.1x + 0.25x$$

$$y = 0.1 + 0.15x \tag{15}$$

and we see that the specific volume is a linear function of the composition. Therefore, if the specific volume is plotted against the composition in the case of any alloy series consisting entirely of mechanical mixtures of pure metals (as in the lead-antimony series), we obtain a straight line. Note that a plot of specific gravity against composition would not give a straight line, for if $z$ = specific gravity:

$$\frac{1}{z} = 0.1 + 0.15x \quad \text{or} \quad 0.15xz + 0.1z = 1 \tag{16}$$

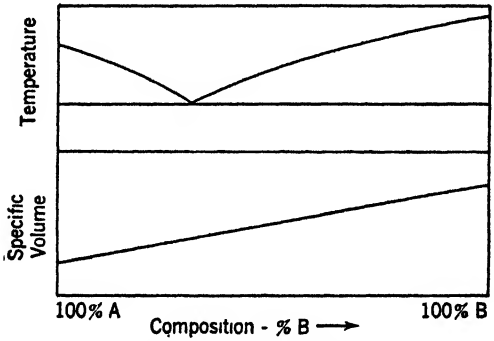


Fig. 27.—Specific Volume of Group I Alloys.

and the curve between $x$ and $z$ is one branch of a hyperbola. (This procedure is followed in calculating the specific gravity of *any* mechanical mixture.)

According to the rule derived above, we may calculate the specific volume (and specific gravity) of all alloys of Group I, since here all the atoms are in their normal lattices, and each metal has its normal specific volume. The rule may also be applied to alloys of Groups II and III with reasonable accuracy, since the distortion of the space lattices does not affect the atomic volumes to any great extent; intermetallic compounds, however, usually involve changes in atomic volume great enough to throw the calculated specific volume several per cent off the true value, so that the rule cannot be applied to alloys of Group IV. These calculations are based upon the assumption that the metals and alloys are sound and free from cavities; a few blow holes in a solid alloy would alter its apparent specific gravity so greatly as to vitiate any calculations.

**Malleability.**—From the work of Leon Guillet, as given by Fulton,[2] the following general rules are taken:

*Group I.* (1) If both components are malleable, all alloys of the series are malleable. Example: Pb-Cd.

(2) If both metals are non-malleable, no alloy of the series is malleable.

(3) If one metal is malleable and the other is not, the malleability of the alloy is largely dependent on the malleability of the eutectic. If the eutectic contains the malleable metal to the extent of more than 50 per cent, the eutectic will probably be malleable; if the concentration of the malleable metal is less than 50 per cent, the eutectic will be non-malleable. Alloys consisting of a malleable eutectic and a malleable excess constituent will be malleable; but when the excess metal is non-malleable, the alloy will be non-malleable, unless only a small amount of excess material is present.

*Group II.* If both metals are malleable, the whole series is malleable; and if neither metal is malleable, the series is non-malleable. In the case of alloys between a malleable and non-malleable metal, those alloys are malleable which are rich in the malleable metal. These same statements apply to alloys in Group III.

*Group IV.* Any alloy containing a considerable amount of an intermetallic compound is non-malleable; the malleability of alloys containing small amounts of a compound depends upon the malleability of the matrix.

The malleability of alloys may be profoundly affected by small amounts of impurities which tend to form weak "networks" at the grain boundaries. For example, phosphorus makes steel cold short because $Fe_3P$ forms a low-melting eutectic with Fe, and this eutectic is very brittle. Because of its low melting point, it is the last material to solidify; and so the eutectic appears as a network between the crystal grains of the steel. Gray cast iron is non-malleable because it contains flakes of graphite which are mechanically weak and brittle. The bulk of a gray cast iron may consist of malleable substances (pearlite and ferrite), but the relatively small amount of free carbon makes the alloy brittle because fracture takes place through the flakes of graphite.

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[2] Fulton, Chas. H.: Principles of Metallurgy, McGraw-Hill Book Co., 1910, New York.

**Specific Heat of Alloys.**—The mean specific heat of an intermetallic compound is the mean of the specific heats of the constituent metals, and so also is the specific heat of conglomerate (Group I) alloys. It would appear that, in the absence of definite data, the mean specific heat of an alloy of any type could be approximated by calculating the average of the specific heats of the component metals.

**Thermal Expansion of Alloys.**—For alloys of Group I, the coefficient of expansion for an alloy containing $n$ per cent $a$ and $(100 - n)$ per cent $b$ may be calculated by the formula:

$$100\alpha_{a+b} = n\alpha_a + (100 - n)\alpha_b \tag{17}$$

i.e., the coefficient of expansion of the alloy is the average of the coefficients of expansion of the two components. For solid solutions and compounds there is no general rule for determining the coefficient of expansion of a given alloy.

## CORROSION OF METALS AND ALLOYS

The phenomenon of corrosion is a familiar one, and the problem of preventing the corrosion of metals and alloys has been the subject of a great deal of research. Corrosion is concerned with the chemical properties of metals rather than with their physical properties, but the topic is included in this chapter because of its relation to certain other topics which have been discussed.

**The Electromotive Series.**—Some of the pure metals are more easily corroded than others; and since corrosion is essentially a chemical action whereby the metals react with a liquid reagent to form oxides or salts, it follows that those metals which are most active chemically should corrode most easily. A rough measure of the corrodibility of a metal is its position in the electromotive series (Table 3) of the metals; a metal will displace any metal below it in the series from a salt solution as

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

The metals which are high in the series are the most active chemically and usually corrode rapidly. The metals near the bottom (noble metals) are much more resistant to corrosion. However, other factors besides position in the electromotive series govern the corrodibility of metals—in some cases, for example, the products of corrosion form an impervious layer on the surface of the metal and prevent further attack by the corrosive liquid.

TABLE 3*

ELECTROMOTIVE SERIES OF METALS

| Metal | Electrode Potential | Metal | Electrode Potential |
|---|---|---|---|
| Alkali: Cs, Rb, K, Na, Li | | Lead | +0.122 |
| Alkaline earth: Ba, Sr, Ca | | Hydrogen | 0.000 |
| Magnesium | | Copper | −0.344 |
| Aluminum | +1.70 | Arsenic | |
| Manganese | +1.10 | Bismuth | |
| Zinc | +0.76 | Antimony | |
| Chromium | +0.557 | Silver | −0.798 |
| Iron | +0.441 | Mercury | −0.799 |
| Cadmium | +0.401 | Palladium | −0.820 |
| Cobalt | +0.278 | Platinum | −0.863 |
| Nickel | +0.231 | Gold | −1.360 |
| Tin | +0.136 | | |

* Hodgman, Charles D : Handbook of Chemistry and Physics, Edition 19; Chemical Rubber Publishing Co., 1934, Cleveland, Ohio. Reprinted by permission.

**The Mechanism of Corrosion.**—All the work which has been done in this field seems to point to the fact that corrosion is essentially an electrolytic action, and that for corrosion to take place there must be an electrolyte in contact with the metal, and a difference in potential must exist between portions of the metal object. Two dissimilar metals in contact with an electrolyte constitute an electrolytic cell. If the two metals are connected by a metallic conductor, a current flows through the circuit and the less noble metal corrodes rapidly. The e. m. f. of the cell depends upon the relative position of the two metals in the electromotive series; and the farther apart they are, the greater will be the voltage of the cell. The corrosion of metals and alloys seems to be due to the same sort of action, for the corrosive medium forms the electrolyte, and the points on the surface which have different potentials correspond to the electrodes of the ordinary cell. These points are electrically short-circuited through the body of the metal, and a metal which is being corroded should be regarded as a collection of a great many small electrolytic cells. The localized effect of this electrolytic action is indicated by the pits and irregularities which always appear on the surface of a corroded metal or alloy.

Any two metals in contact with the same electrolyte have different "single potentials," so that a current flows when the metals are connected electrically. Not only is this true for pure metals, but it is also true of the various constituents of alloys. Differences in single potential exist between compounds or solid solutions and the constituent metals; between two solid solutions of different concentration; between annealed and cold-worked grains of the same metal or solid solution. In fact, any two grains which are not chemically identical and/or which have not undergone the same mechanical and thermal treatment will display different single potentials. From the standpoint of resistance to corrosion, even commercially "pure" metals are alloys, since they always contain certain impurities which increase the corrodibility of the metal. Commercial zinc, for example, corrodes about 10,000 times as fast as chemically pure zinc.

*(Courtesy Dr. F. N. Speller, National Tube Company, Pittsburgh)*

Fig. 28.—Corrosion Pits in Wrought Iron Pipe.

Three factors govern the rate of corrosion in any metallic substance: (1) the chemical behavior of the metal or metals involved, (2) the nature of the corroding liquid, and (3) the homogeneity (or lack of it) of the specimen. Certain of the more noble metals, gold, silver, chromium, etc. have an inherent resistance to corrosion, and this corrosion resistance may be imparted to alloys containing these metals. On the other hand, magnesium is readily attacked by dilute acids, and so are all the magnesium-base alloys. Atmospheric corrosion is the most common and the most important type of corrosion. The corroding medium in this case is a film of water (often merely an invisible condensed film) containing dissolved oxygen, nitrogen, and carbon dioxide. Metals do not corrode to any extent in air-free distilled water; neither do they corrode in a dry atmosphere. In many industrial operations metals and alloys are exposed to more powerful corrosive agents than ordinary wind and water, some of these being sea water, moist air containing corrosive gases such as sulfur dioxide or trioxide, furnace gases, acids, alkalies, salt solutions etc.

**Prevention of Corrosion.**—Because of the enormous amount of metal that is lost every year from corrosion the question of preventing corrosion is important to all users of metals, and mention will be made of some factors which play a part in the control of corrosion losses.

Although aluminum and magnesium are very active chemically, they withstand atmospheric corrosion quite well, because the products of corrosion form an impervious layer on the surface of the metal and prevent further ingress of the corrosive medium. The surface of aluminum becomes covered with an oxide, and the magnesium surface is a hydroxide. Both coatings are very effective protection against further attack, and they form immediately upon any fresh metallic surface exposed to the air. The familiar iron rust, however, is a porous, loosely adherent mass. Not only does it permit the corrosive attack to continue on the underlying metal, but, by holding additional electrolyte in its pores, it usually accelerates the corrosion rate. Old copper and bronze articles often assume a green color owing to the formation of a surface *patina* (in this case a basic copper sulfate) which adds to the appearance of the metal and protects it from further corrosion: Natural patinas are formed only after long exposure to the atmosphere, but artificial patinas may be produced in a short time by heating and/or pickling in a suitable reagent. The black oxide finish which can be produced on copper and iron, and the blued finish on steel gun barrels, are examples of artificial patinas. Resistance to corrosion may also be obtained by covering a metal surface with paint, lacquer, enamel, acid-free grease (slushing compound), etc.

In many cases it is neither possible nor desirable to maintain a protective surface on a metal, and the metal or alloy must have an intrinsic resistance to corrosion. For purposes such as this, pure metals or uniform solid solution alloys should be used if possible. Conglomerate alloys (those containing two or more species of crystallites) invariably corrode much faster than alloys which contain only one kind of grain. The well-known corrosion-resisting alloys, Monel metal, stainless steel, and many others are all uniform solid solution alloys.

If a metal contains punched rivet holes, it may corrode rapidly near the holes because of the potential difference between the cold-worked metal and adjacent metal which has not been worked. Rivets should have the same composition as the metal on which they are used, or the contact will corrode rapidly. Welds are subject to accelerated corrosion if the metal deposited by the weld has a different composition from that of the welded part. If a metal is exposed to stray electric currents, it will corrode more rapidly than under ordinary conditions. All these facts and many others may be considered in fabricating any metal part which is to resist corrosion. A few general suggestions for guarding against corrosion loss are:

1. If possible, cover all exposed parts with a protective film.
2. Use solid solution alloys or pure metals in preference to conglomerate alloys.
3. Avoid having two dissimilar metals or alloys in electrical contact.
4. Metal which is locally cold-worked should be annealed before being exposed to any corrosive medium.
5. Avoid having surfaces which may corrode in such a position that they cannot be easily inspected.

**Metallic Coatings.**—Many metals are protected from corrosion by having their surface covered with a thin layer of a more resistant metal. Examples are tin, nickel, or chromium plating and galvanizing (zinc plating). The surface layer is produced in one of the following ways:

1. Electroplating. One of the most common methods of producing a surface coating on a metallic surface is by electrodeposition. The object to be plated is made the cathode of an electrolytic cell, and the electrolyte contains a salt of the metal to be deposited. The anode may be composed of the metal to be deposited, or it may be insoluble. In the first instance, the anode dissolves to replenish the metal in solution. Gold, nickel, silver, chromium, copper and zinc are commonly deposited in this way. The electroplating of zinc is called cold galvanizing.

2. Hot Dipping. A metal object may be coated by dipping it in molten metal. The liquid metal alloys with the solid metal and forms a coating on the surface. Tin plate and hot galvanized material are the most common products of this process and the foundation metal is practically always iron or mild steel. Most of the tin used in this country goes into the manufacture of tin plate, which is superior to galvanized iron but more expensive. A cheaper coating called terne plate is produced by dipping the iron in a molten alloy containing four-fifths lead and one-fifth tin. An interesting variation

of the hot dipping process is the method used in coating strong aluminum alloys with pure aluminum. The "strong" alloys have a conglomerate structure and corrode much more easily than pure aluminum, so that the desired combination is metal with a "body" of strong alloy and a surface of pure aluminum. The liquid alloys are cast between pure aluminum sheets, and the resulting "sandwich" rolled down to the desired size. The ratio of the thickness of the alloy to that of the metal coating will remain the same for any amount of reduction in the rolls.

In the Schoop process, molten metal (zinc, aluminum, copper, and even bronze) is sprayed on the cold surface to be coated. The metal adheres strongly, but does not actually penetrate and alloy with the metal of the base. This process has an advantage in the fact that it permits metal coatings to be sprayed on such materials as wood or paper, or on large pieces such as tank cars and girders.

3. Vaporizing Processes. Certain metals can be deposited as a surface layer by permitting their vapor to strike a metallic surface with which it will alloy. Zinc and aluminum may be plated in this way—the deposition of aluminum is called calorizing, and the deposition of zinc is called Sherardizing or dry galvanizing.

Most of the metallic coatings are of value only when they are unbroken, for, if a crack develops in the surface, a junction of two dissimilar metals is exposed to the corroding electrolyte, and this tends to accelerate the corrosion. A scratch on the surface of tin plate will cause the exposed iron to rust very rapidly, because the tin is more noble than iron, and it is the less noble metal which corrodes rapidly when two metals are in contact. Zinc, on the other hand, is less noble than iron (zinc is above iron in the electromotive series), and if the contact is exposed, the zinc will corrode and protect the iron. In other words, a coating of tin affords only mechanical protection to an iron sheet; but a zinc coating gives both mechanical and electrochemical protection.

## EXERCISES

1. A round tension specimen ¼ in. in diameter is placed in a testing machine and loads applied with the following results:

| Load, lb. | Elongation in 8 in. |
|---|---|
| 930 | 0.0012 |
| 1,860 | 0.0025 |
| 3,720 | 0.0050 |
| 5,580 | 0.0075 |
| 6,500 | 0.0088 |
| 6,980 | 0.0096 |
| 7,400 | 0.0110 |
| 8,200 | 0.0200 |
| 11,600 | maximum |

Determine the elastic strength (psi).

2. Compare the resilience of mild steel (Young's modulus 30,000,000 psi.; elastic limit 32,000 psi.) with that of spring steel (Young's modulus 29,000,000 psi.; elastic limit 90,000 psi.).

3. If two flat metallic strips of dissimilar metals are riveted together and heated, show that the radius of curvature of the resultant arc is independent of the length of the strips. Design such a bimetallic strip that, when fastened securely at one end and heated 20° C., a lateral motion of the other end of approximately 1 mm. results. Sketch. What is the final radius of curvature?[3]

4. Calculate the specific heats of lead, iron, copper, and aluminum from Dulong and Petit's rule, and compare with values taken from tables. What is the percentage error in each case?

5. From microscopic examination a lead-antimony alloy is found to contain 50 per cent Sb and 50 per cent Pb-Sb eutectic by volume (from comparative areas). Assuming that lead and antimony are completely insoluble in the solid state, calculate the percentage composition of the alloy by weight. The eutectic contains 12 per cent Sb by weight. Sp. gr. Pb. 11.35; Sb 6.32.

6. Calculate, for several metals, the heat of vaporization by Trouton's rule, and the heat of fusion by equation (7). Compare with results in tables.

7. Calculate the sensible heat in 2000 pounds of molten lead at 600° C.

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# CHAPTER V

## SHAPING OF METALS AND ALLOYS

Most extractive processes in metallurgy produce liquid metal. Wrought iron is produced in the form of solid blooms which are relatively soft and plastic at the temperature of the furnace, and solid metallic tungsten is produced by reducing $WO_3$ in a current of hydrogen. All other important metals and alloys, however, begin their careers in the liquid state; and since all these (except mercury, which is liquid at ordinary temperatures) are used in the solid state, the first step in all shaping operations is to permit the liquid metal to solidify. The art of cooling a liquid metal in such a way that the solidified metal takes the desired shape is called *casting*.

Two factors are of prime importance in considering the choice of shaping operations for any given alloy or metal. These processes are designed not only to put the metallic object into the shape desired, but also to modify the physical properties of the metal. It would be possible, for example, to produce a steel bar either by casting the steel to the required shape or by cold-rolling the bar from a larger piece of steel. The two finished bars might have the same size and shape, and the chemical analysis of the steel in both might be the same; but the tensile strength and elastic limit would be much greater in the cold-rolled bar.

### ALLOYING

In the great majority of cases, the desired composition of an alloy is obtained by mixing the metals to be alloyed just before the alloy is cast. Usually the metal which is to be present in the largest amount ("base" of the alloy) is melted, and the other constituents are added as solids which dissolve in the molten metal. In the production of alloy steels, the alloying ingredients are usually added to the metal during or immediately after the refining process.

Since all the commercial alloys consist of metals which are miscible in all proportions in the liquid state, the forming of alloys does not ordinarily offer many difficulties. The chief problem is to prevent the loss of metal by volatilization or oxidation, in order that the composition of the alloy shall not change. In making brass, therefore, copper (the less volatile metal) is first melted, and the more volatile zinc is added in the solid form and dissolved as quickly as possible. Alloys of metals that oxidize readily must be melted in an inert atmosphere or under a protective flux.

## CASTING

There are two principal methods of shaping metallic bodies—by casting and by mechanical working. Mechanical work is done on solid metal and consequently must be preceded by a casting operation. Two aspects of casting come up for consideration: (1) casting in which the solid metal takes the shape of the finished piece (foundry casting or founding); and (2) casting into shapes (ingots, billets, wire-bars. etc.) which are to be mechanically worked.

**Founding.**—The art of producing a finished metallic shape (except for machining to dimensions) by casting liquid metal into a suitable mold is called founding, and plants for the production of such finished castings are foundries. Foundries may be operated in conjunction with a metal-producing plant, so that the metal can be obtained in the molten state and cast directly. However, ordinarily the foundry is some distance from the source of supply and must obtain its raw material in the solid state. This means that the first step in the casting operation is the melting of solid metals, and the foundry must be equipped with suitable melting furnaces. Iron foundries commonly employ cupolas in which to melt pig iron, and foundries which produce non-ferrous castings use coal- or oil-fired melting furnaces or electric furnaces. The electric furnace is becoming more common in all types of foundry work. If the foundry produces alloy castings, the alloying may be done in the melting furnace.

**Foundry Operation.**—After the metal or alloy has been liquefied and brought to the proper casting temperature, it must be poured into a mold and allowed to solidify. The preparation of the mold and pouring the metal call for great skill on the part of the foundryman.

Castings may be made in permanent molds or in sand molds. Permanent molds are usually made of metal (cast iron is most common) and are used to cast metals and alloys which have relatively low melting points. Permanent molds and casting machines are used only where a large number of castings of the same size and shape are to be made.

**Pattern Molding.**—The standard method for producing castings is by means of a sand mold. A wooden *pattern* is made of the same size and shape as the desired metal object (the pattern must be slightly larger to allow for the shrinkage which takes place as the metal freezes), sand is rammed into place about the pattern, and then the pattern is removed, leaving a cavity or mold into which the metal can be poured. In order that the sand may be firmly tamped into place, the mold is made in a *flask* which is the container of the mold proper. The flask must be made in at least two parts, so that the pattern can be removed—the upper part is called the *cope,* and the lower part is the *drag.* For complicated shapes, it may be necessary to design the flask and pattern in several sections to permit withdrawal of the pattern.

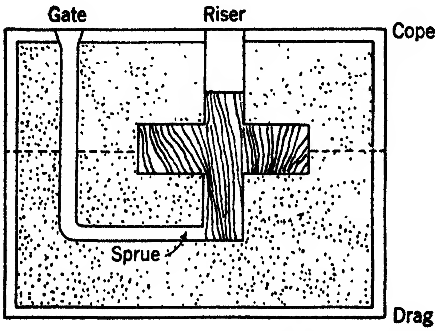

Fig. 1.—Sketch of Sand Mold Showing Pattern in Place.

Metal is poured into the mold through a *gate* (Fig. 1), which is usually so arranged that the metal enters the mold at the bottom through horizontal feeders known as *sprues* (Fig. 1). The *riser* serves as a reservoir of liquid metal to prevent the formation of cavities in the casting proper. In designing and gating a pattern mold, many factors must be considered, among which are the following:

1. The stream of metal must not flow so rapidly as to wear the sand away.
2. Proper allowance for shrinkage must be made when designing the pattern.
3. Sprues, gates, and risers have only the value of scrap and should not be made larger than necessary.
4. If a hollow casting is to be made, the mold must be designed to permit the placing of a suitable *core* before the metal is poured.
5. Freezing of the metal at any time during the pouring operation must be avoided.

**Application of Founding.**—Listed below are the principal reasons for the shaping of metals and alloys by foundry casting.

1. Some metals cannot be mechanically worked and can be shaped only by casting. Examples are cast iron and manganese steel.
2. Mechanical working requires expensive dies, rolls, forges, and other equipment, and unless a given shape is to be produced in large quantity, it is cheaper to make it as a casting.

3. Some shapes are so intricate that they can be formed only by casting. Only a rather limited number of standard shapes can be produced by mechanical working.

4. Very large pieces such as bed-plates for heavy machinery must be cast because of their size.

**Ingot Making.**—Smelters and refineries produce raw metal which must be cast into such shapes as are demanded by the fabricating plant. For example, a copper smelter may cast the metal into anodes for electrolytic refining, and the refinery in turn may cast the remelted cathode copper into wire-bars, cakes, or ingots depending upon the use for which it is intended. Cast iron, both for steel-making and for foundry work, is cast into pigs (if it is not refined into steel while still liquid); steel for rolling mills is cast into large ingots; lead is cast into small pigs suitable for alloying; and zinc is usually cast into small slabs.

With the exception of a few iron blast furnaces where pig iron is cast in sand molds, all the casting at smelters or refineries is carried out in permanent (usually cast-iron, water-cooled) molds, and the product is then ready for sale or for mechanical shaping. For lack of a better term for this general class of castings which is the raw material for mechanical fabrication, this section has been headed "ingot-making," but actually the term "ingot" is generally used in this sense by steel-makers only. Copper and brass sheet is rolled from blanks or cakes, copper rod and wire is rolled and drawn from wire-bars, and the shapes called ingots at the copper refinery are for alloying and are not used directly for mechanical fabrication.

**Defects in Ingots.**—Large ingots (particularly steel ingots) are subject to certain inherent defects which may seriously affect the quality of the product rolled or forged from such ingots.

1. *Piping.* Figure 2 illustrates the manner in which an ingot solidifies. The metal on the outside is the first to freeze, so that, after freezing begins, the ingot consists of a solid shell with a molten interior. Solidification continues to advance toward the center; but, since almost all metals and alloys contract as they freeze, the volume of the solid metal is less than the original volume of the liquid. The frozen outer shell prevents the ingot from shrinking, so that the solid ingot will contain a shrinkage cavity or pipe in the upper central portion. In steel mills the upper third of the ingot is often cropped and scrapped, unless some precaution has been taken to prevent the formation of a pipe.

Shrinkage cavities are relatively unimportant in small flat slabs such as copper anodes and brass slabs, principally because of their short vertical dimension and the rapidity with which they freeze. In foundry castings, it is very important to avoid shrinkage cavities, and therefore the riser is made to act as a reservoir to feed molten metal into the casting and fill the shrinkage space. Cast iron ordinarily freezes without a shrinkage cavity.

Pipes usually contain gases which were dissolved in the molten metal and thrown out of solution on freezing. If this gas does not escape or collect in the pipe, it will form blow holes throughout the mass of an ingot or casting.

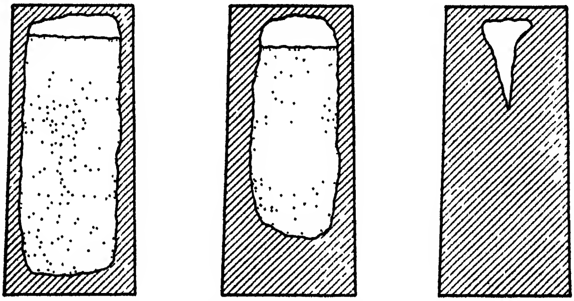

FIG. 2.—Diagram to Illustrate the Formation of a Pipe in an Ingot.

2. *Segregation.* Many impurities in metals and alloys are soluble in the liquid and insoluble in the solid metal. When an ingot solidifies in the manner indicated by Fig. 2, the impurities are rejected from each layer as it solidifies and are eventually concentrated in the center of the ingot. This has a tendency to make the center portion of an ingot inferior to the outer portion in chemical and physical properties.

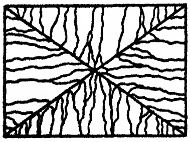

FIG. 3.—Diagram to Illustrate Formation of Planes of Weakness in an Ingot (Ingotism).

3. *Ingotism.* Large ingots cool slowly, and the slow cooling promotes the growth of large crystals. Since the crystal growth is toward the center, the crystals are often large dendrites, normal to the walls of the ingot mold; and if the mold has sharp corners, the intersection of these dendrites forms a plane of weakness (Fig. 3). Crystallization of this type produces an ingot which is likely to crack when rolled or forged.

The size of the pipe in an ingot may be decreased in several ways: by (1) casting with the large end of the ingot upward to diminish the length of the pipe, (2) permitting a large number of small (and relatively harmless) blow holes to form, (3) slow pouring of the liquid metal so that it tends to solidify in layers, (4) using a "hot-top" on the ingot mold, and (5) compressing the ingot during the solidification period.

The formation of blow holes is best prevented by thoroughly degasifying the liquid metal before it begins to freeze. Elimination of sharp corners on ingot molds lessens the harmful effect of coarse crystallization, and the precautions taken to prevent formation of a large pipe also tend to decrease segregation.

## MECHANICAL WORKING

**Preliminary Treatment.**—In a previous chapter we have mentioned the processes of hot- and cold-working and the effects produced by each on a metallic object. Hot-working refines the grains, closes up blow holes, and raises the ultimate strength and elastic limit of the metal; it does not decrease the ductility and sometimes may increase it. Cold-working increases the tensile strength and elastic limit much more than hot-working, but it also decreases the ductility, and leaves mechanical strains in the finished piece. Because of the decrease in strength of metal as the temperature rises, hot-working requires less power than cold-working for equal reduction in cross-sectional area.

Each metal and alloy has a best temperature for rolling or forging and a best finishing temperature. Before mechanical working begins, the ingot or billet must be uniformly heated to this proper temperature. Steel ingots, for example, cannot be rolled as cast because the outside may be cooled below the rolling temperature while the interior is still molten. To insure that the entire ingot is at the proper temperature, it is placed in a heating furnace (soaking pit) and held at the proper temperature until the entire mass is solid and uniformly heated. If a metal cools too rapidly during any mechanical working operation, it may be necessary to reheat it at intervals.

**Rolling.**—Rolling is used in the production of large tonnages of such shapes as plate, sheets, metal foil, rails, bars, beams and girders. It produces a larger amount of finished material than any other shaping process. In the rolling operation the metal is nipped by two rolls rotating in opposite directions and forced between them. This reduces the thickness of the piece and the percentage reduction in thickness (or cross-sectional area) is called the *draft*. Rolling may be either hot- or cold-working. Cold-rolling is used extensively on the ductile metals and alloys such as copper, brass, and the aluminum alloys, but most steel shapes are hot-rolled; and if cold-rolling is used, it is as a finishing operation only. Hot-rolling requires less power than cold-rolling and permits a greater draft; cold-rolling gives a better surface on the finished piece, and cold-rolled material can be made to more exact dimensions than hot-rolled stock.

Rolling is done in several stages, either by passing the metal through a number of rolling mills in series (a "train" of rolls) or by making a number of passes through a set of adjustable reversible rolls. Rolls for breaking down ingots are called blooming or slabbing mills, and the bloom or slab from these mills goes to the intermediate and finishing rolls. Rolls may be plain for the rolling of sheet and plate, or grooved for rolling such shapes as rails and I-beams. Lap- and butt-welded pipe is made by rolling plate (*skelp*) in concave rolls over a mandrel, and the pipe is shaped and pressure welded in a single operation.

*(Courtesy The Dow Chemical Company, Midland, Michigan)*

FIG. 4.—Rolling Sheets of Dowmetal.

**Forging.**—Forging is the shaping of metal either by hammering or by squeezing in a hydraulic press. Hammer forging is the oldest method known for the mechanical shaping of metals and is used today for producing such shapes as car wheels and alloy steel bar stock; most hammer forging is done under a steam hammer. For large forgings a hammer would have to be very large and heavy—so big, in fact, that it would not be practicable—and so for large forgings such as cannon and armor plate a hydraulic press forge is used. Hammer forging has a tendency to work only the surface layers of an object, but the beneficial effects of press forging extend throughout the body of the material. Forging of heavy pieces is invariably hot-working. Cold-pressing (stamping, flanging), used only for shaping thin sheet, produces such shapes as automobile fenders, bolsters, and braces.

*(Courtesy the Midvale Company, Philadelphia)*

FIG. 5.—A 9000-ton Hydraulic Press Forge.

**Wire Drawing.**—Wire is made by drawing rod through a series of dies until the wire has been reduced to the proper diameter. Wire drawing is often cold-working and if the draft is heavy, the wire may work-harden so rapidly that it must be annealed several times during the operation. American practice tends to eliminate the necessity of reheating by drawing so rapidly that the frictional heat more than balances the heat lost by radiation and conduction.

**Drop Forging.**—Drop forging is a method of hammer forging, but, instead of a plain hammer and anvil, the piece is forged between two dies. For complicated shapes, the forgings must be done in stages; and this requires several sets of dies. Drop forging combines the advantages of both casting and mechanical working, for intricate shapes can be made in this way, and the metal has the benefit of the mechanical work. The dies and other equipment required for drop forging are very expensive; the process can be used only where a large number of identical shapes are required.

**Special Methods.**—There are several other methods of shaping metals by mechanical means, most of which are cold-working. In *stamping, cupping, flanging,* and *deep drawing,* the metal is pressed into shape by means of dies and plungers; in *spinning* a flat plate is clamped against a form in a spinning lathe and deformed by a blunt tool until it fits the form. Many of these processes involve severe cold-working and are suitable only for very ductile material.

## OTHER SHAPING METHODS

Two other ways of shaping metallic objects do not come directly under the heading of either casting or mechanical working.

*(Courtesy Aluminum Company of America, Pittsburgh)*

**FIG. 6.—Die-Cast Oil Burner Part; 43 Holes Cored in 4 Directions.**

**Die Casting.**—In this method the metal is cast under pressure in accurately shaped molds or dies. Die casting is used in the quantity production of small objects such as automobile ornaments, valves, and other machine parts; and die castings are usually made of zinc-, lead-, or aluminum-base alloys. *Centrifugal casting* may be used in casting hollow cylinders such as pipes. The casting is done in a rotating cylindrical mold; centrifugal force causes the metal to cling to the walls of the mold, where it freezes. As the surface tension of most liquid metals and alloys is very high, the metal is prevented from filling small crevices and corners in the mold when ordinary casting methods are used. Pressure casting causes the liquid metal to fill the mold completely, and hence gives better detail to the finished castings.

**Extrusion.**—Most metals and alloys pass through a pasty stage near the melting point, and sometimes this pasty liquid can be extruded or forced through a die to emerge as solid metal. Brass, and aluminum and magnesium alloys are often made into tubes, curtain rods, small girders, and similar shapes by extrusion. Lead pipe is usually made by this method, and lead-sheathed cable is made by forcing the freezing metal through a die around the outside of the cable.

## SUMMARY

The methods considered up to this point include all the common methods of shaping metals and alloys. Before considering welding, cutting, and machining, it will be helpful to summarize some of the reasons for the widespread application of mechanical shaping methods.

1. The mechanical properties of worked metal are much superior to those of cast metal. Cannon tubes, for example, must be forged, even though casting would be cheaper, because cast steel would not be strong enough for this purpose.
2. Some very useful metals (copper, steel) cannot be cast satisfactorily without special precautions, and these metals are fabricated by mechanical processes whenever possible.
3. For producing large quantities of standard shapes (rails, rods, beams, plates, and sheets), mechanical processes are much cheaper than casting and yield a better product.
4. Cold-working provides a very convenient way to harden certain non-ferrous metals and alloys, such as brass, copper, aluminum alloys, and magnesium alloys.

## CUTTING AND WELDING

The final shaping operation on a casting or on metal stock (bar, plate, or rod) such as drilling, planing, and turning, are not considered as metallurgical operations. This does not mean, however, that the machinability of metals and alloys is of no interest to the metallurgist.

**Cutting.**—Besides the cutting of metals in machine shops, there is a large amount of cutting of scrap in steel mills, the wrecking of steel buildings and ships, and the cropping of blooms in the rolling mill. Specially designed saws and shears are often used for this purpose, and in recent years the cutting of metals by heat has grown in importance. In the *arc process* of cutting, an electric current of from 350 to 800 amperes is used with a carbon electrode, and the arc melts the metal out of its path. Another method which is very useful in cutting steel is the *oxygen lance* method. A stream of oxygen under pressure impinges on a preheated spot on the steel, and the steel burns to form a fusible oxide which flows out of the cut; the heat generated by the burning metal is sufficient to keep the operation going. The oxygen lance is also used to burn the frozen metal out of the iron tap hole in blast-furnace operation.

Some metals, such as copper, cannot be cut by either of these methods, because the heat generated by the oxidation is not enough for the oxygen lance method, and the thermal conductivity is so high that the heat cannot be confined to a small area.

**Welding.**—When metals are joined in such a manner that they are held firmly together by atomic attractions they are said to be *welded*. Welding may be done by pressing two solid pieces together, or by bringing liquid and solid metal in contact. In all types of welding, it is essential that the metal surfaces to be joined are free from coatings of oxides.

**Pressure Welding.**—The oldest form of welding is pressure welding, and the original method was to bring two heated metal surfaces together and hammer them until they welded. A flux such as borax was used to slag off the oxide coating; the slag was squeezed out by the hammering, leaving clean metallic surfaces in contact. The purpose of hammering was twofold—to expel the slag and to force the metals into intimate contact. The purpose of heating was to increase the thermal energy of the metallic atoms and to promote the diffusion which is essential for the establishment of atomic bonds across the welded joint. This type of welding is still used by blacksmiths for welding steel and wrought iron. Some soft metals, such as gold and lead, can be welded cold by the application of sufficient pressure.

In modern welding practice the principles of pressure welding have been applied to a wide variety of welding methods which are much more efficient and rapid than hammer welding, and which can be applied to a large number of metals and alloys. The essential facts about modern welding practice are: (1) the metals to be welded are held in close contact by steady pressure rather than by hammering, and (2) the heating is done by passing a heavy current of electricity through the junction of the two pieces. Under the general heading of pressure welding (electrical resistance welding) are included flash welding, shot welding, seam welding, spot welding, percussion welding, and projection welding. Pressure welding is very widely used in welding plate and sheet metal, as shown by the following tabulation[1] of the pressure welds performed on a 1938 two-door sedan.

| | |
|---|---|
| Spot welds | 3,154 |
| Butt welds | 35 |
| Seam welds | 2 |
| Total | 3,191 |

**Fusion Welding.**—Fusion welding, brazing, and soldering involve the fusion of parts to be welded or the fusion of an intermediate body such as a solder. In autogenous welding the liquid metal is supplied by the parts to be welded; if a solder, brazing mixture, or filler rod is used, the welded parts are held together by a solid metal which may or may not have the same composition as the welded parts. The fact that molten metal is used in forming the weld makes it easier to get good contact at the joint and accelerates the interdiffusion of the metals involved. Fusion welding does not require pressure or hammering (except as a means of working the finished weld) and can be used in welding large sections which could not be welded by pressure welding. The different methods of fusion welding are classified according to the way the heat is supplied for the fusion. Among the most important are:

1. *Soldering.* A heated soldering iron or a blow torch is used to melt the solder. The parts to be soldered are not melted.

2. *Brazing.* The brazing mixture is melted in a gas furnace while in contact with the joint to be welded.

3. *Welding.* In the following processes, the heat melts either the metals to be welded, or a filler rod (generally of the same composition as the welded metal) or both. In the thermit process the hot liquid metal produced by the chemical reaction is used as the welding medium.

(*a*) *Arc welding.* The heat for welding is supplied by an electric arc discharge.

(*b*) *Oxyacetylene welding.* The heat is supplied by the oxyacetylene flame:

$$2C_2H_2 + 5O_2 \rightarrow 4CO_2 + 2H_2O + 608{,}000 \text{ calories}$$

(*c*) *Oxyhydrogen welding.* Heat is supplied by the oxyhydrogen flame:

$$2H_2 + O_2 \rightarrow 2H_2O + 115{,}800 \text{ calories}$$

(*d*) *Thermit welding.* A metal (usually iron) is reduced from an

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[1] Ford Motor Company, private communication.

oxide by metallic aluminum, the reaction generating a large amount of heat:

$$2Al + Fe_2O_3 \rightarrow Al_2O_3 + 2Fe + 197{,}900 \text{ calories}$$

(*e*) *Atomic hydrogen welding.* Molecular hydrogen is dissociated into atomic hydrogen by an electric arc, and the atoms recombine to form molecular hydrogen:

$$2H \rightarrow H_2 + 50{,}400 \text{ calories}$$

The hydrogen does not burn to water as in the oxyhydrogen flame (at least not in the vicinity of the weld). The atomic hydrogen flame gives a higher temperature than any of the fuel flames and provides a reducing atmosphere at the weld. These facts make it possible to weld many oxidizable metals which could not be welded by other methods.

**Metallurgy of Welds.**—The metal in a pressure weld is essentially hot-worked metal, and that in a fusion weld is essentially a casting. These facts, together with the heat-treating effects of the localized heating used in welding, mean that there are many physicometallurgical considerations to be taken into account in order that a welded joint shall have the best possible properties.

**Uses of Welding.**—In the past, when welding was principally a last resort in attempting to salvage broken machinery, it did not receive a great deal of attention from metallurgists, but today conditions are different. Welding has come to be one of the most useful and efficient methods of joining metallic bodies, and now it is essentially a fabricating process rather than a repairing process. One very important application of modern cutting and welding technique is the manufacture of heavy machine parts from cut and welded stock. These are usually superior to castings in their mechanical properties, and are cheaper than castings.

## EXERCISES

Determine how each of the following are shaped, and give reasons why the particular process is used in each case:

1. Automobile door handles.
2. Automobile engine blocks.
3. Aluminum cooking utensils.
4. High-grade wrenches.
5. Razors.
6. Balls for ball bearings.
7. "Tinfoil."
8. Seamless copper tubing.

9. Airplane fuselages.
10. Manganese steel crusher mantles and linings.
11. Structural steel I-beams.
12. Trolley wire.
13. Stainless-steel cutlery.
14. Spot-welded pipe.
15. Lap-welded pipe.
16. Cast-iron pipe.
17. Brass curtain rods, "trim," etc.
18. Automobile fenders.
19. Heat-treated axe heads.
20. Armor plate.
21. Cannon.

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# CHAPTER VI

## THE HEAT-TREATMENT OF METALS AND ALLOYS

**Heat-treatment** is the name given to heating and cooling operations performed upon solid metals and alloys in order to cause certain changes in their properties. The heat-treating is usually performed upon the finished object, and after the heat-treatment the metal is ready for use, except for small amounts of machining, polishing, or burnishing.

In previous chapters we have considered various changes which take place in solid metals and alloys, such as phase changes in the solid state, recrystallization, and grain growth. In all these discussions, the fact was either stated or implied that we were speaking of equilibrium conditions—in other words, it was assumed that sufficient time was allowed in each case for the process involved to go to completion; and we designated our "maps" showing the phase changes in various alloys as "equilibrium diagrams" to indicate the fact. In this chapter we shall have occasion to refer to the iron-carbon equilibrium diagram (Fig. III-22) in the discussion of the heat-treatment of steels; probably this is the best diagram to use to illustrate the meaning of equilibrium and non-equilibrium. Consider any point in the field *AESG* on the diagram. The alloys in this region consist of austenite, or the solid solution of carbon in gamma iron; if we cool such an alloy, we eventually reach a point on the line *GSE*. Here our uniform solid solution becomes saturated—with iron (ferrite) if our point is to the left of *S*, with carbon (or rather cementite, $Fe_3C$) for points to the right of *S*, with both carbon and iron at the point *S*. At any point in the field *GPS*, we have ferrite + saturated austenite, and in the field *SRE* we have cementite + saturated austenite. At any point just above the line *PSR*, we have saturated austenite of the eutectoid composition (0.85 per cent) + either excess ferrite or excess cementite; and when we cool below the line *PSR*, this austenite decomposes into Fe + $Fe_3C$ to form the eutectoid pearlite; this transformation takes place at constant temperature. The point *G* on the diagram is a critical point of pure iron; and on cooling through this point, the iron undergoes an allotropic change from gamma iron to beta iron. We may regard the line *GS* in the same way as we considered the line *GE* in the lead-antimony diagram (Fig. III-9). The presence of antimony lowers the incipient freezing point of lead, and the presence of carbon lowers the gamma-beta transformation point in iron.

Any one of the steels must originally exist as the uniform solid solution of carbon in gamma iron. When the steel is cooled below the line *PSR*, all the austenite disappears, and in its stead we have a mechanical mixture of Fe and $Fe_3C$. For this transformation to take place, there must be a certain amount of diffusion of the atoms of carbon and iron in the original solid solution. The carbon is originally uniformly distributed throughout the austenite; and when the transformation takes place, the carbon atoms must migrate to certain regions where they unite with iron to form $Fe_3C$ (cementite), leaving other regions which are virtually free of carbon (ferrite or pure iron). At the normal temperatures of these transformations the mobility (thermal energy) of the iron and carbon atoms is sufficiently great so that the necessary diffusion takes place with reasonable speed. If, however, a steel in the austenitic stage is cooled rapidly or quenched, there is not sufficient time for the diffusion to become complete; and the transformation is arrested in an incomplete or metastable state. If the steel is cooled to room temperature by the quenching operation, the thermal energy of the atoms becomes so low that diffusion is virtually impossible, and the steel remains indefinitely in the metastable condition. Although we have "frozen" the normal transformation at an intermediate stage, the tendency to assume the normal, or stable, condition is still present and is prevented only by the lack of mobility of the atoms. If the thermal energy is increased by reheating the steel after quenching, the alloy can be made to approach its stable condition as closely as desired.

The foregoing discussion concerns the phase changes upon which depend all the methods for heat-treating steel. Steel may exist at room temperature in its normal, or stable, form, or as a metastable form produced by quenching from above its transformation point. Note that the equilibrium diagram recognizes none of the metastable states, since by its definition it is concerned only with stable forms (equilibrium conditions). The reason for making use of such heat-treating operations is simply that the steels in the metastable condition have properties which differ widely from the properties of normal steels.

## TYPES OF HEAT-TREATMENT

All methods of heat-treating deal either with (1) the production of a metastable condition in an alloy, or (2) the removal of metastable conditions caused either by heat-treatment or by mechanical working.

**Annealing.**—Any heating operation which is followed by slow cooling is called annealing; i.e., the heated object is constrained to cool much more slowly than if it were allowed to cool in the open air. This end may be attained by packing the hot metal in an insulating material, such as lime or ashes, or by leaving it to cool in the furnace. Annealing is used to restore (partially or completely) normal conditions in a metal or alloy which is already in a metastable state, and its efficacy is due to the increased mobility of the atoms which permits them to reassemble in more stable positions. A short heating period followed by relatively rapid cooling gives a partial or "light" anneal; "dead" annealing is a process of prolonged heating followed by slow cooling which completely restores the metal or alloy to its stable form.

The principal use of annealing is to soften work-hardened metals or alloys and cause equiaxing of the distorted grains. Cold-worked metals are in a metastable condition, and annealing permits the atoms in the deformed crystals to reassemble into equiaxed grains. Annealing also relieves any mechanical strains set up in a metallic object by cold-working operations. Annealing may be applied to either alloys or pure metals.

**Grain Refining.**—Grain refining of most non-ferrous metals and alloys consists of heating cold-worked metals to a point just above the recrystallization temperature and cooling. At such a temperature a new set of grains is formed, and these grains have their minimum size. The rate of cooling is immaterial, since the rate of cooling has no effect on the size of the grains. If the cooling is slow, the grain-refining operation is the same as annealing.

**Quenching.**—When a body is heated and then plunged into cold water or some other fluid which cools it more rapidly than it would cool in still air, it is said to have been *quenched*. The fluid used is the quenching medium; water is most common for this purpose. Oils, salt solutions, molten salts, air blasts, liquid air, and iced brine are other quenching baths which serve special purposes. The object of quenching is to preserve some structural form which is stable at high temperatures but which would ordinarily alter to something else if permitted to cool slowly.

Quenching is used only on alloys and not on pure metals. As an example to illustrate this, let us return to the iron-carbon diagram (Fig. III-22). At the point *G*, pure iron transforms from the gamma to the beta form on cooling, and no quenching operation can be made rapid enough to prevent this change and retain iron in the gamma form at room temperatures. In the quenching of steels, however, the transformation involves not only the gamma-beta change in iron (the beta phase later alters to alpha iron), but also the diffusion of carbon out of austenite into cementite, and it is probably the time required for this diffusion which makes it possible to arrest the process before it becomes complete. The gamma-beta transformation in pure iron, however, involves only the rearrangement of iron atoms in a space lattice (with no diffusion necessary), and hence the transformation is more difficult to arrest. As a matter of fact, not only does quenching have no effect upon pure iron, but it has very little effect upon the low-carbon ("mild") steels so that as a rule only the high-carbon steels are treated by quenching.

Pure metals can be obtained in a metastable state at room temperatures only if the transformation point is close to room temperature. Tin, for example, undergoes an allotropic change at just a few degrees below room temperature to form "gray" tin, and it is possible to have this metal at ordinary temperature (for example 25° C.) in either the normal "white" (beta) form, or in the form of metastable "gray" (alpha) tin. The formation of the brittle, powdery, gray tin gives rise to what is known as "tin disease."

The legendary "tempering of copper" has received considerable attention for many years, and this common phrase illustrates both an error in usage of terms and a misconception of the limitations of heat-treating operations. In the first place, the process referred to is one of hardening, and "tempering" does not mean hardening, but rather the removal of hardness. The only possibility of hardening pure copper by heat-treatment would be to preserve an allotropic form by quenching—copper, however, has no allotropic modifications. Moreover, if it had such a modification it would probably be impossible to preserve it by quenching. "Hard copper" has been produced by heat-treatment, it is true; but the "copper" in question always contains one or more other elements; and the heat-treatment involved is well known and has been applied to many other types of alloys (see Precipitation Hardening below).

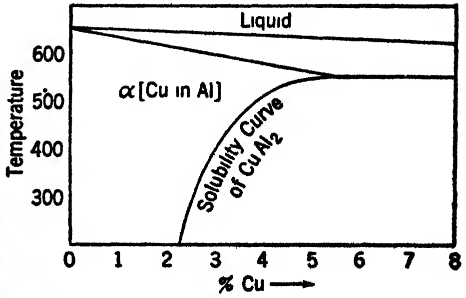
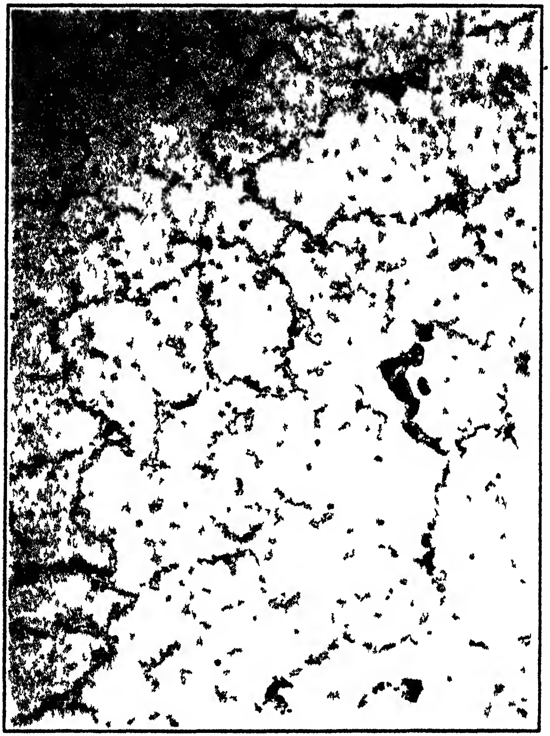


Fig. 1.—Portion of the Aluminum-Copper Equilibrium Diagram.

**Precipitation Hardening.**—Figure 1 is part of the aluminum-copper equilibrium diagram. From this sketch it is seen that copper is slightly soluble in solid aluminum, and that the solubility decreases as the temperature drops (compare with the discussion of Fig. III-17). An alloy containing 4 per cent Cu would be a homogeneous solid solution immediately after freezing, but by the time it had cooled to 200° C., the solution would contain only about 2.5 per cent Cu; and the rest of the copper would have been precipitated as $CuAl_2$. Examination of a slowly cooled alloy of 4 per cent Cu and 96 per cent Al would reveal host crystals of the alpha solid solution + visible crystals of $CuAl_2$. If, however, the alloy were quenched from 500° C., the decomposition would be arrested, and the alloy would appear to consist of uniform alpha solution. The separation of excess compound in the quenched alloy would still be possible, but would be largely prevented by the lack of mobility of the atoms—if the alloy were now heated slightly (for example, to 200° or 300° C.), the delayed precipitation would take place, and many extremely fine particles of $CuAl_2$ would be formed throughout the grains of the alpha solution.

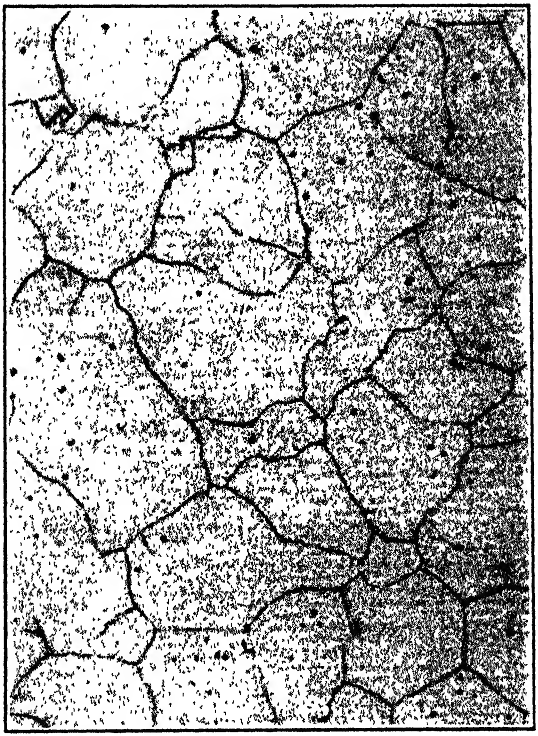


*(Courtesy The Dow Chemical Company, Midland, Michigan)*

FIG 2—Cast Alloy for Precipitation Hardening (× 100).

Note the visible grains of the segregated compound

These are invisible under the microscope, but their presence is revealed by the increase in hardness of the alloy after treatment. Since the compound $CuAl_2$ is very hard, the presence of great numbers of these fine particles throughout the alpha crystal grains keys most of the slip planes; and as slip is made more difficult, the alloy becomes harder. It will be seen that the critical condition is the size of the $CuAl_2$ particles—if they are too large, as in the normal alloy, the keying action is negligible.



(*Courtesy The Dow Chemical Company, Midland, Michigan*)

FIG. 3.—Same Alloy after Heating and Quenching. (× 100).

**Most of the segregate has gone back into solution. The alloy is now ready to be hardened by the precipitation of minute grains of the hard compound, either by gentle heating or by aging.**

The example given above illustrates the mechanism of precipitation hardening; aluminum-base and magnesium-base alloys are most commonly treated by this method. In some cases the precipitation of the hardening medium takes place at room temperature, and the process is then called *age-hardening.*

## HEAT-TREATMENT OF STEELS

The heat-treatment of steels is by far the most important aspect of the general problem, and several types of heat-treatment are used with steels which are not used for non-ferrous metals and alloys.

**Hardening.**—Steel is hardened by quenching from just above the line *GSE* (Fig. III-22). The quenching arrests the decomposition of the austenite and preserves one or more of the metastable transition substances which exist between austenite and the normal (pearlitic) structure. As a general rule, steels containing more than 0.75 per cent C. are the only ones which harden sufficiently to make this treatment applicable, and even with the most drastic quenching, none of the original austenite remains. Steels which are very high in carbon (1.5–1.6 per cent) will show some austenite when cooled very rapidly from a high temperature, but as a rule no austenite will be left in these steels after quenching.

The normal constituent of drastically quenched steels is *martensite*, which is the first material to be formed when austenite decomposes. Martensite has a characteristic needlelike structure under the microscope, and it is very hard and quite brittle. Martensite is exceeded in hardness by only one other constituent of steels—cementite. Austenite is relatively soft and ductile as compared with martensite.

Consequently, the hardening process results in producing a very hard material—a steel containing 0.85 per cent C may be made hard enough to scratch glass by such treatment. The hardening treatment, however, is attended by certain undesirable features, for a steel which has its maximum hardness will also be very brittle; and if the piece is large, the quenching operation will set up tremendous mechanical strains in the piece. In order to secure the best possible properties between the soft, ductile pearlitic steel and the hard, brittle martensitic steel, we resort to the process of tempering.

**Tempering.**—A previously quenched or hardened steel is tempered by reheating to some point *below* the line *PSK* (Fig. III-22) and cooling. The cooling may be either rapid or slow. The additional thermal energy imparted to the atoms by the heating permits the martensite to continue its alteration toward the stable pearlitic form. As martensite decomposes, there are formed in order *troostite*, *sorbite*, and finally pearlite, each of which is softer but tougher and more ductile than the preceding substance. The degree of alteration, or the amount of tempering, in any case is determined by the temperature to which the steel is reheated. The higher the temperature, the softer and more ductile the final product will be. Proper tempering permits the production of a steel having any desired properties between the two limits. Tempering also tends to relieve the mechanical strains set up in the object by quenching.

Relatively slow quenching has approximately the same effect as rapid quenching followed by tempering—quenching in oil, molten lead, or molten salts is really a combined hardening and tempering operation. Tempering is often called *drawing.*

**Normalizing.**—This process corresponds most nearly to the grain refining which is used for non-ferrous metals and alloys. The grain size of the ferrite in hypoeutectoid steels depends upon the size of the parent austenite grains; if the original grains of austenite are large, the ferrite grains will be large. When such a coarse-grained steel is heated to a point just above the line *GS* in Fig. III-22, a new set of austenite grains are formed, and these grains have their minimum size. If the steel is now cooled in air (it must not be quenched unless it is desired to harden it), the steel will have the finest possible grain size. Such a steel is then said to be normalized.

A similar treatment designed to decrease the size and alter the shape of the cementite needles in hypereutectoid steel is known as *spheroidizing.* In spheroidizing the steel is heated to a point just above *SK* in Fig. III-22, and often several repetitions of the treatment are necessary.

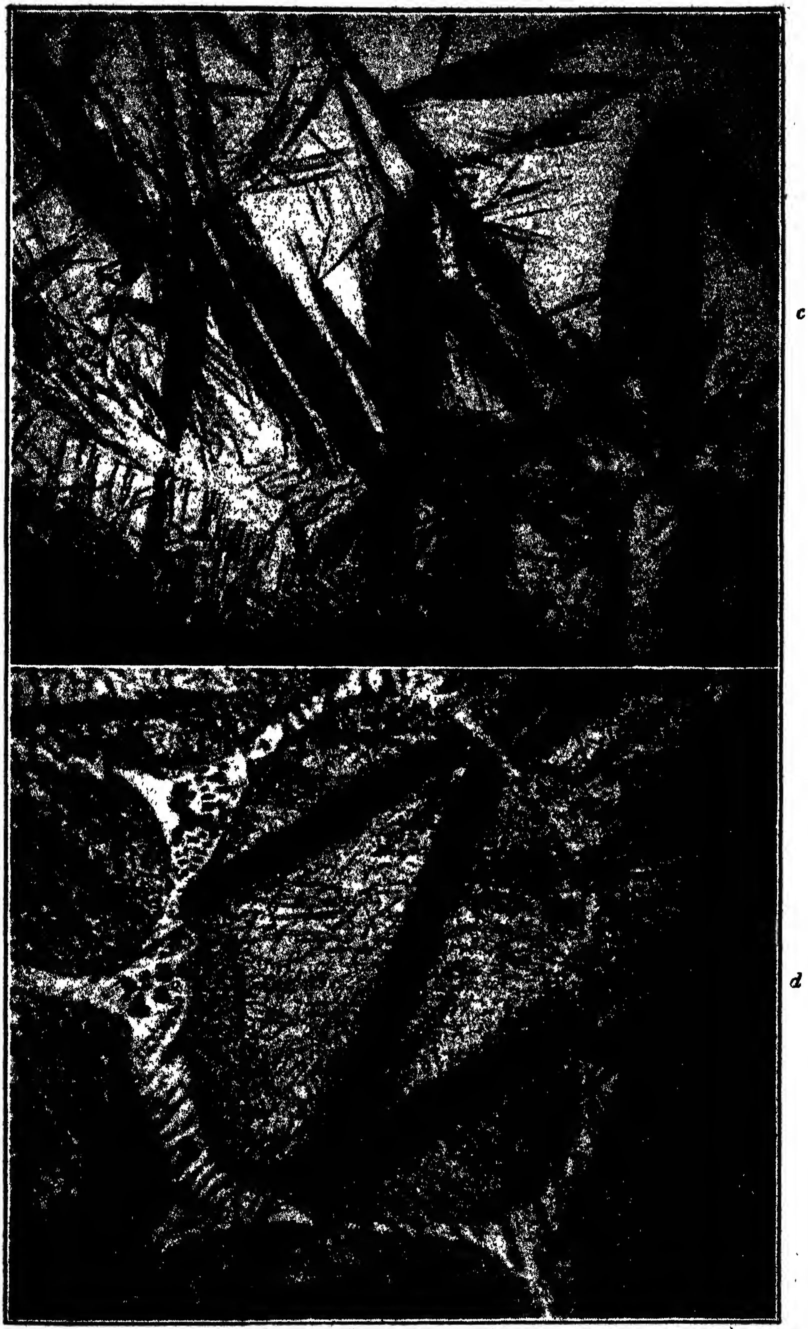
**Case-Hardening.**—The operation of case-hardening differs from the other heat treating operations which we have considered in that it involves a chemical change in the steel. Usually low-carbon steels are used for case-hardening, since the object is to produce a metal having a tough, ductile core and a hard surface or *case.*

*Carburizing* (*cementation*) consists of heating a piece of low-carbon steel for a long period (8 to 24 hours) while packed in contact with a carbonaceous material, such as charcoal, graphite, potassium ferrocyanide, leather, potassium cyanide, etc. At the temperature of cementation (about 900° C.), the carbon penetrates into the steel to form a high-carbon case on the outside of the piece. Subsequent quenching then greatly hardens the case but has very little effect upon the low-carbon interior. Apparently most of the carbon diffuses into the steel in the form of CO gas.

In *nitriding,* the steel is heated in an atmosphere of ammonia at a relatively low temperature (about 500° C.) until a thin surface layer of iron nitrides is formed by the reaction of iron and the nitrogen in the ammonia. The resultant nitrided case is harder than a carburized case.

*(Courtesy H. O. Walp, SKF Industries, Inc., Philadelphia)*

**Fig. 4.**—Illustrating the Progressive Decomposition of the Fe-C Solid Solution (Austenite) with Tempering (all × 1000).



*(Courtesy H. O. Walp, SKF Industries, Inc., Philadelphia)*

FIG. 4.—Illustrating the Progressive Decomposition of the Fe-C Solid Solution (Austenite) with Tempering (all × 1000).

(*Courtesy H. O. Walp, SKF Industries, Inc., Philadelphia*)

FIG. 4.—Illustrating the Progressive Decomposition of the Fe-C Solid Solution (Austenite) with Tempering (all × 1000).

*a.* Quenched; not annealed (Austenite).
*b.* Tempered at 200° C.
*c.* Tempered at 300° C.
*d.* Tempered at 500° C.
*e.* Tempered at 700° C.

**Heat-Treatment of Alloy Steels.**—Alloy steels (steels containing important amount of elements other than carbon and iron) respond to much the same heat-treatments as do the carbon steels. Because of their higher cost, practically all alloy steels are heat-treated before use in order to develop the very best properties possible. The presence of foreign elements in steel, however, often alters the position of the critical points; and this, of course, has considerable effect upon heat-treating procedures. In the case of manganese steel (containing 14 per cent Mn) and stainless steels (e.g., "18–8" steel containing 18 per cent Cr and 8 per cent Ni), the gamma-beta transformation is lowered so much that the austenitic form is stable at room temperature. These austenitic steels are homogeneous under the microscope (showing only one species of grain), are non-magnetic, and work-harden very rapidly when subjected to any cold-working.

**Heat-Treatment of the Non-Ferrous Metals and Alloys.**—Heat-treatment of most non-ferrous metals and alloys is limited almost entirely to annealing operations, except for certain aluminum, magnesium, and copper alloys which respond to precipitation hardening.

**Temper.**—The condition of a metallic object as determined by its mechanical and heat-treatment is often called its temper. This nomenclature is used principally in referring to non-ferrous metals and alloys, because "temper" has a more restricted meaning when applied to steels. In describing brass sheet, for example, the temper may be denoted as: (1) annealed; or (2) cold-rolled; or (3) 0.0325 gauge, 3 Nos. hard, which means that after the last anneal the thickness was reduced by cold rolling, 3 Brown and Sharpe gauge numbers to 0.0325 inch.

## HARDNESS

At various points in the preceding chapters the ways in which the hardness and strength of a metal may be increased have been mentioned. For the sake of convenient reference, the important methods of hardening will be listed at this point.

*Alloying.* An alloy of two metals may be harder than the component metals. If the alloy is a conglomerate, its hardness will be an average of the hardness of the constituent grains. If the alloy is a compound or solid solution, it will usually be considerably harder than either.

*Hardening.* Here we use the special meaning of the word to refer to the hardening of iron-carbon alloys by quenching. *Tempering* is a reheating operation which removes some of the hardness.

*Strain-Hardening.* This is due to the increased resistance to slip caused by cold-working.

*Age- or Precipitation-Hardening.* In this the hardness (resistance to slip) is caused by the precipitation of submicroscopic particles of a hard compound which serve to key the slip planes.

*Case-Hardening and Nitriding.* These two processes result in the formation of a hard case on steel or iron. Case-hardening or carburizing produces a surface which is high in carbon, and this is generally further hardened by quenching. Nitriding produces a case which contains considerable amounts of iron nitrides, and this nitrided case requires no heat treatment.

## EXERCISES

1. Prepare a report on some definite heat-treatment operation performed on a production basis (e.g., heat-treatment of certain standardized motor-car parts). List the type of furnaces and other equipment used, temperature control methods, etc.

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# CHAPTER VII

# THE INDUSTRIAL METALS AND THEIR ALLOYS

**Relative Importance of the Metals.**—In a sense it is impossible to list the metals in the order of their importance, because each metal has unique properties which make it suitable for certain purposes; and often there is no adequate substitute which can replace a given metal for some particular use. Because of its low resistivity, copper is invaluable for many electrical uses; iron has unique magnetic properties; aluminum and magnesium alloys are very useful in aircraft where lightness combined with strength is desired; and tungsten is the most satisfactory metal available for lamp filaments.

From the standpoint of the amount produced and consumed each year, iron is by far the most important of all the metals, and it is followed by copper, lead, and zinc in order. During the last few years, the use of aluminum and magnesium has been increasing rapidly. Table 1 is a list of the elements used in commercial metals and alloys.

TABLE 1

Elements in Commercial Metals and Alloys

| Used as Metals or Alloys | | Used Only in Alloys | |
|---|---|---|---|
| *Engineering Metals* | *Others* | *Metals* | *Metalloids* |
| ✓ Iron (steel) | Sodium | Manganese | Carbon |
| ✓ Copper | Gold | Titanium | Silicon |
| ✓ Lead | Silver | Molybdenum | Boron |
| ✓ Zinc | Platinum | Vanadium | |
| ✓ Aluminum | Chromium | Cobalt | *Non-Metals* |
| ✓ Tin | Cadmium | Bismuth | Nitrogen |
| ✓ Nickel | Mercury | Antimony | Phosphorus |
| ✓ Tungsten | Palladium | Rhodium | Sulfur |
| ✓ Magnesium | Iridium | Arsenic | Oxygen |
| | Tantalum | Zirconium | |
| | Selenium | Calcium | |
| | | Barium | |
| | | Uranium | |
| | | Cerium | |

## IRON AND STEEL

**Properties.**—Pure iron is a silvery white metal, very ductile, and highly magnetic. Its atomic weight is 55.84, atomic number 26, melting point 1535° C., boiling point 3000° C., specific gravity 7.85–7.88, and valence 2 or 3. Iron has four allotropic forms: alpha, which is stable at ordinary temperatures; beta, which is stable from 800° C. to 906° C.; gamma, which is stable from 906° C. to 1425° C.; and delta, which is stable above 1425° C. Gamma iron has a face-centered cubic lattice; all the other forms have a body-centered cubic space lattice.

Iron in the form of commercially valuable ore is the most abundant of the metals found in the earth's crust. In total amount it is surpassed only by the metal aluminum. The widespread use of iron in the arts and industries is due primarily to two important facts, viz.:

1. Iron forms a remarkable series of useful alloys with carbon.
2. The widespread distribution of high-grade iron ores permits the metal to be produced cheaply and on an enormous scale. Iron is the cheapest of all the metals.

In addition, iron has unique magnetic properties which make it invaluable for many purposes.

Chemically pure iron is difficult to prepare, and electrolytic iron (which is produced only on a small scale) is the only commercial metal which approaches the composition of pure iron. Practically all commercial iron exists in the form of iron-carbon alloys.

**Alloys of Iron.**—In all the normal iron-carbon alloys, the iron exists as free iron (alpha iron; ferrite) or as $Fe_3C$ (cementite), and the carbon may be present as cementite, as graphite, or partly as cementite and partly as graphite.

1. *Cast iron* (*pig iron*) is the original form of all primary iron (iron extracted from ore, as distinguished from secondary iron recovered from scrap metal) and is produced in the iron blast furnace. Cast iron is high in carbon (2.5 to 4.0 per cent) and in the solid state would contain from 35 to 50 per cent cementite, if all the carbon remained combined with iron. In most cast irons, however, some or all of the carbide decomposes to yield iron and elemental carbon in the form of graphite. Consequently, an ordinary or gray cast iron contains ferrite either in large crystals, in pearlite, or both; combined carbon in the form of cementite either in large crystals, in pearlite, or both; and free or graphitic carbon. In the limiting case, all the carbide would be decomposed, and the alloy would consist of ferrite and graphite only.

The free carbon in gray cast iron separates in the form of relatively large plates; and since graphite is neither strong nor ductile, the alloy will break through the flakes of graphite. It is this graphite showing on a fractured surface that gives the iron its gray color, and hence its name. Gray cast iron may be regarded as a highly impure steel; the impurity is graphite, and it is present in such large amounts that it virtually determines the properties of the cast iron. Gray cast iron is not malleable in any temperature range and can be shaped only by casting. Cast iron has a lower melting point than either pure iron or the steels (*vide* Fig. III-22). The separation of graphite causes an expansion which counteracts the normal shrinkage on cooling, so that gray cast iron freezes without forming shrinkage cavities.

II *White cast iron* or *chilled cast iron* is obtained by cooling a cast iron rapidly enough to prevent decomposition of any of the carbide. White cast iron has all its carbon in the combined form, and it contains so much cementite that its properties resemble those of cementite. It shows a white fracture and is extremely hard and very brittle. White cast iron is too brittle to be used alone; it is generally used (1) as a chilled surface on a gray iron casting, or (2) as a raw material for the manufacture of malleable cast iron. Gray iron itself is very brittle as compared with such malleable alloys as the steels, but it is considerably tougher and more resistant to shock than white cast iron.

The amount of silicon and other substances present in a cast iron is of great importance in determining the rate at which the carbides decompose, so that a white cast iron can be produced only when the iron has the proper chemical composition.

III *Malleable cast iron* is prepared by annealing white cast-iron articles so that the carbon separates in the form of finely divided graphite or *temper carbon,* rather than as the large flakes which are found in gray cast iron. Simple annealing of this material gives *black-heart malleable* iron; if the iron is packed in an oxidizing agent such as $Fe_2O_3$ and annealed, most of the carbon is oxidized and escapes as CO. When the carbon is almost completely removed by the annealing operation, the product is known as *white-heart malleable* iron. Malleable castings are used only for small articles such as pipe fittings and harness buckles. The shape of the object is obtained by casting the white iron before annealing, and the term "malleable iron" means that the alloy is less brittle and more resistant to shock than gray cast iron, and not that it is shaped by forging or rolling.

IV *Steel* is an alloy of iron and carbon containing less than 1.7 per cent C and is formed by (1) the refining of liquid pig (cast) iron, or (2) remelting and refining steel scrap. Steel never contains free carbon or graphite; it consists of a mechanical mixture of soft, ductile ferrite and hard cementite. *Ingot iron* and *wrought iron* are both very low in carbon, and their physical properties approximate those of pure iron. Wrought iron can always be distinguished by the fact that it contains stringers of slag owing to the methods of manufacture. Ingot iron does not contain slag stringers and under the microscope appears to consist almost entirely of ferrite grains. Neither ingot iron nor wrought iron contains enough carbon to harden by quenching.

We can best define steel as an alloy of carbon and iron which (1) consists of ferrite and cementite, and has a carbon content less than 1.7 per cent; (2) contains sufficient carbon so that it can be hardened appreciably by quenching; and (3) is malleable enough to be worked mechanically in at least one temperature range. Items (1) and (3) distinguish steel from the cast irons, and (2) distinguishes it from ingot iron and wrought iron.

The low-carbon or mild steels are rather soft and ductile and do not harden very much when quenched. High-carbon steels are harder, stronger, and less ductile, and their hardness can be greatly increased by quenching. Ordinary steels always contain small amounts of Mn, Si, and S (sometimes P), but if these are kept below certain limits, they have little effect upon the properties of the steels. The following table illustrates what is ordinarily meant by such terms as "mild" steel, "low-carbon" steel, etc.

TABLE 2[*]

| | % C | U.T.S. (psi.) | E.L. (psi.) | El. % in 2 in. |
|---|---|---|---|---|
| Very mild steel | 0.05–0.15 | 40– 48,000 | 24–30,000 | 34–28 |
| Mild steel | 0.15–0.25 | 48– 60,000 | 30–36,000 | 28–25 |
| Low carbon steel | 0.25–0.40 | 60– 70,000 | 36–40,000 | 25–22 |
| Medium C steel | 0.40–0.60 | 70– 80,000 | 40–48,000 | 22–18 |
| Higher C steel | 0.60–0.70 | 80– 94,000 | 48–56,000 | 18–14 |
| Spring steel | 0.70–0.80 | 94–108,000 | 56–64,000 | 14–8 |
| Pearlitic steel | 0.85 | 120,000 | 70,000 | 5 |
| High carbon steel | 1.00–1.10 | 115–110,000 | 55–60,000 | Slight |
| Very high carbon steel | 1.10–1.70 | 110,000– 90,000 | 55–50,000 | Slight |

[*] Stoughton and Butts: Engineering Metallurgy. McGraw-Hill Book Co., New York, 1930. Reprinted by permission.

The lower the carbon content, the greater the ductility, electrical conductivity, and magnetic permeability; the higher the carbon content, the greater the hardness and the hardenability on quenching. Note that the U.T.S. and the E.L. (Table 2) increase to a maximum at 0.85 per cent C and then diminish as the carbon content increases beyond 0.85 per cent.

Steel is more widely used than all other metals and alloys combined. It is employed for building construction, bridges, machinery, tools, rails, etc. The following tabulation illustrates the type (carbon content) of steel suitable for a few specific purposes:

### TABLE 3

### Carbon Content of Steel for Various Uses

| | Carbon Content % |
|---|---|
| Boiler plate | 0 08–0.18 (or wrought iron) |
| Boiler tubes | 0.08–0.18 (or wrought iron) |
| Case-hardening stock | 0.10–0.20 |
| Nails | 0.10 |
| Rivets | 0.05 |
| Structural steel | 0.25 |
| Machinery steel | 0.35 |
| Rock drills | 0.85 |
| Springs | 0.8 –0.9 |
| Circular saws | 0.85 |
| Metal cutting dies | 0.85 |
| Lathe tools | 1.00–1.20 |
| Machinists' tools | 0.70–1.20 |
| Stone cutting tools | 1.35 |
| Cold-rolled steel | Not over 0.4 |
| Dies for wire-drawing | 1.30–1.70 |

**Alloy Steels and Alloy Cast Irons.**—The alloy steels may be defined as steels which contain one or more other elements in addition to iron and carbon in quantity sufficient to alter noticeably the properties of the alloy. A similar definition applies to alloy cast iron. Steels with one additional ingredient are binary steels (chrome steel, nickel steel, manganese steel, tungsten steel); with two additional ingredients ternary steels (chrome-nickel steel, nickel-vanadium steel); and with three additional ingredients quaternary steels (nickel-chromium-molybdenum steel).

Silicon and manganese are present in small amounts in almost all steel and cast iron, and a steel is not a silicon steel unless it contains 2 or 3 per cent Si, nor a manganese steel unless it contains from 7 to 14 per cent Mn. The other alloying ingredients (nickel, cobalt, tungsten, molybdenum, etc.) cause the steel to be classified as an alloy steel, even when present only in small amounts.

In general, the purpose of alloying steel is to produce an alloy with better properties than those of plain carbon steel. Alloy steels are often made in electric furnaces in order to assure the best possible quality, and they are usually heat-treated in order to bring out their best physical properties. Because of the care exercised in their manufacture and because of the cost of some of the alloying elements, the alloy steels are much more expensive than plain carbon steel; they are used where quality is the first consideration. Alloying ingredients have pronounced effects upon the properties of steel, and these effects may take one or more of the following forms:

1. The alloying ingredients may alter the location of critical points and the rate at which critical changes occur. For example, the eutectoid point may be moved to the left so that a eutectoid steel may contain less than 0.85 per cent C or the transformation range may be lowered so far that austenite is stable at room temperatures.

2. The alloying ingredients may form solid solutions or compounds with iron and carbon, and these new constituents will have better physical properties than those of plain carbon steel.

3. The alloying elements may remove gases and oxides to produce a sounder alloy; silicon and manganese are especially useful for this purpose. Hence they are added in small amounts to all steels.

Probably the most common characteristic of alloy steels is that they remain fairly ductile, even when they are very hard and strong. This is not true of plain carbon steel which loses most of its ductility when it becomes hard (*vide* Table 2).

At this point we shall consider briefly a few of the most common alloy steels.

*Nickel steel* ordinarily contains from 1.5 to 4.0 per cent Ni, and 0.25 to 0.4 per cent C. These steels have a pearlitic structure, but they have greater tensile strength, higher elastic limit, and better fatigue resistance than carbon steel. These steels are used in motor shafts, axles, connecting rods, structural work, engine forgings, etc. *Invar*, which contains 36 per cent Ni, has the lowest coefficient of thermal expansion of any known metal or alloy and is used in making clock pendulums, surveyor's tapes, and similar articles. *Platinite* containing 42 per cent Ni has the same coefficient of expansion as glass and is used in making electrical connections to be sealed in glass. Before the discovery of platinite, platinum was the only known metal with the proper coefficient of expansion for such a purpose—hence the name "platinite."

*Chrome steel* is not common, since most of the chromium alloy steels are ternary (or higher) steels, such as the chrome-nickel steels. Steels containing 12 per cent Cr or more are austenitic at room temperature, and because of their great resistance to corrosion are included in the classification of stainless steels.

*Chrome-nickel steel* usually contains from 0.45 to 0.95 per cent Cr and 1.00 to 3.25 per cent Ni with the nickel-chromium ratio generally about 2 or 2½ to 1. These steels have very good mechanical properties, fine grain, and respond well to heat-treatment. They are widely used in crankshafts, axles, and other motor and machine parts.

The most widely used of the stainless steels is "18–8" steel, which contains about 18 per cent Cr, 8 per cent Ni, and 0.1 per cent C. This is an austenitic, non-magnetic steel.

*Manganese steel* commonly contains about 14 per cent Mn and 1 per cent C. This is an austenitic steel and hence non-magnetic. Manganese steel is extremely tough as well as strong, and it has the remarkable work-hardening ability which is characteristic of austenitic steel. When a manganese-steel piece is subjected to blows, its surface work-hardens and offers greater resistance to abrasion. Manganese steel is used for such purposes as ball-mill liners, crusher jaws and mantles, power shovel buckets, railroad frogs and crossings, and burglar-proof safes.

Other elements which may be added to alloy steels (usually in small amounts) are tungsten, vanadium, molybdenum, and cobalt.

*Alloy cast iron* usually contains small amounts of nickel and chromium or nickel alone (1–4 per cent Ni; 0.2–0.8 per cent Cr). These cast irons are stronger, denser, and have a finer grain than ordinary cast iron, and they machine well. This last property is of special importance in all cast irons. Other alloy cast irons contain higher percentages of alloying elements and are used because of their resistance to corrosion.

**Consumption and Prices.**—In 1934 there were produced in the United States 15,686,442 gross tons of pig iron.[1] In addition to this, 114,488 gross tons of pig iron were imported (chiefly from the Netherlands and India), and 4096 gross tons were exported (chiefly to Japan and Canada). The general average value for all grades of pig iron at the furnaces was $16.93 a gross ton.

The total production of steel in the United States for 1934 was 26,055,289 gross tons,[2] of which 6.19 per cent were alloy steels.[3] Note that considerably more steel was produced than pig iron; and, of course, not all the pig iron is made into steel. The difference is due to the large amount of scrap used by the steel-makers, the general

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[1] Minerals Yearbook, 1935; U. S. Bureau of Mines.

[2] Minerals Yearbook, 1935; U. S. Bureau of Mines.

[3] Cone, Edwin F.: Trends in American Alloy Steel Production; Metals and Alloys, Vol. 7, June, 1936, page 162.

average being about one ton of scrap to each ton of pig used.[4] About 85 per cent of the pig iron produced goes into steel manufacture, and about 70 per cent is never cast—it goes from the blast furnace to the steel furnaces while still liquid.

Open-hearth steel billets at Pittsburgh in 1934 were priced at $26 to $29 per gross ton;[5] tank plates and structural shapes were 1.7 to 1.85 cents per pound, and hot-rolled sheets were 2.25 to 2.65 cents per pound.

The automobile industry was the largest steel consumer in 1934,[6] taking 21 per cent of finished steel consumption; the construction industry second with 13.5 per cent; railroads third with 10.5 per cent; and the container industry ("tin" cans) fourth with 10 per cent. Of all finished steel products, sheets and strip steel accounted for 32.3 per cent.

## COPPER

**Properties.**—Copper is a reddish metal, very ductile and malleable, and a very good conductor of heat and electricity. (Silver is the only metal which is a better electrical conductor than copper.) Its atomic weight is 63.54, atomic number 29, melting point 1083° C., boiling point 2310° C., specific gravity 8.93–8.95, and valence 1 or 2. Copper crystallizes in the face-centered cubic system and has no allotropic modifications.

Unlike iron, copper in commercially pure form is produced in large quantities, and is used in this form largely for electrical transmission. Electrolytic copper ordinarily contains more than 99.9 per cent Cu.

**Alloys of Copper.**—The bulk of the copper-base alloys are of the solid solution type with the alloying metal (or metals) dissolved in the copper. These alloys are harder and stronger than pure copper, and as a rule display better casting and machining properties.

*Brass* is a copper-zinc alloy (see Fig. III-38), and most brasses consist of the uniform alpha solid solution. "High" or "yellow" brass contains enough zinc (20 to 30 per cent) to produce an almost saturated alpha solution. "Low" or "red" brass contains smaller amounts of zinc (0 to 20 per cent). Some brasses contain enough zinc to exceed the solubility of the alpha solution, and consist of a mixture of alpha and beta phases (e.g., Muntz metal). Very seldom, however, do the commercial brasses contain any of the other phases shown in Fig. III-38, since alloys containing these phases generally are very brittle.

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[4] Stoughton, Bradley: Metallurgy of Iron and Steel; Edition 4, McGraw-Hill Book Co., 1935, New York.

[5] Minerals Yearbook, 1935; U. S. Bureau of Mines.

[6] The Mineral Industry During 1934 (Vol. 43); edited by G. A. Roush, McGraw-Hill Book Co., New York.

Many brasses contain other metals in addition to copper and zinc. Lead is often added to give the brass better machining qualities; aluminum and/or nickel may be present in some brasses.

*Bronze* originally referred to the group of copper-tin alloys, but since the true bronzes are superior to brass in many respects, and also since tin is considerably more expensive than zinc, it has become customary to designate as "bronzes" many alloys which might be denoted as brasses. The various brasses and bronzes, as well as special bronzes and proprietary copper-base alloys, are used for many different purposes. The following is a list of several of the common alloys with their compositions:

TABLE 4 *

| Name | Composition, % |
|---|---|
| Bronze | Cu; Sn, 20 |
| Best bronze | Cu, 90; Sn 10 |
| Cartridge brass | Cu, 67–70; Zn 33–30; Pb; Fe |
| Coinage bronze | Cu, 95; Sn, 4; Zn, 1 |
| Commercial bronze | Cu, 90; Zn, 10; Pb; Fe |
| Common high brass | Cu, 65; Zn, 35 |
| Constantan | Cu, 60–45; Ni, 40–55; Mn, 0–1.4; C, 0.1; Fe |
| Copel | Cu, 55; Ni, 45 |
| Copper (electrolytic) | Cu, 99.90–99.993 |
| Free cutting bronze | Cu, 89; Zn, 10; Pb, 1.5 |
| German silver (best) | Cu, 46; Zn, 34; Ni, 20 |
| Hard phosphor bronze | Cu, 93; Sn, 7; P, 0.2 |
| Low brass | Cu, 80; Zn, 20; Pb; Fe |
| Muntz metal | Cu, 60; Zn, 40 |
| Nickel silver (10%) | Cu, 65–56; Zn, 25–34; Ni, 10 |
| Red brass | Cu, 89–83; Zn, 5–12; Pb, 3–10; Sn, 2–5 |
| Tobin bronze | Cu, 60–59; Zn, 38–39; Sn, 2; Pb; Fe |

* International Critical Tables (Vol. II); McGraw-Hill Book Co., 1927, New York. Reprinted by permission.

**Consumption and Prices.**—Tables 5 and 6 show the statistics for the consumption of copper in the United States for the year 1934.

TABLE 5 *

PRODUCTS OF COPPER (63% OF TOTAL)

| | % Used as Copper | % of Total Copper |
|---|---|---|
| Wire and rod | 59.3 | 37.1 |
| Sheet and strip, etc. | 32.2 | 20.1 |
| Tube | 8.3 | 5.7 |
| Miscellaneous | 0.2 | 0.1 |
| | 100.0 | 63.0 |

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*The Mineral Industry During 1934 (Vol. 43); edited by G. A. Roush; McGraw-Hill Book Co. New York. Reprinted by permission.

TABLE 5—*continued* *

PRODUCTS OF BRASS AND OTHER COPPER ALLOYS
(37% OF TOTAL)

| | % of Copper Used for Copper Alloys | % of Total Copper |
|---|---|---|
| Sheet | 52.7 | 19.5 |
| Rod and wire | 32.6 | 12.0 |
| Tube | 11.9 | 4.4 |
| Miscellaneous | 2.8 | 1.1 |
| | 100.0 | 37.0 |

* The Mineral Industry During 1934 (Vol. 43); edited by G. A. Roush; McGraw-Hill Book Co., New York. Reprinted by permission.

TABLE 6 *

ESTIMATED USE OF COPPER IN THE UNITED STATES

| | Tons of 2000 Pounds |
|---|---|
| Electrical manufactures (*a*) | 101,000 |
| Telephone and telegraphs | 18,000 |
| Light and power lines (*b*) | 40,000 |
| Wire cloth | 4,600 |
| Other wire | 40,000 |
| Ammunition | 12,200 |
| Automobiles (*c*) | 63,000 |
| Buildings | 36,000 |
| Castings n.e.s. (*d*) | 36,000 |
| Clocks and watches | 1,800 |
| Coinage | 900 |
| Copper bearing steel | 2,100 |
| Fire-fighting apparatus | 1,000 |
| Radiators, heating | 2,400 |
| Radio receiving sets | 12,600 |
| Railway equipment | 2,600 |
| Refrigerators | 16,200 |
| Shipbuilding | 3,700 |
| Washing machines | 1,900 |
| Water heaters (household) | 1,500 |
| Other uses | 42,000 |
| Manufactures for export | 25,500 |
| Total | 465,000 |
| Use in pounds per person | 7.36 |

* The Mineral Industry During 1934 (Vol. 43); edited by G. A. Roush, McGraw-Hill Book Co., New York. Reprinted by permission.

(*a*) Generators, motors, electric locomotives, switchboards, light bulbs, etc.

(*b*) Transmission and distribution wire and bus bars.

(*c*) Does not include starter, generator, and ignition equipment.

(*d*) Bearings, bushings, lubricators, valves and fittings.

The average price of domestic copper for 1934 was 8.775 cents per pound,[7] and the average prices for some other copper products were as follows:

| | Cents per Pound |
|---|---|
| Copper sheets | 15.562 |
| High brass sheet (66% Cu) | 14.125 |
| Low brass wire (80% Cu) | 15.535 |
| Commercial bronze rod (90% Cu) | 16.125 |
| Seamless copper tube | 16.638 |

## LEAD

**Properties.**—Lead is a bluish-white metal, very soft and malleable, fairly ductile, and of low tensile strength; it is a relatively poor conductor of electricity. Its atomic weight is 207.22, atomic number 82, melting point 327.5° C., boiling point 1620° C., specific gravity 11.35, and valence 2 or 4. Lead crystallizes in the face-centered cubic system and has no allotropic modifications. It has such a low recrystallization temperature that it cannot be work-hardened. Lead is used not only in the metallic state, but also in chemical compounds, the most important of these being the pigment white lead, $2PbCO_3 \cdot Pb(OH)_2$. Lead is very resistant to most corrosive liquids, and is used for such purposes as pipes and containers for sulfuric acid.

**Alloys of Lead.**—The important lead-base alloys include hard lead, antimonial lead, and the various white metal alloys. The white metal alloys contain lead and other low-melting metals such as antimony, tin, zinc, bismuth, cadmium, and arsenic. Bearing metals usually contain particles of a compound such as SbSn embedded in a soft matrix; the hard particles of the compound take the wear, and the soft matrix permits the bearing to adjust itself to the moving shaft. These bearing metals also permit good circulation of the lubricant; and if the bearing gets hot, the low-melting bearing metal melts before harm can be done to the moving shaft. Solders and type-metal are also lead-base alloys. Antimonial lead is widely used for storage-battery plates; often the term hard lead is used for antimonial lead, although other elements besides antimony impart hardness to lead.

Most of the lead alloys are conglomerate alloys of metals or metals and compounds; very few solid solutions are found in this group of alloys. Table 7 contains a list of some common lead alloys and their compositions.

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[7] Minerals Yearbook 1935; U. S. Bureau of Mines.

TABLE 7 *

| Name | Composition, % |
|---|---|
| Antimonial lead | Pb, 100–75; Sb, 0–25 |
| Battery plates | Pb, 94; Sb, 6 |
| Babbitt metals | Pb and Sn–base bearing alloys |
| Light duty bearings | Pb, 90–80; Sb, 10–17; Sn, 10–0; Cu, 0–1 |
| Expanding alloy | Pb, 67; Sn, 25; Bi, 8.3 |
| Hard bearing metal | Pb, 98.7; Mg, 1.3 |
| Hard lead | Pb–Sb; Pb–As; Pb–alkali metal; or Pb–alkaline earth metal |
| Lead foil | Pb, 86; Fe, 6.9; Al, 5.5; Sn, 1.9 |
| Lead shot | Pb, 99.8; As, 0.2 |
| Linotype, standard (English) | Pb, 83; Sb, 12; Sn, 5 |
| Solder (half-and-half) | Pb, 50; Sn, 50 |
| Solder (plumbers') | Pb, 67; Sn, 33 |
| Type-metal (standard) | Pb, 58; Sn, 26; Sb, 15; Cu, 1 |

* International Critical Tables (Vol. II); McGraw-Hill Book Co., New York, 1927. Reprinted by permission.

**Consumption and Prices.**—Table 8 lists the consumption of lead for various purposes in the United States for 1934.

TABLE 8 *

LEAD CONSUMPTION IN THE UNITED STATES

| | Tons of 2000 Pounds |
|---|---|
| White lead | 64,500 |
| Red lead and litharge (*a*) | 28,000 |
| Storage batteries | 163,000 |
| Cable covering | 34,100 |
| Building | 30,000 |
| Automobiles | 7,300 |
| Railway equipment | 800 |
| Shipbuilding | 200 |
| Ammunition | 34,800 |
| Terneplate | 2,400 |
| Foil | 16,200 |
| Bearing metal | 16,500 |
| Solder | 16,000 |
| Type-metal | 13,000 |
| Calking | 10,000 |
| Castings | 5,000 |
| Other uses (*b*) | 35,000 |
| Total | 476,800 |

* The Mineral Industry During 1934 (Vol. 43); edited by G. A. Roush; McGraw-Hill Book Co., New York. Reprinted by permission.

(*a*) Not including oxides for storage batteries.

(*b*) Conjectural. Under "Other uses" the largest item in recent years has been the manufacture of lead tetraethyl for tempering gasoline, which has been increasing rapidly. Also included are lead for brass-making, collapsible tubes, lead-lined pipe, lead-headed nails, and many miscellaneous uses.

The average New York price for lead in 1934 was 3.860 cents per pound.[8]

## ZINC

**Properties.**—Zinc is a bluish-white metal, quite brittle at ordinary temperatures but malleable at 100° C. It is a fairly good conductor of electricity. Its atomic weight is 65.38, atomic number 30, melting point 419.4° C., boiling point 907° C., specific gravity 7.14, valence 2. Zinc crystallizes in the hexagonal close-packed system and has no allotropic modifications. Pure zinc is used for protective coatings on iron (galvanizing), as sheet for roofing, and as electrodes in dry-cell batteries. The oxide of zinc is also of considerable commercial importance.

**Alloys of Zinc.**—The largest consumption of zinc for alloys is in the making of brass, which was discussed in connection with copper. A number of the white metal alloys (bearing metals, solders, etc.) are zinc-base alloys, and recently there has been a growing demand for zinc-base die-casting alloys. Table 9 contains a number of typical zinc-base alloys.

TABLE 9 *

| Name | Composition, % |
|---|---|
| Battery plates | Zn, 63; Sn, 21; Pb, 12; Cu, 3.2 |
| Die-casting alloy | Zn, 85; Sn, 8; Cu, 4; Al, 3 |
| Die-casting alloy No. 5 † | Zn; Al, 4.10; Cu, 1.00; Mg, 0.03 |
| Brazing solder | Zn, 57–45; Cu, 34–45; Ni, 8–10 |
| White solder | Zn, 60; Cu, 40 |
| Zinc babbitt | Zn, 69; Sn, 26; Cu, 5; Sb, 3 |

* International Critical Tables (Vol. II); McGraw-Hill Book Co., New York, 1927. Reprinted by permission.

† Apex Smelting Co., Chicago, Ill.

**Consumption and Prices.**—Table 10 summarizes the industrial uses of zinc in the United States for 1934.

The average price for zinc in 1934 at St. Louis was 4.16 cents per pound, and at New York 4.51 cents per pound.[9]

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[8] The Mineral Industry During 1934 (Vol. 43); edited by G. A. Roush; McGraw-Hill Book Co., New York.

[9] Minerals Yearbook 1935; U. S. Bureau of Mines.

TABLE 10 *

ESTIMATED USE OF ZINC IN THE UNITED STATES

| Purpose | Tons of 2000 Pounds |
|---|---|
| Galvanizing | |
| Sheets | 83,300 |
| Tubes | 22,000 |
| Wire | 20,000 |
| Wire cloth | 4,000 |
| Shapes (*a*) | 22,700 |
| Total for galvanizing | 152,000 |
| Brass and castings (*b*) | 98,000 |
| Rolled zinc | 40,900 |
| Die castings | 32,000 |
| Other purposes (*c*) | 37,000 |
| Total | 359,900 |

* Minerals Yearbook, 1935; U. S. Bureau of Mines.

(*a*) Includes pole-line hardware, hollow ware, chains, and all articles not elsewhere mentioned. The estimates for the use of slab zinc under this head, and also for wire cloth, are probably incomplete.

(*b*) Includes all casting other than die casting, slush casting, and battery zinc.

(*c*) Includes slab zinc for the manufacture of French oxide, lithopone, atomized zinc dust, wire, zinc for wet batteries, slush castings, and for the desilverization of lead. In 1934 25,000 tons of zinc were used in making French-process zinc oxide.

## TIN

**Properties.**—Tin is a silver white metal, soft, quite malleable, and fairly ductile. Its atomic weight is 118.70, atomic number 50, melting point 231.9° C., boiling point 2270° C., specific gravity (gray) 5.75, (rhombic) 6.55, (tetragonal) 7.31, and valence 2 or 4. Common, or white, tin (beta tin) has a tetragonal double body-centered space lattice; and gray (alpha tin), an allotropic modification, has a face-centered cubic lattice. Tin is resistant to corrosion, and the largest use of the metal is in the manufacture of "tin plate"—tin-coated mild steel. Tin is widely used as lining or plating for food containers where there might be danger of metallic poisoning if other metals were used.

**Alloys of Tin.**—Tin is used in bronzes, and other copper-base alloys, and in many of the white metal alloys. Tin-base solders, babbitts, etc., are generally conceded to be the best of all, but the high price of tin makes for the use of lead- or zinc-base alloys whenever the cheaper metals will do. Table 11 lists some of the common tin-base alloys.

TABLE 11 *

| Name | Composition, % |
|---|---|
| Babbitt (genuine) | Sn, 89; Sb, 7.3; Cu, 3.7 |
| Britannia metal (plate) | Sn, 91–90; Sb, 7–8; Cu, 1.4 |
| Diesel bearings | Sn, 80; Sb, 15; Cu, 5 |
| Hard babbitt | Sn, 83; Cu, 8.4; Sb, 8.3 |
| Pewter | Sn, 89–74; Pb, 0–20; Sb 0–7.6; Cu, 0–3.5; Zn |
| Solder (tinner's) | Sn, 67; Pb, 33 |
| Tinfoil | Sn, 88; Pb, 8; Cu, 4; Sb, 0.5 |
| Tinsel | Sn, 60; Pb, 40 |

* International Critical Tables (Vol. II); McGraw-Hill Book Co., New York, 1927. Reprinted by permission.

**Consumption and Prices.**—The United States is the world's largest consumer of tin, owing largely to its great canning and motor vehicle industries. Table 12 shows the consumption of virgin tin in the United States for 1930 and indicates the relative distribution of tin among its various uses. This table does not account for the secondary tin used.

TABLE 12 *

VIRGIN TIN CONSUMED IN THE UNITED STATES IN 1930

| Use | Long Tons |
|---|---|
| Tinplate and terneplate | 27,753 |
| Solder | 11,407 |
| Babbitt | 5,438 |
| Bronze | 3,499 |
| Foil | 3,061 |
| Collapsible tubes | 3,826 |
| Chemicals | 3,268 |
| Tin oxide | 666 |
| Tinning (brass, copper tubes, sheets, shells, wire, nails, etc.) | 2,814 |
| White metal | 1,117 |
| Type metal | 223 |
| Castings | 74 |
| Other alloys | 306 |
| Miscellaneous | 1,996 |
| Total | 65,448 |

* Minerals Yearbook, 1935; U. S. Bureau of Mines.

The apparent consumption of virgin tin in the United States for 1934 was 43,638 long tons.[10] The average New York price for tin in 1934 was 52.16 cents per pound.

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[10] Minerals Yearbook, 1935; U. S. Bureau of Mines.

## NICKEL

**Properties.**—Nickel is a white metal, rather hard and strong, and quite ductile and malleable. Its atomic weight is 58.69, atomic number 28, melting point 1452° C., boiling point 2900° C., specific gravity 8.90, and valence 2 or 3. Nickel exists in two crystallographic forms; alpha nickel which has a hexagonal close-packed lattice, and beta nickel which has a face-centered cubic lattice. The beta form is stable at room temperatures. Nickel shows more pronounced magnetic properties than any metal except iron.

Nickel, as pure metal, is used principally for nickel plating. Nickel is resistant to corrosion and takes a high polish.

**Alloys of Nickel.**—The most important use of nickel is in the alloy steels and in Monel metal. Most of the nickel-base alloys have properties which approach those of the noble metals—they show considerable resistance to corrosion, heat, and oxidation. The large number of nickel alloys in use makes it almost impossible to give a brief classification. Table 13 gives a few of the nickel-base alloys.

TABLE 13 *

| Name | Composition, % |
|---|---|
| Alumel (*a*) | Ni, 94; Mn, 2.5; Al, 2; Si, 1; Fe, 0.5 |
| Chromel A (*a*) | Ni, 80; Cr, 20 |
| Chromel P (*a*) | Ni, 90; Cr, 10 |
| Illium (*b*) | Ni, 63; Cr, 21; Cu, 6.5; Mo, 5; W, 2; Fe, 1; Mn, 1; Al, 1 |
| Monel metal (cast) | Ni, 68; Cu, 28; Fe, 1.9; Si, 1.1 |
| Nichrome II (*a*) | Ni, 75; Fe, 12; Cr, 11; Mn, 2 |

* International Critical Tables (Vol. II); McGraw-Hill Book Co., New York, 1927.

(*a*) Type used for electrical resistance elements, thermocouples, etc.
(*b*) Corrosion-resisting alloy. Illium may be used as a substitute for platinum for some purposes.

**Consumption and Prices.**—In 1934 the United States consumed about 28,558 short tons of nickel, and its use was distributed as shown in Table 14.[11]

In 1934 the average price of nickel was 35 cents per pound. Nickel has held steady at this price since 1929.

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[11] Minerals Yearbook, 1935; U. S. Bureau of Mines.

TABLE 14 *

| Use | Per Cent of Total |
|---|---|
| Structural nickel steel | 30 |
| Corrosion-resistant steel | 4 |
| Nickel cast iron | 4 |
| Nickel-steel castings | 2 |
| Other iron-nickel alloys (Invar, Permaloy, etc.) | 2 |
| Monel metal | 31 |
| Nickel plating | 7 |
| Malleable nickel | 6 |
| Nickel silver | 5 |
| Heat-resisting or electrical alloys | 5 |
| Miscellaneous (*a*) | 4 |
| Total | 100 |

* Minerals Yearbook, 1935; U. S. Bureau of Mines.

(*a*) Includes nickel catalysers, storage batteries, coinage, and minor alloys.

## GOLD

**Properties.**—Gold is an orange-yellow metal, quite soft, and the most malleable and ductile of all the metals. It is a good conductor of heat and electricity and is highly resistant to corrosion. Its atomic weight is 197.2, atomic number 79, melting point 1063° C., boiling point 2600° C., specific gravity 19.32, and valence 1 or 3. Gold crystallizes in the face-centered cubic system and has no allotropic modifications. It is used principally as money (either as actual coin or as a gold reserve), for jewelry, and for dental work.

**Alloys of Gold.**—Gold which is used simply as a money reserve is usually stored in the form of bars of practically pure gold. For coin and articles of jewelry, however, the gold is ordinarily hardened by alloying it with other metals. Table 15 indicates the composition of a few of the commoner gold alloys.

TABLE 15 *

| Name | Composition, % |
|---|---|
| 22 carat | Au, 92; Ag, 4.2; Cu, 4.2 |
| 10 carat | Au, 42; Cu, 38–46; Ag, 12–20 |
| Green gold | Au, 75; Ag, 11–25; Cd, 13–0 |
| Standard gold coin (British) | Au, 92; Cu, 8 |
| Standard gold coin (United States) | Au, 90; Cu, 10 |
| White gold | Au, 85–75; Ni, 10–8; Zn, 2–9 |
| Yellow gold | Au, 53; Ag, 25; Cu, 22 |

* International Critical Tables (Vol. II); McGraw-Hill Book Co., New York, 1927. Reprinted by permission.

While the United States was on the gold standard, gold was valued at $20.67 per troy ounce. It is now worth $35 per ounce. In 1934 the United States produced 2,742,161 fine ounces of gold valued at $95,975,600.00.

## SILVER

**Properties.**—Silver is a pure white metal, slightly harder than gold, and second only to gold in malleability and ductility. Its atomic weight is 107.88, atomic number 47, melting point 960.5° C., boiling point 1950° C., specific gravity 10.50, and valence 1. Silver crystallizes in the face-centered cubic system and has no allotropic modifications. Silver has the highest electrical and thermal conductivity of all the metals.

Silver is used as money (coinage and monetary reserves), and for jewelry and tableware. In recent years the use of silver in photography has been of importance because of the growth of the motion-picture industry. Other uses of the metal are in dental alloys, the sterilization of water, and certain base-metal alloys.

**Alloys of Silver.**—Table 16 lists some of the common silver-bearing alloys.

TABLE 16 *

| Name | Composition, % |
|---|---|
| Silver (rupee) | Ag, 92; Cu, 8 |
| Silver (United States coins) | Ag, 90; Cu, 10 |
| Silver solder (common) | Ag, 63; Cu, 30; Zn, 7.5 |
| Sterling silver † | 925 fine (92.5% Ag) |
| Bearing alloy † | Cd; Ag, 2.5 |

* International Critical Tables (Vol. II); McGraw-Hill Book Co., New York, 1927. Table reprinted by permission.

† Modern Uses of Nonferrous Metals; edited by C. H. Mathewson; copyrighted by the American Institute of Mining and Metallurgical Engineers, 1935.

In 1934, 31,157,683 fine ounces of silver were produced in the United States.[12] The government price was 64.6 cents per troy ounce, and the average price in the open market was 48.3 cents per ounce.

## THE LIGHT METALS

The two light metals, aluminum and magnesium, are relatively recent additions to the group of commercial metals, but the growth of their importance in the last twenty or thirty years has been remarkable, and they apparently have a brilliant future. Commercially, aluminum is the older of the two, since its metallurgy was developed before that of magnesium.

The outstanding characteristic of these two metals is their low

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[12] The Mineral Industry During 1934 (Vol. 43); edited by G. A. Roush; McGraw-Hill Book Co., New York.

specific gravity, and the fact that strong alloys of these metals can be made without noticeably sacrificing the advantage of their light weight.

Aluminum is a white metal, fairly soft, very malleable, and quite ductile. Its atomic weight is 26.97, atomic number 13, melting point 658.7° C., boiling point 1800° C., specific gravity 2.70, and valence 2 or 3. Aluminum crystallizes in the face-centered cubic system and has no allotropic modifications. The specific electrical conductivity of aluminum is about 0.60 that of copper, but the conductivity per unit weight is greater than that of copper. Aluminum is quite resistant to corrosion because of the protective coating that forms on exposed surfaces.

Aluminum is used in making strong alloys for such purposes as automotive, aircraft, and railway construction; metal foil; kitchen utensils; aluminum powder for paint; and as a deoxidizer of molten steel.

Magnesium is a white, fairly tough metal, fairly ductile and malleable. Its atomic weight is 24.32, atomic number 12, melting point 651° C., boiling point 1110° C., specific gravity 1.74, and valence 2. Magnesium crystallizes in the hexagonal close-packed system and has no allotropic modifications. Magnesium is very active chemically, and the metal and its alloys are readily attacked by acids.

Magnesium metal is used to make strong light alloys for constructive purposes, and it is also used for flashlight photography and for pyrotechnic purposes.

**Alloys of the Light Metals.**—Table 17 lists some of the "strong" alloys of aluminum and magnesium. Many of these alloys can be work-hardened, and others can be age-hardened.

TABLE 17 *

| Name | Composition, % |
|---|---|
| *Aluminum alloys* (*a*) | |
| Casting alloy 43 | Al; Si; Fe, 1 |
| Casting alloy 145 | Al; Zn, 10; Cu, 2.5; Fe, 1.25 |
| Wrought alloy 5S | Al, 95; Cu, 2; Zn, 2; Mn, 1.5 |
| Wrought alloy 17S (Duralumin) | Al, 92; Cu, 3.5–4.5; Mn, 0.4–1.0; Mg, 0.2–0.75 |
| Wrought alloy 51S | Al; Si, 0.6–1.2; Mg, 0.45–0.8 |
| Die casting alloy | Al, 92–82; Cu, 8–18; Fe, 0–3; Mg; Mn; Si; Zn |
| *Magnesium alloys* | |
| Dowmetal A | Mg, 92; Al, 8 |
| Dowmetal D | Mg, 88; Al, 8.3; Cu, 2.0; Cd, 1.0; Zn, 0.5; Mn, 0.2 |
| Dowmetal T | Mg, 92; Cu, 3.8; Cd, 2; Mn, 0.2 |

* International Critical Tables (Vol. II); McGraw-Hill Book Co., New York, 1927. Reprinted by permission.

(*a*) Numbers are the Aluminum Company of America's designations for these alloys.

**Consumption and Prices.**—The apparent consumption of aluminum in the United States for 1934 was about 89,000 tons,[13] and the price was stationary at 23.3 cents per pound. The domestic production of magnesium in 1934 was 4,248,838 pounds,[13] an increase of 196 per cent over the production for 1933. The price of magnesium metal was 26 cents per pound. Magnesium constituted 5.4 per cent of the total light metal output of the United States in 1934.

### OTHER METALS

**Mercury** is the only common metal which is liquid at ordinary temperatures. It has a variety of uses as shown by Table 18.

TABLE 18 *

CONSUMPTION OF QUICKSILVER IN THE UNITED STATES IN 1928

| | Flasks *(a)* |
|---|---|
| Drugs and chemicals | 14,000 |
| Fulminate | 6,500 |
| Vermilion | 2,500 |
| Amalgamation | 500 |
| Felt manufacture | 2,000 |
| Electrical apparatus | 2,500 |
| Industrial and control instruments | 3,000 |
| General laboratory use | 500 |
| Manufacture of caustic soda and glacial acetic acid | 1,000 |
| Miscellaneous | 2,500 |
| Total | 35,000 |

* Modern Uses of Nonferrous Metals; edited by C. H. Mathewson, copyrighted by the American Institute of Mining and Metallurgical Engineers, 1935. Reprinted by permission.

(a) A "flask" of mercury is 76 pounds.

In 1934 the output of mercury in the United States was 15,445 flasks,[14] and about 10,000 flasks were imported. The average price was $73.865 per flask.

**Manganese, cobalt, molybdenum,** and **vanadium** are used principally as alloying ingredients in steels. **Tungsten** is used in steels and in the manufacture of filaments for electric lamps. **Chromium** is used in alloy steels and also for chromium plating.

The **platinum metals** compose a group of six metals (platinum, iridium, osmium, rhodium, palladium, and ruthenium), of which

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[13] Minerals Yearbook, 1935; U. S. Bureau of Mines.

[14] The Mineral Industry During 1934 (Vol. 43); edited by G. A. Roush, McGraw-Hill Book Co., New York.

platinum is the most important. These are noble metals, highly resistant to corrosion, and are used for jewelry and for laboratory equipment (crucibles, tongs, etc.)

Other metals, such as **cadmium, antimony, arsenic,** and **bismuth,** are used primarily as minor alloying ingredients in a large number of non-ferrous alloys (particularly white metal alloys). Cadmium is also used to some extent for cadmium plating. All these metals have fairly low melting points.

**Miscellaneous Alloys.**—Table 19 lists a few common alloys not included in other lists in this chapter. The alloys marked (*a*) are the low-melting or fusible alloys (some melt below 100° C.). The stellites, Haynes metal, and cemented carbides are extremely hard alloys and retain their hardness at high temperature. They are used for resistance to severe abrasion and for high-speed cutting tools.

TABLE 19 *

| Name | Composition, % |
|---|---|
| Rose's alloy (*a*) | Bi, 50; Pb, 28; Sn, 22 |
| Lipowitz alloy (m.p. 70–74° C.) (*a*) | Bi, 50; Pb, 27; Sn, 13; Cd, 10 |
| Eutectic alloy (m.p. 96° C.) (*a*) | Bi, 53; Pb, 32; Sn, 15 |
| Stellite | Co, 80–55; Cr, 20–35; W, 0–10 |
| Stellite (No. 3) | Co, 55; Cr, 20–23; W, 20–15; Fe, 5–3; C, 1.5–4 |
| Permalloy | Ni, 78; Fe, 21; Co, 0.4; Mn, 0.2; Cu, 0.1; C, 0.04; S, 0.04; Si, 0.03 |
| Resistance (high, non-magnetic) | Cr, 70; Ni, 30 |
| Spark-plug wire | Ni; Mn, 2–6; Fe, Cu |
| Cemented tungsten carbide | WC; Co; Ni |
| Haynes metal (hard) | Co, 45; W, 40; Cr, 15 |

* International Critical Tables (Vol. II); McGraw-Hill Book Co., New York, 1927. Reprinted by permission.

## EXERCISES

1. Make a report on the various commercial grades of such "pure" metals as zinc, lead, copper, or aluminum. Give names, limits of composition, relative prices, and uses.

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# *PART B*

# EXTRACTIVE METALLURGY

# CHAPTER VIII

## THE SOURCES OF METALS

All metals and alloys originally come from natural deposits (ores) in the earth's crust. In many cases, metal may be used over again, so that the metal in any given object may have passed through several metamorphoses before reaching its present form. Metallurgical and commercial usage has made it convenient to classify metals according to their source as *primary* and *secondary* metals. Primary metal is metal which has been produced directly from ore; secondary metal is metal extracted from scrap. This distinction does not reflect upon the quality of the metal in any way, and there is no physical or metallurgical test which will determine whether a metal object is "primary" or "secondary." Practically all the steel produced in this country contains some secondary metal, and often a steel-refining furnace will carry more than 90 per cent scrap on the charge.

Our subsequent discussion of metallurgical processes will be concerned principally with the recovery of metal from ores, or the production of primary metal. The treatment of secondary metals and alloys does not involve any principles which differ from those employed in recovering and refining primary metal, and often both ores and scrap metal are consumed by the same producer. Many metallurgical plants, however, utilize nothing but scrap metal as raw material. The term "secondary metal" is somewhat ambiguous; generally it refers to the scrap metal itself, but it is also applied to metal products which are made from scrap.

### PRIMARY METAL

**Ores.**—An ore may be defined as *a naturally occurring aggregate of minerals from which a metal or metals may be extracted at a profit.* The phrase "at a profit" is the factor which determines whether or not a given deposit is an ore or worthless rock; and a complete elaboration of this simple statement would involve not only a detailed study of the processes of extractive metallurgy, but also a study of many phases of mining, geology, geography, and economics. An iron ore, for example, may be worthless if it is located too far from a coal field and/or an industrial center. A deposit may contain large amounts of a metal (aluminum in clay, for example) but still be worthless as a metallic ore for lack of an economic reduction process. The great "prophyry copper" deposits of southwestern United States were not ores until the invention of the flotation process made their treatment feasible. The student of metallurgy should never become so involved in the technical aspects of the subject as to lose sight of the fact that all metallurgical operations are commercial enterprises operated with the hope of realizing a profit. The best metallurgical process is always the one which produces the maximum profit, all things considered.

Disregarding certain local terminology (in the Tri-state district, concentrate is called "ore," and in the Lake Superior copper country the ore is called "rock"), the word "ore" usually refers to ore in place or "hard-rock" ore. Some valuable metallic minerals are found in *placer deposits* (gold, tin, platinum), in which the valuable minerals are not consolidated with other minerals but are free. These deposits may correspond in all respects to the definition we have given, but nevertheless they are seldom called ores. The term ore is restricted to the hard-rock material.

The metal-bearing minerals in an ore are the *ore minerals* or *values*. The term "values" is widely used and may refer to the ore minerals or the metals themselves. Non-valuable minerals in the ore are the *gangue* or *gangue minerals,* and wall-rock broken with ore is called *waste*. For example, a typical lead-zinc ore may contain the minerals galena ($PbS$), sphalerite ($ZnS$), pyrite ($FeS_2$), siderite ($FeCO_3$), and quartz ($SiO_2$). The galena and sphalerite are the ore minerals, and pyrite, siderite, and quartz are the gangue minerals. The dividing line between ore minerals and gangue minerals is fixed by the "profit phrase" in the definition of an ore. The extraction of iron from pyrite and siderite in an ore such as this is not economically possible, and therefore these are gangue minerals. A large deposit of fairly pure siderite, however, might be a valuable iron ore. If the pyrite in our lead-zinc ore happened to contain gold, then it would be classed as an ore mineral.

**The Ore Minerals.**—The valuable metal in an ore may occur as native metal, or as a chemical compound of the metal. The common ore minerals are native metals, sulfides, oxides, silicates, chlorides, carbonates, and sulfates. Table 1 summarizes the way in which the important metals commonly occur. Table 2 lists a few of the most common ore minerals. With the exception of pyrite, these are ore minerals of the metal contained in the mineral. Pyrite may be exploited for its sulfur content or for associated gold and silver values, but it is hardly an iron ore. Likewise, the iron in bornite and chalcopyrite is not recovered.

TABLE 1

OCCURRENCE OF COMMON METALS

| Native | Oxide | Sulfide | Carbonate | Silicate | Chloride |
|---|---|---|---|---|---|
| Au | Fe | Cu | Fe | Ni | Ag |
| Cu | Al | Pb | Zn | Cu | Cu |
| Pt | Sn | Zn | Cu | Zn | Mg |
| Ag | Cr | Ni | Mg | Mn | Na |
| Pd | Mn | Ag | Mn |  | K |
| Hg | W | Co | Pb |  |  |
| Ir | Cu | Sb |  |  |  |
|  |  | Hg |  |  |  |
|  |  | Mo |  |  |  |
|  |  | Cd |  |  |  |
|  |  | Bi |  |  |  |

TABLE 2

COMMON ORE MINERALS

Native Metals: Gold, silver, copper, platinum, electrum (alloy of gold and silver).

Oxides: Hematite $Fe_2O_3$; magnetite $Fe_3O_4$; limonite ("bog iron ore") $Fe_2O_3 \cdot xH_2O$; bauxite $Al_2O_3 \cdot 2H_2O$; corundum $Al_2O_3$; cassiterite ("tin-stone," "stream-tin") $SnO_2$; zincite $ZnO$; franklinite $ZnO \cdot (Fe, Mn)_2O_3$; wolframite $(Fe, Mn)WO_4$; scheelite $CaWO_4$; chromite $FeCr_2O_4$; cuprite $Cu_2O$; psilomelane $4MnO_2 \cdot (Ba, K)O \cdot xH_2O$; pyrolusite $MnO_2$.

Sulfides: Galena ("lead glance") $PbS$; sphalerite ("zinc blende") $ZnS$; chalcocite ("copper glance") $Cu_2S$; covellite ("indigo copper") $CuS$; chalcopyrite ("copper pyrites") $CuFeS_2$; bornite $Cu_5FeS_4$; pyrite ("pyrites," "fool's gold") $FeS_2$; millerite $NiS$; pentlandite $(Ni, Fe)_{11}S_{10}$; cinnabar $HgS$; molybdenite $MoS_2$; stibnite ("antimony glance") $Sb_2S_3$; bismuthinite $Bi_2S_3$; argentite ("silver glance") $Ag_2S$.

Carbonates: Siderite $FeCO_3$; smithsonite $ZnCO_3$; malachite $CuCO_3 \cdot Cu(OH)_2$; azurite $2CuCO_3 \cdot Cu(OH)_2$; cerussite $PbCO_3$; magnesite $MgCO_3$; rhodochrosite $MnCO_3$.

Silicates: Chrysocolla $CuSiO_3 \cdot 2H_2O$; calamine $Zn_2(OH)_2SiO_3$; rhodonite $MnSiO_3$; garnierite $H_2(Ni, Mg)SiO_4$; willemite $Zn_2SiO_4$.

Chlorides: Cerargyrite ("horn silver") $AgCl$; atacamite $CuCl_2 \cdot 3Cu(OH)_2$.

Sulfates: Brochantite $CuSO_4 \cdot 3Cu(OH)_2$; chalcanthite ("bluestone") $CuSO_4 \cdot 5H_2O$.

Arsenides and Antimonides: Smaltite $(Co, Ni)As_2$; tetrahedrite ("gray copper") $Cu_3SbS_3$; polybasite $(Ag, Cu)_{16}Sb_2S_{11}$; enargite $Cu_3AsS_4$; pyargyrite ("ruby silver") $Ag_3SbS_3$.

Fig. 1b.—(× 78).
(*Courtesy Dr. Alfred L. Anderson*)

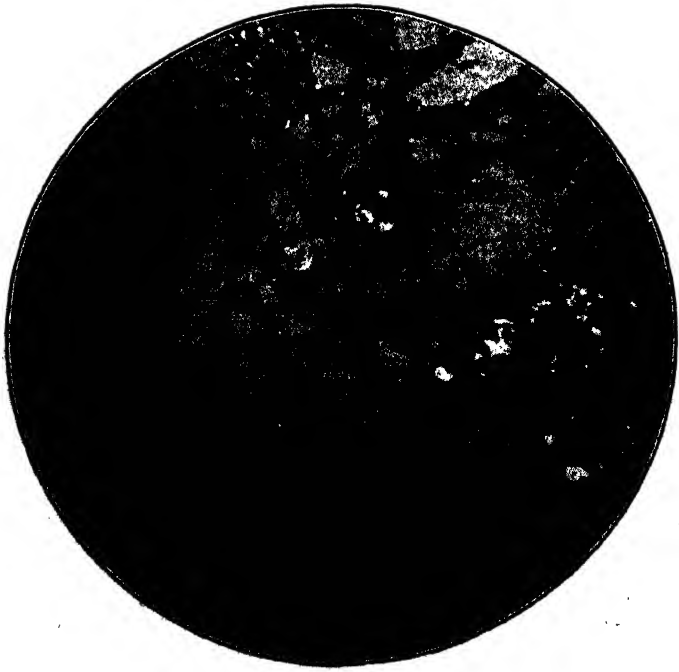

Fig. 1a.—(× 80).
(*Courtesy Dr. Alfred L. Anderson*)

(*Courtesy Dr. Alfred L. Anderson*)

Fig. 1*c*.—(× 145).

(*Courtesy Thomas H. Hite*)

Fig. 1*d*.—(× 50).

Fig. 1.—Photomicrographs of Ore Minerals.

*a*. Black—calcite.
Gray—sphalerite.
White—native gold.

*b*. White—galena.
Light gray—tetrahedrite.
Dark gray—sphalerite.

*c*. Black—quartz.
Gray—pyargyrite.
White—galena.

*a*, *b*, and *c*, are polished sections of vein ore; *d* is a picture of gold "colors" panned from a placer deposit.

**Tenor of Ores.**—The tenor of an ore means the amount of valuable metal in the ore. This is given in percentage of metal or metallic oxide, except in the case of gold, silver, and platinum ores, where the analysis is reported in troy ounces per avoirdupois ton (1 ton = 29,167 troy ounces). In countries employing the metric system, the precious metals are reported in grams per metric ton. Examples of the tenor of some typical ores are:

| | |
|---|---|
| Copper ores: | 2.5% Cu (average). |
| | 0.75% Cu (porphyry coppers). |
| | 0.50% Cu (native copper ores). |
| Iron ores: | 50% Fe (United States). |
| | 30% Fe (Europe). |
| | 30% Fe (United States—limestone gangue). |
| | 20% Fe (rare—must be concentrated). |
| Zinc ores: | 4% Zn (Joplin district). |
| | 12% Zn (Butte district). |
| Lead ores: | 8% Pb (average). |
| | 5% Pb (Joplin district). |
| Silver ores: | 10 oz. per ton. (Silver ores are rare, since most silver is obtained as a by-product in treating lead, gold, and copper ores.) |
| Gold ores: | 0.2 oz. per ton (0.2 represents about the minimum). |
| Tin ores: | 2.0% Sn. |
| Mercury ores: | 1.0% Hg. |
| Aluminum ores: | 50–60% $Al_2O_3$ (bauxites). |
| Tungsten ores: | 1.0% $WO_3$. |
| Molybdenum ores: | 0.5–3.0% Mo. |
| Vanadium ores: | 1.0–5.0% $Va_2O_5$. |
| Magnesium ores: | 12% Mg ($MgCl_2 \cdot 6H_2O$). |
| Nickel ores: | 2.0% Ni. |
| Manganese ores: | 40% Mn. |
| Chromium ores: | 40% $Cr_2O_3$. |

The tenor of a placer, or alluvial deposit of a given metal, in general may be lower than the tenor of a vein ore of the same metal. Thus, gold ore in "hard-rock" as a rule should assay more than 0.2 ounce per ton, but gold placers containing as little as 0.0025 ounce per "yard" (a cubic yard = about 1.5 tons) have been worked profitably. This is due to the fact that placer deposits may be mined and treated more easily and cheaply than vein deposits.

Some metals are not found alone in ores but are practically always associated with other metals, and are considered as by-products from the other metals. Examples are cadmium (found in zinc ores), platinum (with nickel and copper ores), cobalt (with nickel ores), and arsenic, antimony, and bismuth (with lead ores). A large part of the gold and most of the silver produced in the United States come from base-metal (lead, copper, zinc) ores. The examples quoted above represent the average tenor required for ores containing a single metal. If the ore contains two or more valuable metals, these figures may be modified considerably.

Because of the fact that many ores contain two or more metals, it is difficult to present statistics showing the relative amounts of different ores mined and the amount of each metal produced from them. The following tabulations will give some idea of the relation between amount of ore mined and metal produced for the four leading base metals and gold and silver in the United States and Alaska for 1933.

**Classification of Ores.**—There is no scientific classification of ores from the standpoint of the metallurgist, but many names are given to various ores because of certain characteristics. The classifications listed below cover much of the ordinary nomenclature of ores. Obviously, several of these names may apply to a single ore.

A. Ores named for the useful metal: lead ores, copper ores.
B. Ores named for two or more valuable metals: lead-zinc ores, gold-silver ores, copper-cobalt-nickel ores. (These ores may be called complex ores.)
C. Ores named from the form of the useful metal: sulfide ores, oxide or oxidized ores. (Sulfide ores may contain arsenides and antimonides.)
D. Ores named from the type of gangue material: siliceous ores (gangue principally silica); argillaceous ores (gangue principally clay); calcareous ores (gangue principally calcite); ferruginous ores (gangue principally oxides of iron); acid ores (siliceous ores); basic ores (gangue largely metallic oxides or carbonates); self-fluxing ores (ores in which the gangue contains acids and bases, or silica and metallic oxides, in such amounts that in smelting a fusible slag is formed without the addition of flux.)
E. Ores named from the metal content: rich or poor ores, first or second class ores.
F. Ores named from size of material: coarse or fine ores; *run-of-mine ore* signifies ore as it comes from the mine, containing all sizes, as distinguished from the crushed and sized material found at certain stages of the milling process.
G. Ores named from the treatment required:
    Direct smelting ore.
    Milling ore.
    Leaching ore.
    Amalgamating ore.
    Cyaniding ore.
H. Special classifications:
    1. Bessemer ore—a term applied only to iron ores. In a Bessemer ore the iron content is at least 1000 times the phosphorus content.
    2. Dry ores—a name given at lead and copper smelters to ores which contain precious metals (gold and silver) but insufficient lead or

TABLE 3 * (*a*)

| | Weight of Ore in Short Tons | Assay (Average) | Tons of Metal Produced (Calculated) |
|---|---|---|---|
| Iron ore | 27,600,000 | 50% Fe | 13,800,000 Fe |
| Dry gold and silver ores | 8,680,000 | 0.18 oz. Au/ton<br>0.42 oz. Ag/ton<br>+ some copper | 53.7 Au<br>125.0 Ag |
| Copper ore | 8,385,000 (practically all contain Au and Ag) | 2 11% Cu<br>0 0126 oz. Au<br>0 696 oz. Ag | 177,000 Cu<br>3 6 Au<br>197.0 Ag |
| Lead-zinc ore | 4,894,000 | 4 – 10% Zn<br>3 – 5% Pb | ......<br>...... |
| | (1,182,000 tons bearing Au and Ag) | 0 036 oz. Au/ton<br>5 20 oz. Ag/ton | 1 3 Au<br>193 0 Ag |
| Zinc ore | 3,236,000 | 4 0 – 10 0% | ...... |
| | (122,000 tons bearing Au and Ag) | 0 002 oz. Au/ton<br>0 58 oz. Ag/ton | 0.01 Au<br>1 8 Ag |
| Lead ore | 3,213,000 | *Circa* 4.0% | ...... |
| | (717,000 tons contain Au and Ag) | 0 019 oz. Au/ton<br>5.47 oz. Ag/ton | 0.5 Au<br>135 0 Ag |
| Copper-lead and copper-lead-zinc ores | 126,000 (all carry Au and Ag, | 0 9 – 10 0% Cu<br>Pb, Zn, variable<br>1.001 oz. Au/ton<br>27.49 oz. Ag/ton | 0.01 Au<br>109.0 Ag |

Placer gold = 578,000 ounces = 20.0 tons.

Total Production from Domestic Ores and Placers

| | |
|---|---|
| Pig iron ........ .. . | 16,100,000 short tons |
| Copper ........ . . . . | 225,000 short tons |
| Lead ................ | 259,616 short tons |
| Zinc .................. . | 306,010 short tons |
| Gold .. ...... .... ... | 2,303,000 troy oz. (79 tons) |
| Silver ............ ..... | 23,000,000 troy oz. (785 tons) |

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* Minerals Yearbook, 1935; U. S. Bureau of Mines.

(*a*) This table shows the distribution of metals in the various types of ores and is not intended to be an accurate statistical analysis. As far as possible, the figures were taken from the Minerals Yearbook for 1935, but many approximations and simplifications have been made from the extensive data given in the Yearbook.

copper to be smelted without the addition of richer lead or copper ores.

3. Base and free-milling ores—a common system of naming gold ores. The upper portion of a gold vein usually contains free gold because the accompanying sulfide minerals have weathered or oxidized. Ore of this type is called oxidized, or free-milling ore, while the ore in which the gold is still intimately associated with sulfides is called base ore.
4. Refractory ore—ore which for one reason or another is difficult to treat by ordinary methods.

## SECONDARY METAL

Table 4 gives the amount of various secondary non-ferrous metals recovered in the United States during 1933. Comparison with the data in Table 3 brings out some interesting facts. Note that the amount of secondary copper exceeds the amount of primary copper, and that the secondary lead appears to be almost equal to the production of primary lead. Table 5 is compiled from further data from the section on secondary metals in the Minerals Yearbook for 1935, and it shows the undoubted importance of secondary metal in the market.

TABLE 4 *

SECONDARY METALS OF CERTAIN CLASSES RECOVERED IN THE UNITED STATES IN 1933

| | Short Tons |
|---|---|
| Copper, including alloys other than brass | 247,100 |
| Brass scrap re-treated | 130,000 |
| Lead as metal | 131,800 |
| Lead in alloys | 92,700 |
| Zinc as metal | 48,100 |
| Zinc in alloys other than brass | 7,600 |
| Tin as metal | 7,250 |
| Tin in alloys and chemical compounds | 14,850 |
| Aluminum as metal | 14,500 |
| Aluminum in alloys | 19,000 |
| Antimony as metal and in alloys | 7,400 |
| Nickel as metal | 300 |
| Nickel in non-ferrous alloys and salts | 1,350 |
| Total | 721,950 |

* Minerals Yearbook, 1935; U. S. Bureau of Mines.

No data were available on the amount of iron and steel produced from secondary sources, but probably about 50 per cent of the ferrous metals were produced from scrap.

TABLE 5 *

| Metal | Total Secondary Production in 1933 (tons) | Total Primary Production in 1933 (tons) | Percentage of Total (a) Represented by Secondary Metal |
|---|---|---|---|
| Copper | 338,100 | 225,000 | 60 |
| Lead | 224,500 | 273,000 | 45 |
| Zinc (as metal or alloys) | 112,357 | 306,010 | 27 |
| Aluminum | 33,500 | 47,500 (b) | 41 |
| Tin | 19,700 | 63,700 (c) | 24 |
| Antimony | 7,400 | 5,470 (c) | 57 |
| Nickel | 1,650 | 26,000 (c) | 6 |

* Minerals Yearbook, 1935; U. S. Bureau of Mines.

(a) Computed from columns 1 and 2.

(b) Domestic and import.

(c) Imports.

Scrap includes all types of metal products that have outlived their usefulness ("junk") and such by-products of the foundry, rolling mill, or machine shop as clippings, turnings, sprues, scale, faulty ingots, skimmings, etc. Much alloy scrap is used as such to make new alloys, because the manufacturer of alloys does not necessarily have to use virgin (pure or unalloyed) metal.

The importance of scrap as a source of metal should not lead to optimistic hopes about the scrap value of worn-out machinery. The actual value of the metal in a machine is only a small fraction of its cost—most of the cost comes from such items as manufacturing costs, patent royalties, transportation, and advertising. When the machine is worn out (or becomes obsolete), only the value of the metal at the current scrap quotation remains. Now, by the time that the machine has been dismantled or "scrapped," transported to the melting furnaces, remelted and recast, the net amount received for the metal will be very small in comparison with the original cost. In a few special cases the scrap value of metals may be relatively high, as, for example, the scrap value of copper wire or bus-bars. With a rising price of copper, it is possible that the scrap value of material of this kind might be greater than the original cost.

Metal in the form of scrap naturally commands a lower price than refined virgin metal. In 1934,[1] for example, heavy copper scrap ranged in price from 5.12 to 6.62 cents per pound; old zinc scrap from 1.187 to 2.25 cents per pound; cast aluminum scrap from 6.87 to 9.75

cents per pound; and heavy lead scrap from 2.75 to 3.37 cents per pound. The average prices of refined virgin metals in 1934[1] were: copper, 8.0 cents per pound; zinc, 4.16 cents per pound; aluminum, 22.9 cents per pound; and lead 3.7 cents per pound.

The scrap-metal industry[1] has laid down a number of specifications by means of which scrap is classified for buying and selling. Steel mills use such designations as "heavy melting scrap," "light scrap," and "plate scrap." A few typical classifications of non-ferrous scrap metal are:

*(Courtesy United States Metals Refining Company, Carteret, New Jersey)*

FIG. 2.—View of Scrap Plant Showing Scrap on Floor Ready for Classifying.

No. 1 heavy copper. This shall consist of untinned copper, not less than 1/16 inch thick, and may include trolley wire, heavy armature wire that is not tangled, and also new untinned and cleaned copper clippings and punchings, and copper segments that are clean.

No. 1 yellow brass turnings. This shall consist of yellow brass turnings, free of aluminum, magnesium, manganese, and composition turnings; not to contain over 3 per cent of free iron, oil, or other moisture; to be free of grindings and babbitts. To avoid dispute, to be sold subject to sample.

Old scrap sheet aluminum. This shall consist of clean, old, unalloyed sheet or manufactured sheet aluminum, guaranteed free from iron, dirt, or any other foreign substance, and to be free from hub caps, radiator shells, and airplane sheet.

No. 1 pewter. This shall consist of tableware and soda-fountain boxes, but in any case must test 84 per cent tin. Siphon taps to be treated for separately.

The handling of scrap material usually involves sorting and classifying into different grades before the metal goes to melting or refining furnaces. Light scrap, such as turnings and borings, is often compressed (briquetted) into solid blocks before being melted down.

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[1] Minerals Yearbook, 1935; U. S. Bureau of Mines.

## EXERCISES

1. An ore contains 14.53 ounces of gold per ton. Express this as percentage, as grams per metric ton, and as dollars per ton.

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# CHAPTER IX

# ORE DRESSING

The first process which most ores undergo after they leave the mine is *ore dressing*, also called *milling, mineral dressing*, or *beneficiation.* Of the 28 million odd tons of non-ferrous ores referred to in Table VIII-3, practically all were treated by one or more ore dressing processes. Only a small portion of the iron ores were beneficiated (dressing of iron ores is usually called beneficiation), but each year the amount increases.

Ore dressing is *a process of mechanically separating the grains of ore minerals from the gangue minerals,* to produce an enriched portion or *concentrate* containing most of the ore minerals, and a discard or *tailing* containing the bulk of the gangue minerals. Since most base metals occur in the form of chemical compounds, the metal-bearing minerals must eventually be subjected to a chemical treatment (pyrometallurgical and hydrometallurgical processes) to break up the chemical union and liberate the metallic elements. Such chemical processes are quite expensive as a rule, and the cost is proportional to the bulk of material treated. Thus, it would cost as much (or more) to smelt one ton of 5 per cent lead ore as to smelt a ton of 50 per cent lead ore, and the yield of metal would only be one-tenth as much in the first case as in the second. Smelting a 5 per cent lead ore is economically impossible, but, by using the relatively cheap ore dressing operations to make a high-grade concentrate which can be smelted profitably, the 5 per cent ore can be treated economically. Most of the high-grade, direct smelting ores have been mined, and each year the producers become more and more dependent upon low-grade ores. Treatment of such ores would be impossible without the resources of modern ore dressing methods. As a concrete illustration of the economics of ore dressing, we reproduce the following example from Taggart's "Handbook of Ore Dressing":

### EXAMPLE 1[1]

Assume an ore consisting of galena scattered as grains and small veinlets through a body of dolomite. Assume that the mass as mined assays 5 per cent

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[1] Taggart, A. F.: Handbook of Ore Dressing; John Wiley & Sons, New York, 1927.

lead, that the market price for lead is $0.07 per pound, that mining and delivery at the surface costs $3.00 per ton, that freight to the nearest smelter costs $5.00 per ton, that the smelter charge for treating material containing 5% lead is $10.00 per ton, that 97 per cent of the lead in the ore is recoverable by smelting and that the smelter pays 95 per cent of the market price for the lead recovered. Assume further that by a process of ore dressing the galena from the ore as mined can be separated from the dolomite in the form of a concentrate assaying 60 per cent lead, that in the process 5 per cent of the lead will be lost, that the process costs $0.75 per ton, that the freight charge on concentrate is $10.00 per ton, the smelter charge $2.00 per ton, and that 97 per cent of the lead in the concentrate is recovered and paid for at 95 per cent of the market price. The comparative receipts and expenditures on 100 tons of ore are tabulated below. In this case, which is typical, concentration changes a deficit of $11.55 per ton into a profit of $1.43 per ton.

Solution: 100 tons of ore produce 7.92 tons of 60 per cent concentrate under the conditions stated.

*Without Concentration*

Expenditures

| | | |
|---|---|---|
| Mining 100 tons at | $ 3.00 | $ 300.00 |
| Freight 100 tons at | 5.00 | 500.00 |
| Smelting 100 tons at | 10.00 | 1,000.00 |
| | | $1,800.00 |

Receipts

| | |
|---|---|
| 100 tons of ore produce 9,700 lb. of lead which at 95% of $0.07 per lb. is | $ 645.05 |
| Deficit | 1,154.95 |
| | $1,800.00 |

*With Concentration*

Expenditures

| | | |
|---|---|---|
| Mining 100 tons at | $ 3.00 | $300.00 |
| Milling 100 tons at | 0.75 | 75.00 |
| Freight 7.92 tons at | 10.00 | 79.20 |
| Smelting 7.92 tons at | 2.00 | 15.84 |
| Profit | | 142.76 |
| | | $612.80 |

Receipts

| | |
|---|---|
| 100 tons of ore produce 7.92 tons of concentrate containing 9,500 lb. of lead. This, when smelted, produces 9,215 lb. of lead which, at 95% of $0.07 per lb., is | $612.80 |
| | $612.80 |

The fact that most ore minerals are usually finely disseminated and intimately associated with gangue minerals (*vide* Fig. VIII-1) means that the various minerals must be broken apart or *liberated* before they can be collected in separate products. This liberation is accomplished by *comminution* or *crushing* and *grinding* of the ore. After the ore has been ground to the proper size, it is subjected to some process of *concentration* which separates the mixture of mineral grains into two or more products.

Comminution and concentration are the two primary operations in ore dressing, but many other important subjects are involved, among which are sizing and classification of mineral mixtures, and thickening, de-watering and filtering of ore-water pulps. With this brief introduction we shall proceed to consider the various ore-dressing operations.

## COMMINUTION

**Laws of Crushing.**—*Rittenger's law* states that the energy consumed in crushing or grinding is proportional to the amount of new surface formed. This law, which has been verified by a number of experimenters,[2] means that the useful work done in comminution is equal to the surface energy of the new surface produced by the operation.

Let us assume that we have a cubic particle, $d$ cm. on an edge; the area of this particle will be $6d^2$ sq. cm. Now let us, by means of some ideal crushing machine, fracture this into 8 cubes $\frac{d}{2}$ cm. on an edge. The area of each small cube will be $6\left(\frac{d}{2}\right)^2 = \frac{3d^2}{2}$ sq. cm., and the total area $8 \times \frac{3d^2}{2} = 12d^2$ sq. cm. The increase in area in this operation will be $12d^2 - 6d^2 = 6d^2$ sq. cm.

Now, let us crush each of the small cubes into still smaller cubes, having an edge equal to $\frac{d}{4}$ cm. The area of each cube will be $6\left(\frac{d}{4}\right)^2 = \frac{3d^2}{8}$ sq. cm. Now, however, we have $8 \times 8$ or 64 cubes, so that the total surface will be $64 \times \frac{3d^2}{8} = 24d^2$, and the increase in area will be $24d^2 - 12d^2 = 12d^2$.

Note that in each case we have reduced the diameter of the particle by ½, but that the second operation produced twice as much new surface as the first. If we had proceeded farther, we should find the same relation to hold, namely, that the increase in surface is

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[2] Gross, John, and Zimmerley, S. R.: Crushing and Grinding III; Transactions A.I.M.E., Vol. 87, page 35, 1930.

greater, the smaller the particle size, for equal reductions in diameter. In other words, much more new surface is produced by crushing a ton of 1-cm. particles down to 0.5-cm. particles than by crushing a ton of similar material from 12-inch particles down to 6-inch particles. This general rule follows from simple geometry, and will hold in any case, even though the particles are far from cubical in shape.

Since the energy required for crushing or grinding is directly proportional to the amount of new surface produced, we can see at once that fine grinding will require more power than coarse crushing, and will therefore be more expensive. The machinery used in fine grinding is different from that used in coarse crushing; but entirely apart from the consideration of types of machinery, the fact must be kept in mind that fine grinding is intrinsically more difficult (i.e., expensive) than coarse crushing.

Apart from this general consideration is the fact that certain rocks and ores are harder and tougher than others and offer more resistance to crushing. Using an arbitrary scale of "resistance to crushing," Gross[3] tabulates the following minerals:

| Mineral | Resistance to Crushing | Mineralogical Hardness |
|---|---|---|
| Quartz | 1.000 | 7 |
| Pyrite | 0.788 | 6 – 6.65 |
| Sphalerite | 0 311 | 3.5 – 4 |
| Calcite | 0 231 | 3.0 |
| Galena | 0.192 | 2.5 |

Many of the tougher rocks such as diabase and trap are more difficult to crush than brittle rocks, such as quartz and granite. Rocks or ores containing much clayey material may be difficult to get through a crusher, even though they are relatively soft.

**Primary Crushing.**—The crushing and grinding in ore-dressing plants is almost invariably done in two or more stages, and usually a different type of machine is used for each stage. Experience has shown that stage crushing and grinding usually is more efficient than an attempt to perform the necessary comminution by means of a single machine.

The first stage is called coarse crushing or primary breaking, and for this purpose one of two machines are ordinarily used: (1) some modification of the Blake jaw crusher, or (2) a gyratory crusher. These primary breakers take the run-of-mine ore and reduce it to a size small enough to be taken by the next crusher in the series.

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[3] Gross, John, and Zimmerley, S. R.: Crushing and Grinding III; Transactions A.I.M.E., Vol. 87, page 35, 1930.

The jaw crusher is illustrated by the cross-section in Fig. 1. This machine consists of a heavy main frame carrying a fixed jaw and a swing jaw. The swing jaw is pivoted at the top and is given an oscillating motion by means of toggles and pitman actuated by the eccentric on the main driving shaft. Rock is fed down between the crushing jaws, and is nipped and crushed by them as the swing jaw closes. The crusher is usually driven by means of a pulley mounted on the main shaft. The rear toggle is seated against an adjusting block, which is the wedge-shaped block shown on the diagram. This block may be raised or lowered by means of a bolt, and this permits adjustment for *set;* i.e., the distance between the fixed jaw and the swing jaw. Crushing takes place only while the swing jaw is advancing; and while the jaw is receding, the crusher is running idle. This accounts for the heavy flywheels used on these crushers to store energy during the idling period and give it up again during the crushing period—without flywheels there would be a severe strain on the prime mover caused by the intermittent loading.

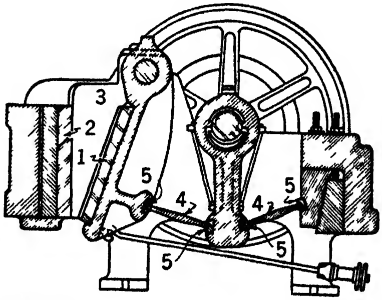

Fig. 1—Section Through a Blake-Type Jaw Crusher.

The jaw plates and cheek or side plates are subjected to severe abrasion by the ore being crushed; these are made of chilled cast iron, manganese steel, or some other wear-resistant alloy, and are removable to permit replacement when worn out. The wear on these plates depends upon the amount of rock crushed and the nature of the rock, and is usually given in terms of pounds of steel consumed per ton of ore crushed. Taggart[4] reports that the average steel consumption for manganese steel liners is from 0.01 to 0.06 pound per ton of ore

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[4] Taggart, A. F.: Handbook of Ore Dressing; John Wiley & Sons, New York, 1927.

*crushed, and for chilled cast iron liners* 0.02 to 0.2 pound per ton. *These figures include the weight of the worn-out liners* which were rejected when new plates were installed. The *angle of nip* is the largest angle made by the two jaws that will allow the pieces of rock to be nipped and crushed—if the angle made by the jaws is greater than this, the piece will not be nipped, but simply squeezed out of the jaws and thrown back out of the crusher. The angle of nip in jaw crushers varies with the size of the machine from 11° to 23°. The angle of nip gives little concern to users, because a well-designed crusher is built so that it will nip and crush any piece small enough to enter the crusher. In some crushers vertically corrugated jaw plates are used instead of smooth plates.

The point at which rock enters is known as the *mouth* of the crusher, and the dimensions of the mouth are given by the width of the crushing jaws, and the *gape* or opening at the mouth measured at right angles to the fixed jaw. The size of a crusher is measured by the dimensions at the mouth in inches; a 66 × 84 crusher, for example, means a crusher with a 66-inch gape and a jaw width of 84 inches. The gape is always given first, width of jaw second. The gape is invariably the smaller of the two, and it is this dimension that determines the size of the largest piece that will enter the crusher. A 66 × 84 crusher, therefore, would take any rock less than 66 inches in diameter.

The *throat* of a crusher is the point at which the rock is discharged, and of course its short dimension varies, depending upon whether the swing jaw is in the open or closed position. The difference in inches between the open and closed positions measured at the throat is known as the *stroke* or *throw* of the crusher. For small crushers the throw is about 3/8 inch to 3/4 inch, and for large crushers from 1 inch to 2 inches. For brittle rock which fractures readily (acid rocks, quartz), a short throw is used; but for crushing tough rock (basic rocks, weathered material, etc.), a long throw is necessary because these materials tend to deform without actually breaking apart.

Rock is discharged from the crusher at all times, but naturally most of the discharge takes place while the swing jaw is receding. This means that many pieces will be discharged which are larger than the minimum throat opening, and some pieces may be discharged which are almost as large as the maximum opening at the throat. The average opening at the throat is the best measure of the size of the product discharged, and this is known as the set of the crusher (very often the minimum opening is given as the set). The ratio of gape to set is called the *reduction ratio,* and this is the same as the ratio of the largest particle in the feed to the largest particle in the discharge.

### TABLE 1 *

### Reduction Ratio and Nip Angle in Blake Crushers

| Size of Crusher, Inches | Minimum Set | | | Intermediate Set | | | Maximum Set | | |
|---|---|---|---|---|---|---|---|---|---|
| | Inches | Reduction Ratio | Angle of Nip, Degrees | Inches | Reduction Ratio | Angle of Nip, Degrees | Inches | Reduction Ratio | Angle of Nip, Degrees |
| 7 × 10 | 0.75 | 9.3 | 13.5 | 1 | 7 | 12.1 | 1.5 | 4.7 | 11.1 |
| 10 × 20 | 0.75 | 13.3 | 21.1 | 1.25 | 8 | 20.0 | 1.5 | 6.7 | 19.5 |
| 15 × 24 | 2 | 7.5 | 21.5 | 3 | 5 | 20.0 | 3.5 | 4.3 | 19.2 |
| 18 × 30 | 2.5 | 7.2 | 20.2 | 3 | 6 | 19.6 | 3.5 | 5.1 | 19.0 |
| 56 × 72 | 7 | 8 | 23.8 | 8 | 7 | 23.4 | 10 | 5.6 | 22.5 |
| 84 × 120 | 10 | 8.4 | 23.2 | 12 | 7 | 22.6 | 14 | 6 | 22.1 |

* Taggart, A. F.: Handbook of Ore Dressing; John Wiley & Sons, New York, 1927. Reprinted by permission.

The actual "reduction ratio" of any crusher is usually less than the figures as calculated above, since the largest pieces in the feed ore usually are smaller than the gape at the mouth, and the average piece considerably smaller. The size of a primary crusher depends upon the size of the ore to be crushed. In most underground mining operations, the ore is broken to pass chute grizzlies before it is hoisted, and consequently the maximum piece will be not more than 10 to 18 inches in diameter. A primary crusher for ore of this type would not require a gape of more than 18 inches, and most primary crushers are not larger than this. The very large primary crushers (gape, 56 to 84 inches) are used to handle ore from steam-shovel mining, etc., where very large boulders are likely to find their way to the crushing plant.

The *capacity* of a crusher is defined as the number of tons of finished product made per hour. Manufacturers' tables usually give approximate values for average capacity, but the actual capacity may vary considerably from these figures. Capacity will increase with the speed of the crusher (r.p.m. of driving shaft), and it will also depend upon the character of the ore being crushed. Capacity decreases as the reduction ratio increases. The following table illustrates the capacities of some typical jaw crushers under certain specified conditions.

The horsepower required to operate these crushers is also shown

TABLE 2

| Size Opening, Inches | Approx. Shipping Weight, Pounds | App. Cap. per Hr.—Tons of 2000 lb.[†] |  |  |  |  | Size Driving Pulley, Inches | Size Flywheel, Inches | Max. H. P. Required | Dia. Swing Jaw Shaft, Inches | Dia. Eccentric Shaft, Inches | Size Opening, Inches |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  | Max. R. P. M. Dr. Pulley | Ring Sizes, Inches |  |  |  |  |  |  |  |  |  |
|  |  |  | Largest |  | Smallest |  |  |  |  |  |  |  |
| **24 × 72** | 162,000 | 150 | 4 | 200 | 2½ | 110 | 78 × 18 | 78 × $10_F$ × 7½ | 150 | 13J × $13\frac{1}{16}$ | 14J × 17 | **24 × 72** |
| **36 × 42** | 108,000 | 175 | 6 | 144 | 4 | 76 | 78 × 18 | 78 × $10_F$ × 7½ | 115 | 11½J × $11\frac{9}{16}$ | 11½J × 14 | **36 × 42** |
| **36 × 48** | 115,000 | 160 | 6 | 160 | 4 | 86 | 78 × 18 | 78 × $10_F$ × 7½ | 125 | 11½J × $11\frac{9}{16}$ | 11½J × 14 | **36 × 48** |
| **42 × 48** | 171,500 | 150 | 8 | 260 | 5 | 118 | 96 × 20 | 96 × $12_F$ × 8 | 150 | 13J × $13\frac{1}{16}$ | 14J × 17 | **42 × 48** |
| **48 × 60** | 265,000 | 120 | 10 | 450 | 6 | 235 | 120 × 26 | 120 × $12_F$ × 6 | 180 | 15J × $15\frac{1}{16}$ | 15½J × 19 | **48 × 60** |
| **56 × 72** | 410,000 | 95 | 10 | 535 | 7 | 310 | 144 × 30 | 144 × $14_F$ × 10 | 250 | 17½J × $17\frac{9}{16}$ | 17½J × 20½ | **56 × 72** |
| **60 × 84** | 490,000 | 90 | 12 | 980 | 8 | 450 | 144 × 44 | 144 × $14_F$ × 16 | 300 | 19¾J × 20 | 20J × 23 | **60 × 84** |
| **66 × 86** | 560,000 | 90 | 12 | 1,110 | 8 | 510 | 144 × 44 | 144 × $14_F$ × 16 | 300 | 19¾J × 20 | 20J × 23 | **66 × 86** |

[*] Reproduced by permission from Bulletin 3097 of the Traylor Engineering Co.

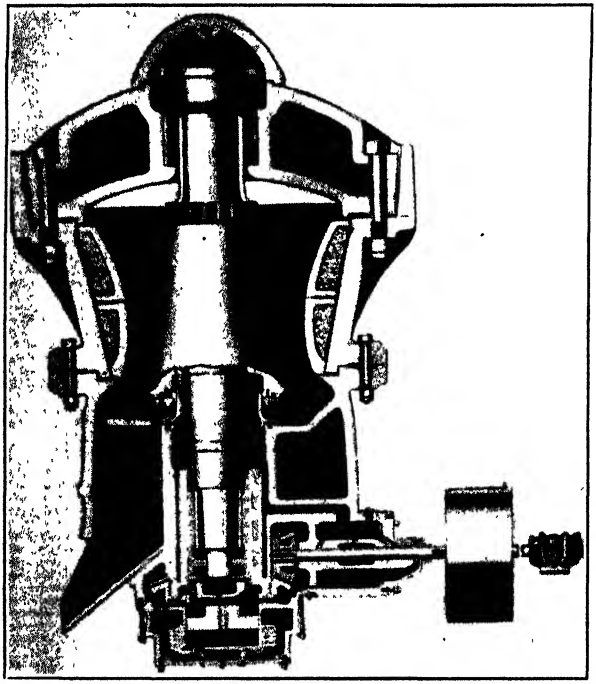
[†] Capacities are based on materials weighing 100 pounds per cubic foot when crushed.

in Table 2. As a rule, the power required per ton of ore crushed is greater for small crushers than for large. In any type of crusher, however, the power is proportional to the amount of crushing done, and any increase in the duty of a crusher means increased power consumption. Note that, for the same maximum power requirement, the capacity of a given crusher is always smallest for the largest reduction ratio (minimum set).

Many adjustments are possible on a jaw crusher, such as variation of speed, adjustment of stroke by changing the pitman or eccentric, and change of nip angle by adjustment of the swing jaw. However, changes such as these are seldom made unless the character of the crusher feed changes radically; these alterations would require much time and money. If the crusher is properly selected for the task at hand, there is seldom any need to change the speed, stroke, etc., from those recommended by the manufacturer. One adjustment, however, which must be made continually is the adjustment for the set of the crusher. As we have noted before, this is made by the use of a wedge (or shims) behind the rear toggle block. The abrasive action of the rock gradually wears away the jaw faces and enlarges the set; and consequently this must be "taken up" at intervals by closing the throat opening with the mechanism provided for the purpose. Crushers of all types must have frequent adjustments for set if the size of the discharged rock is to be kept the same.

The principle of operation of the suspended-spindle gyratory crusher is shown in Fig. 2. This crusher consists essentially of a fixed crushing surface in the form of the frustum of an inverted cone within which is a moving crushing surface in the form of the frustum of an erect cone. The ore is crushed in the downward-converging annular space between the two crushing surfaces. The crushing head is mounted on a spindle which is supported by a spider mounted on the upper part of the crusher frame. The lower end of the spindle passes through an eccentric sleeve which runs in a vertical bearing set in the bottom plate. Rotation of the eccentric sleeve is accomplished by means of a bevel gear and pinion, shaft and pulley. The action of the eccentric sleeve causes the spindle and the crushing head to gyrate; i.e., the axis of the spindle describes a cone with its apex at the point of suspension. The amplitude of the base of this cone is determined by the eccentricity of the sleeve, and this in turn determines the stroke of the crusher. The spindle is free to turn in its bearings; it is given a positive gyratory motion; but it is not positively rotated. The rotation of the crushing head when the crusher is in operation is caused by the impact of the ore being crushed, and the crushing head rotates slowly in a direction opposite that of the gyration.

The action of the gyrating head is such that the head is alternately approaching and receding from the outer shell at any point, and as the particles of rock fall into this space, they are nipped and crushed. The covering or mantle on the breaking head is usually made of manganese steel, as is the bowl liner or concave, which forms the other crushing surface. Steel consumption per ton of ore crushed is about the same as for jaw crushers.



*(Courtesy Traylor Engineering and Manufacturing Company, Allentown, Pennsylvania)*

FIG. 2.—Section of a Gyratory Crusher.

**This Is a Reduction (Intermediate) Crusher, But Is Similar In Action to a Primary Gyratory Crusher.**

The size of a gyratory crusher is expressed by the maximum opening at the mouth in inches; thus, a 12-inch gyratory crusher would have a gape of 12 inches and would crush any rock smaller than this size. The set of a gyratory is the average opening at the throat or discharge points, and this determines the size of the crushed product. The stroke is the distance in inches between the open and closed positions of the throat at a given point.

The throw or stroke in the gyratory crusher is usually shorter than that of jaw crushers. Adjustment for set is made by raising or lowering the spindle and crushing head by means of an adjusting nut at the top support of the spindle. The angle of nip in gyratory crushers ranges from 21° to 23°. The reduction ratio (theoretical) is usually figured as the ratio of the gape to the minimum throat opening.

TABLE 3 *

Capacity of Gyratory (Primary) Crushers. Bulldog Gyratory, Type T

| Size, Inches | Size of Receiving Opening, Inches | Maximum Speed | | Maximum Size of Discharge | Capacity (*c*) | Minimum Size of Discharge | Capacity (*c*) |
|---|---|---|---|---|---|---|---|
| | | (*a*) | (*b*) | | | | |
| 20 | 20 × 80 | 330 | 130 | 5 inches | 275 | 3 inches | 150 |
| 36 | 36 × 136 | 300 | 122 | 7 inches | 600 | 4½ inches | 370 |
| 48 | 48 × 166 | 250 | 96 | 9 inches | 1890 | 5½ inches | 1100 |
| 72 | 72 × 242 | 175 | 70 | 12 inches | 3400 | 9 inches | 2500 |

* Traylor Engineering Co., Bulletin 3100. Reprinted by permission.

(*a*) R.p m. of drive shaft.

(*b*) Gyrations per minute of crushing head.

(*c*) Tons (2000 pounds) per hour of material weighing 100 pounds per cubic foot.

The Telsmith breaker is another type of gyratory crusher often used for primary crushing. It has a fixed spindle; i.e., the spindle is not suspended from above, but is mounted in a long eccentric sleeve. Rotation of the sleeve imparts a gyratory motion to the crushing head, but gives a parallel stroke; i.e., the axis of the spindle describes a cylinder rather than a cone as in the suspended spindle gyratory. Adjustment for set in the Telsmith breaker is accomplished by placing shims between the bottom of the breaking head and an adjusting plate—the addition of shims at this point raises the crushing head and decreases the throat opening.

It is difficult to make a brief comparison of the comparative advantages of primary jaw and gyratory crushers because of the many factors which must be considered. In general, a jaw crusher is more satisfactory for small installations than the gyratory. Taggart[5] gives the following empirical rule which will roughly indicate the proper crusher to use; viz.: "If the hourly tonnage to be crushed

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[5] Taggart, A. F.: Handbook of Ore Dressing; John Wiley & Sons, New York, 1927.

## TABLE 4 *

### Telsmith Primary Breaker—Sizes, Capacities, etc.

| Number | 6B | 8B | 10B | 13B | 16B | 20B | 25B |
|---|---|---|---|---|---|---|---|
| Dimension of each receiving opening, inches (A × B). | 6¾ × 35 | 8 × 41 | 10 × 51 | 13 × 59 | 16 × 74 | 20 × 88 | 25 × 106 |
| Both about | 6¾ × 70 | 8 × 82 | 10 × 102 | 13 × 118 | 16 × 148 | 20 × 176 | 25 × 212 |
| Net weight of crusher in pounds, about | 10,000 | 12,500 | 19,000 | 29,000 | 44,500 | 62,500 | 108,000 |
| Weight of crusher crated for export in pounds, about | 11,000 | 13,500 | 20,600 | 31,500 | 46,000 | 67,000 | 113,000 |
| Cubical contents of crusher crated for export, cubic feet, about | 180 | 200 | 325 | 450 | 650 | 900 | 1,500 |
| Driving pulley: Dia. inches | 20 | 20 | 24 | 30 | 36 | 40 | 40 |
| Driving pulley: Face, inches | 10 | 12 | 12 | 14 | 16 | 20 | 24 |
| Driving pulley: Bore, inches | 2⅞ | 2⅞ | 3⅜ | 3⅜ | 3⅞ | 3⅞ | 4¾ |
| Driving pulley: R.p.m. | 750 | 750 | 700 | 560 | 500 | 440 | 480 |
| Horsepower required (Note 1) | 15–20 | 20–25 | 25–30 | 40–50 | 60–75 | 75–90 | 100–125 |
| Size of elevator required (for crusher output only) | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| Hourly capacity—<br>with 1" discharge opening, tons | 18–20 | | | | | | |
| with 1¼" discharge opening, tons | 20–23 | 30–33 | | | *See Note 1* | | |
| with 1½" discharge opening, tons | 23–26 | 33–36 | 38–44 | | | | |
| with 1¾" discharge opening, tons | | 36–40 | 44–50 | | | | |
| with 2" discharge opening, tons | | | 50–57 | 70–80 | | | |
| with 2½" discharge opening, tons | | | | 80–90 | 120–135 | | |
| with 3" discharge opening, tons | | | | 90–100 | 135–145 | 200–220 | 300–330 |
| with 3½" discharge opening, tons | | | | | 145–160 | 220–250 | 330–365 |
| with 4" discharge opening, tons | | | | | | 250–280 | 365–400 |

**Note.** 1—Where no rating is specified in this section of the table, for any certain discharge opening, crusher cannot be operated economically at that opening. The above capacities are based on stone, weighing loose about 2600 pounds per cubic yard and having a specific gravity of 2.6.

* Smith Engineering Works, Bulletin 261-K. Reprinted by permission.

divided by the square of the gape expressed in inches yields a quotient less than 0.115, use a jaw crusher; otherwise, a gyratory."

The gyratory crusher is more likely to clog than the jaw crusher, when the rock is clayey or fibrous. On the other hand, the discharge of a gyratory crusher is more uniform than that of a jaw crusher because the curved discharge opening does not permit the passage of flat slabs which might pass through a jaw crusher unbroken.

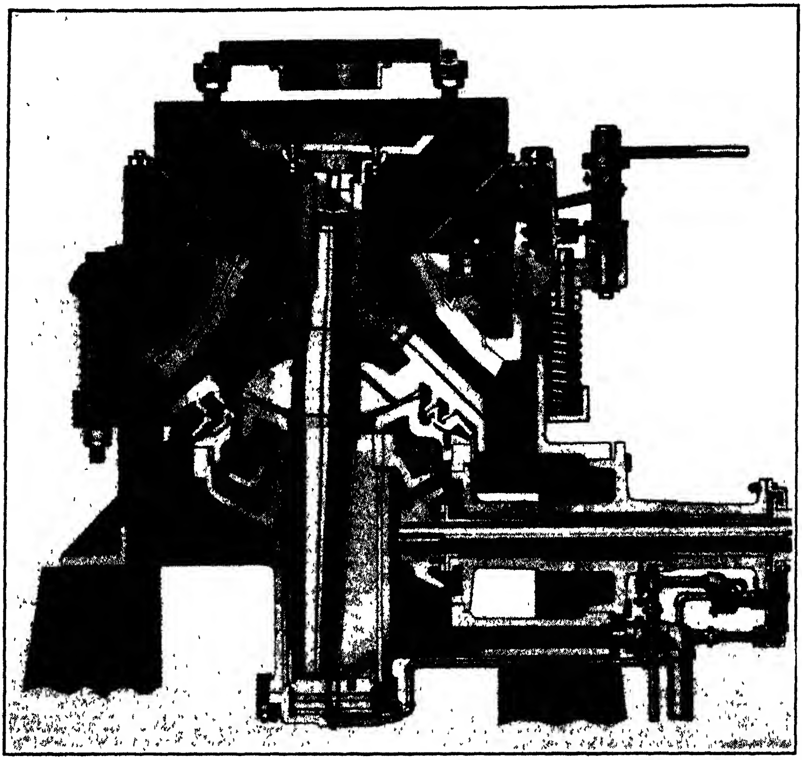
**Secondary Crushing.**—In general, a secondary or intermediate crusher is intended to take the discharge from the primary crusher and break it down to a size suitable for feed to fine grinding machines. Often two or more secondary crushers will be needed if the primary crusher discharge is fairly coarse.

There are a number of types of secondary crushers, and for our purposes we may divide them into the two most important groups: (1) those crushers which are essentially modifications of jaw or gyratory crushers, and (2) crushing rolls. As a general rule, these secondary crushers consume more power and use up more steel per ton of ore crushed than primary crushers, because they are working on finer material and must produce more new surface than a primary crusher would produce for an equal reduction ratio.

To illustrate the construction of secondary crushers of the first group, we shall consider briefly the Symons cone crusher which applies the principle of the gyratory crusher. Figures 3 and 4 illustrate the construction and action of the Symons cone.

The Symons cone crusher consists of a downward-flaring bowl within which is gyrated a conical crushing head (Fig. 3). The main shaft is gyrated by means of a long eccentric which is driven by bevel gears like those of the standard gyratory or Telsmith breaker. A crushing mantle covers the breaking head, and this mantle and the bowl liners are made of manganese steel or other wear-resisting alloy. The bowl is held in place by a heavy screw thread (Fig. 3) which is prevented from turning by means of lock nuts. The loosening of these lock nuts permits the bowl to be turned on these threads and thus raised or lowered. Adjustment, therefore, can be made for set even while the crusher is in operation. Since secondary crushers perform heavy crushing duty, and the wear on crushing surfaces is quite great, and also since the size of the product must usually be held within narrow limits, the secondary crusher must be provided with facilities for quick and easy adjustment for set. Another feature of the Symons cone is the feed distributing plate mounted on top of the main shaft.

The size of the standard Symons cone is denoted by the bottom diameter of the crushing head, or cone, in feet. Each crusher can be fitted with either a coarse or fine crushing bowl and liner. Performance data for Symons cone crushers are given in Table 5.



*(Courtesy Nordberg Manufacturing Company, Milwaukee)*

FIG. 3.—The Standard Symons Cone Crusher.

### CAPACITIES OF STANDARD SYMONS CONE CRUSHERS

In the tables below are given the feed openings and capacities in tons per hour with various discharge settings. The 20-inch, 2-, 3-, 4-, and 4¼-foot sizes are furnished with fine and coarse bowls, these being designated by "A" and "C", while the 5½- and 7-foot sizes have in addition to these, medium bowls as shown by "B." The discharge setting is indicated by "D," this dimension being the width of the opening between the bowl and mantle, measured at the bottom of the parallel zone when the head is at the extreme closed position.

### TABLE 5 *

### FEED OPENINGS FOR STANDARD CONE CRUSHERS

Fine—Medium—Coarse Bowls

| Size of Crusher | Fine Bowl Feed Opening "A" | Medium Bowl Feed Opening "B" | Coarse Bowl Feed Opening "C" |
|---|---|---|---|
| 20 in. | 1½ in. | Not Furnished | 3 in. |
| 2 ft. | 1⅝ in. | Not Furnished | 3 in. |
| 3 ft. | 3 in. | Not Furnished | 4½ in. |
| 4 ft. | 4½ in. | Not Furnished | 6¾ in. |
| 4¼ ft. | 6¾ in. | Not Furnished | 9½ in. |
| 5½ ft. | 7 in. | 8½ in. | 9¾ in. |
| 7 ft. | 9 in. | 11 in. | 14 in. |

### CAPACITIES

| Size of Crusher | Capacities in Tons (2000 pounds) per hour with Discharge Settings "D" | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Fine Bowl with Feed Opening "A" | | | | Medium and Coarse Bowls with Feed Openings "B" and "C" | | | | | | | |
| | ¼ in. | ⅜ in. | ½ in. | ⅝ in. | ½ in. | ⅝ in. | ¾ in. | 1 in. | 1¼ in. | 1½ in. | 2 in. | 2½ in. |
| 20 in. | 10 | 15 | 20 | ..... | 20 | 25 | 30 | 35 | ..... | ..... | ..... | ..... |
| 2 ft. | 14 | 20 | 25 | ..... | 25 | 30 | 35 | 45 | 50 | 60 | ..... | ..... |
| 3 ft. | 25 | 35 | 40 | ..... | 40 | 55 | 70 | 80 | 85 | 90 | 95 | ..... |
| 4 ft. | ..... | 60 | 80 | 100 | 80 | 100 | 120 | 150 | 170 | 177 | 185 | ..... |
| 4¼ ft. | ..... | ..... | 100 | 125 | ..... | ..... | 140 | 160 | 175 | 185 | 190 | ..... |
| 5½ ft. | ..... | 100 | 130 | 160 | ..... | 160 | 200 | 275 | 300 | 340 | 375 | 450 |
| 7 ft. | ..... | ..... | 225 | 280 | ..... | ..... | 330 | 450 | 560 | 600 | 800 | 900 |

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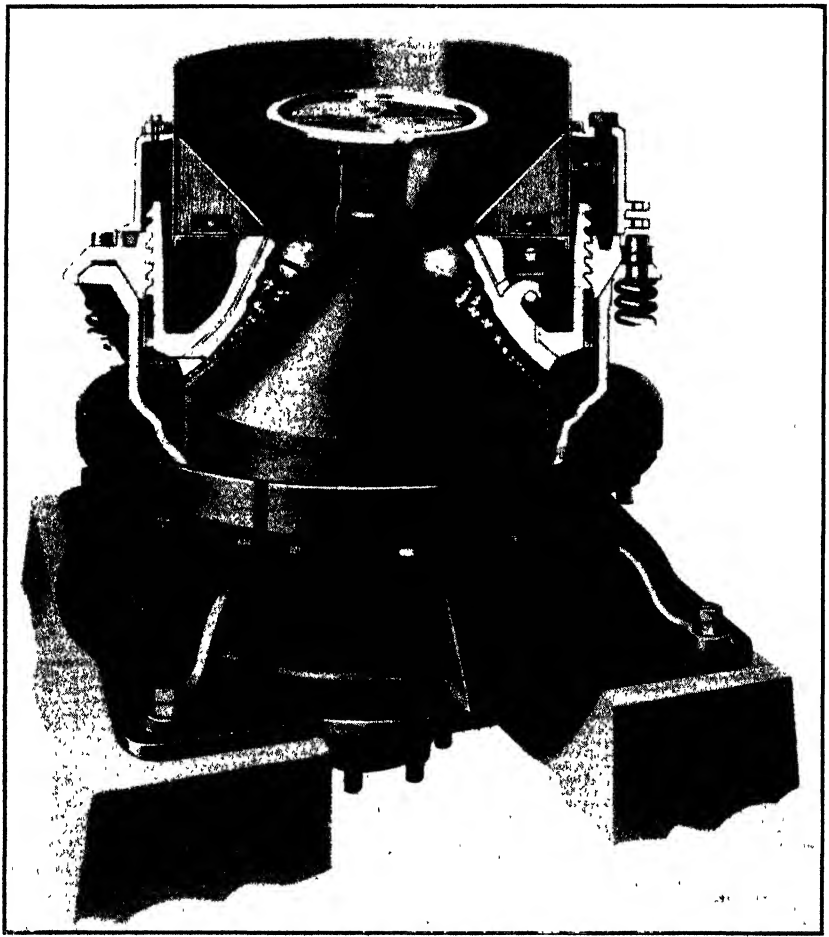
* Reprinted by permission from Bulletin 66, Nordberg Mfg. Co.

The Telsmith Gyrasphere is another type of secondary crusher which utilizes the gyratory principle; it has a hemispherical crushing head. Other types of secondary gyratories utilize the gyratory parallel-stroke principle as illustrated by the Telsmith breaker. The Telsmith Reduction Crusher is an example of this.



*(Courtesy Nordberg Manufacturing Company, Milwaukee)*

FIG. 4.—The Symons Cone in Action.

**Some notes on Crushers in General.**—Figure 4 illustrates a point that is common to all gyratory and jaw crushers; namely, the fact that large pieces are crushed in several stages, and that a piece of rock may receive several crushing blows before it passes through the crushing zone. The fact that the crusher is working on coarse pieces at the mouth and smaller pieces at the throat means that more work is being done at the throat, and consequently the capacity of the crusher must be greater at the throat than at the mouth. The crushing capacity has been defined as the amount of finished product made in unit time—we may also think of the capacity as being determined by the volume displacement of the crushing jaw or head per unit of time. It is easy to see, then, that in all the types of crushers illustrated so far the capacity is greatest at the throat. In the jaw crushers the volume displacement is greater at the throat than at the mouth because the stroke is longest there. In the standard gyratory and the Symons cone, the volume displacement is largest at the throat for two reasons—the stroke is longest here, and the crushing surface has the greatest area. In the parallel-stroke gyratory crushers the larger area of crushing surface results in greater capacity at the throat, but the stroke is the same in all parts of the crushing zone. The Dodge-type jaw crusher has never had a great deal of success—largely because it violates the principle noted here. The Dodge crusher has a swing jaw pivoted at the bottom so that the greatest length of stroke is at the mouth. This means that the greatest capacity is at the mouth, and there is very little crushing capacity at the throat.

Another point which is of particular interest in secondary crushers is the angle of flow of the rock through the crushing zone. In the primary breakers the rock falls almost vertically, but in the secondary crushers the rock has to slide down a surface which is inclined considerably from the vertical. In a vertical crushing zone where the rock falls freely, the crushing zone is always full of rock if the rock is being fed to the machine rapidly enough, and if the crusher is choke-fed (i.e., rock is kept heaped up in the feed hopper so that it will flow in as fast as the machine will take it), there is danger that the machine will stall unless (1) the capacity of the throat is great enough to take everything that comes through the mouth, or (2) the machine is provided with plenty of excess power. In secondary crushers the possibility of stalling may be avoided by making the angle of flow shallow enough so that the rock cannot feed too rapidly down into the throat. This means that the crushing zone never becomes packed full, and there is always sufficient capacity at the throat to handle all that can come through the mouth. Design of this sort results in a more uniformly sized crusher discharge, because the small particles slide through uncrushed, and are not crushed against one another as they would be if the crushing zone were always filled.

Crusher discharge is never uniformly sized, although some crushers may produce better results than others in this respect. A crusher rated to make a 2-inch product will invariably discharge a large amount of material much smaller than 2 inches and usually some material larger than 2 inches. The fact that the size of the discharge opening is always changing is largely responsible for the oversize, and the presence of undersize is unavoidable, since when rock of any size is crushed, a certain amount of fine material is always produced. The Dodge crusher is the only machine which can give a product all below a certain definite size, but its disadvantages far outweigh this advantage. On this point Taggart[6] states, "The Dodge-type breaker is made in smaller sizes than the Blake and is, therefore, suitable for small sample plants where power consumption is so small as to be unimportant, and where uniformity of size of product, caused by the small throw at the throat, is of distinct advantage."

**Roll Crushing.**—The roll crusher is a type of secondary or reduction crusher, but it differs greatly from the crushers we have been considering up to this point. It consists of a heavy frame on which two rolls are mounted. These rolls are driven so that they rotate toward one another in the manner of the rollers in a clothes-wringer. Each roll shaft has its own pulley and is driven independently, but both rolls should have the same peripheral speed. Rock fed in from above is nipped between the moving rolls, crushed, and discharged at the bottom.

Roll crushers are heavy and require heavy foundations. They consume large amounts of power and have a rather small reduction ratio. This last may be caused by the fact that a particle usually gets only one crushing blow in the rolls, whereas it may be struck several times in passing through a jaw or gyratory crusher. To offset these disadvantages, however, there is the fact that crushing rolls have enormous capacity—much greater than that of a comparable jaw or gyratory crusher. Consequently, they are most commonly found in large mills where the daily tonnage is sufficient to warrant the installation of rolls rather than of some other secondary crusher.

The roll centers are usually made of cast iron, and are covered by a roll shell of manganese steel or other wear-resistant alloy. One roll is mounted in fixed bearings (fixed roll), and the other is mounted on movable bearings (movable roll) and is held in position by the tension of several strong springs (*vide* Fig. 5.) These springs permit the rolls to separate and pass any uncrushable object (tramp steel, etc.) that happens to get into the feed. (Reference to Fig. 3 will show that this crusher has protective springs which serve a similar

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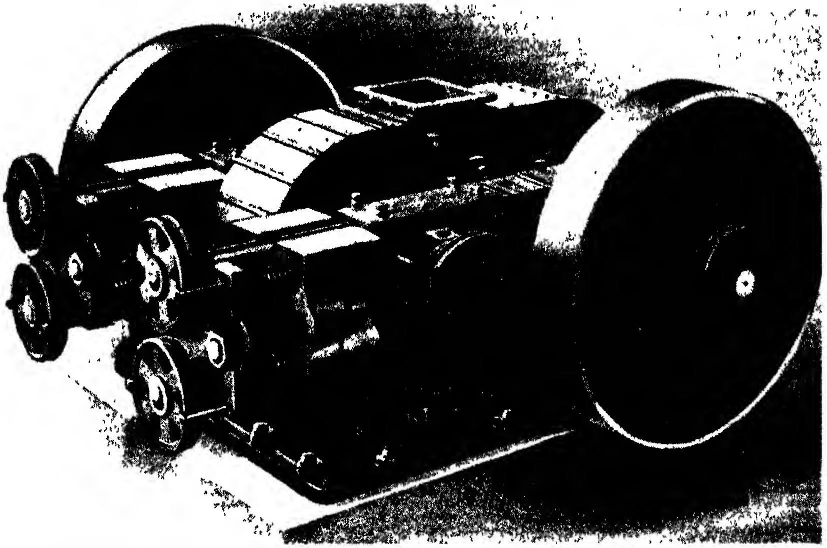
[6] Taggart, A. F.: Handbook of Ore Dressing; John Wiley & Sons, New York, 1927.

purpose.) The set of the rolls is the smallest distance between roll faces, and adjustment for set is easily made on the movable roll. Some rolls are provided with a "fleeting device" which keeps one of the rolls moving slowly back and forth in a lateral direction. This eliminates the annular corrugation which soon forms on the shells of crushing rolls which have no lateral motion.

Rolls may be free fed by feeding only enough material to keep a ribbon of ore between the rolls, or they may be *choke fed* by feeding all the material the rolls will take. In free feeding there is very little movement against the tension springs, the set remains practically constant, and the product is remarkably uniform. When rolls are choke fed, the rolls are generally set close, and the movement of the movable roll against the tension springs allows the particles to pass through the rolls. The product of choke-fed rolls is never as uniform as when free feeding is used. Choke feeding is used only on feed of about ¼-inch diameter or less.



*(Courtesy Traylor Engineering and Manufacturing Company, Allentown, Pennsylvania)*

FIG. 5.—Crushing Rolls.

The angle of nip is important in rolls crushing because it determines the maximum size of particle that will go through the rolls. The maximum angle of nip for rolls is about 33°; i.e., if the angle made by the tangents to the roll faces at the two points where a particle touches the rolls is greater than 33°, the particle will not be nipped and drawn through, but will simply roll about on top of the rolls. The angle of nip depends upon the diameter of the rolls and the width of the set.

The size of roll crushers is given by the dimensions of the roll expressed as the product of the diameter by the length of the face in inches. Thus, 30 × 16 rolls have a diameter of 30 inches, and the face of the roll is 16 inches long.

**Stamp mills** are essentially a mechanical form of mortar and pestle. The mortar is made of cast iron or steel and is mounted on a heavy concrete foundation. Within the mortar are several (usually 5) dies, and for each die there is a stamp which strikes the die and crushes the ore on its surface. The stamp consists of a vertical shaft or stem with a crushing shoe at the bottom. Gravity stamps are lifted by means of cams and tappets and then allowed to fall. Steam stamps have the upper portion of the stem fitted into a steam cylinder and the stamps are lifted and driven down upon the die by the action of the steam. In the United States steam stamps have been used only in the Michigan district for crushing native copper ores. Gravity stamps have been widely used all over the world for crushing gold ore previous to amalgamation. For this purpose the stamp mill is very well adapted, but it never has had extensive application in any other field.

All the crushers we have considered up to this point generally operate on dry ore (ore free from water, not the "dry" ore mentioned in the previous chapter), but the stamp mill is a wet crusher. The ore to be crushed is fed into the mortar in sufficient amounts to keep the dies covered at all times, and for every ton of ore fed to the mortar from 4 to 6 tons of water are added. The front of the mortar contains a screen through which the water can flow, and this outflowing water carries with it all the ore which has been ground fine enough to pass the screen. This pulp is then allowed to flow over amalgam plates to extract the gold.

Gravity stamps weigh from 750 to 1500 pounds apiece, drop from 7 to 10 inches, and make about 100 drops per minute. The capacity depends upon the weight of the stamps, height of drop, frequency of the drop, and especially upon the size of the discharge (screen aperture). The capacity is smaller, the smaller the screen opening, since, with a small screen aperture, the ore must remain in the mortar a longer time before it is crushed fine enough to pass the screen.

The stamp mill combines the functions of an intermediate crusher and a fine grinding machine. The feed to the stamps is ordinarily about 1.5 to 2 inches in diameter, and the maximum size of the dis-

## TABLE 6 *

## SIZE AND CAPACITIES OF ROLLS CRUSHERS

### Traylor Type AA

| Size of Roll. Diameter by Face, Inches | Approx. Capacity Tons of 2000 Pounds per Hour † | | | Rolls without Automatic Lateral Adj. Mechanism | | Rolls with Automatic Lateral Adjustment Mechanism | | | R.P.M. (Usual Range) | H.P. Req. | Size of Roll. Diameter by Face, Inches |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Size Pro., Inches | Max. Feed, Inches | Cap., Tons | Movable and Fixed Pulley, Inches | Approx. Shipping Weight, Pounds | Movable Pulley, Inches | Fixed Pulley, Inches | Approx. Shipping Weight, Pounds | | | |
| **36 × 14** | ¼ | 1¼ | 30 | 72 × 10 | 58,200 | 36 × 8 | 72 × 16 | 56,800 | 100–150 | 35 | **36 × 14** |
| **36 × 16** | ¼ | 1¼ | 35 | 72 × 10 | 59,300 | 36 × 8 | 72 × 16 | 57,900 | 100–150 | 40 | **36 × 16** |
| **42 × 16** | ¼ | 1½ | 40 | 72 × 12 | 64,400 | 42 × 12 | 84 × 16 | 65,700 | 95–120 | 50 | **42 × 16** |
| **42 × 18** | ¼ | 1½ | 45 | 72 × 12 | 65,700 | 42 × 12 | 84 × 16 | 67,000 | 95–120 | 55 | **42 × 18** |
| **48 × 18** | ⅜ | 1⅞ | 50 | 84 × 12 | 79,900 | 42 × 16 | 84 × 20 | 78,200 | 75–105 | 60 | **48 × 18** |
| **48 × 20** | ⅜ | 1⅞ | 60 | 84 × 12 | 81,500 | 42 × 16 | 84 × 20 | 79,700 | 75–105 | 65 | **48 × 20** |
| **54 × 16** | ⅜ | 2 | 55 | 84 × 16 | 94,400 | 48 × 16 | 84 × 20 | 92,200 | 70–95 | 65 | **54 × 16** |
| **54 × 20** | ⅜ | 2 | 65 | 84 × 16 | 99,300 | 48 × 16 | 84 × 20 | 97,100 | 70–95 | 70 | **54 × 20** |
| **54 × 24** | ⅜ | 2 | 75 | 84 × 16 | 103,200 | 48 × 16 | 84 × 24 | 101,500 | 70–95 | 75 | **54 × 24** |
| **54 × 30** | ⅜ | 2 | 95 | 84 × 18 | 112,000 | 54 × 14 | 84 × 24 | 110,200 | 70–95 | 85 | **54 × 30** |
| **60 × 24** | ½ | 2⅜ | 90 | 96 × 16 | 145,800 | 54 × 14 | 96 × 24 | 143,000 | 65–85 | 90 | **60 × 24** |
| **60 × 30** | ½ | 2⅜ | 115 | 96 × 16 | 154,000 | 54 × 14 | 96 × 24 | 151,200 | 65–85 | 100 | **60 × 30** |
| **72 × 20** | ½ | 3 | 85 | 108 × 18 | 218,600 | 60 × 16 | 108 × 24 | 216,900 | 50–75 | 100 | **72 × 20** |
| **72 × 24** | ½ | 3 | 100 | 108 × 18 | 226,100 | 60 × 18 | 108 × 24 | 224,600 | 50–75 | 100 | **72 × 24** |
| **72 × 30** | ½ | 3 | 130 | 108 × 18 | 237,400 | 60 × 18 | 108 × 24 | 235,800 | 50–75 | 125 | **72 × 30** |
| **72 × 36** | ½ | 3 | 155 | 108 × 18 | 248,800 | 72 × 18 | 108 × 24 | 248,600 | 50–75 | 150 | **72 × 36** |

* Traylor Engineering Co. Bulletin 3627. Reprinted by permission.

† Capacities are based on materials weighing 100 pounds per cubic foot when crushed.

charge varies from 0.5 inch down to 0.02 inch. The stamp mill makes a finished product—i.e., enough of the valuable mineral has been liberated so that the ore is ready for some concentration (or extraction) process; but the stamp mill cannot compete economically with ball mills for the production of material having an average diameter of less than 0.02 inch.

TABLE 7 *

EFFECT OF SCREEN APERTURE ON STAMP PERFORMANCE

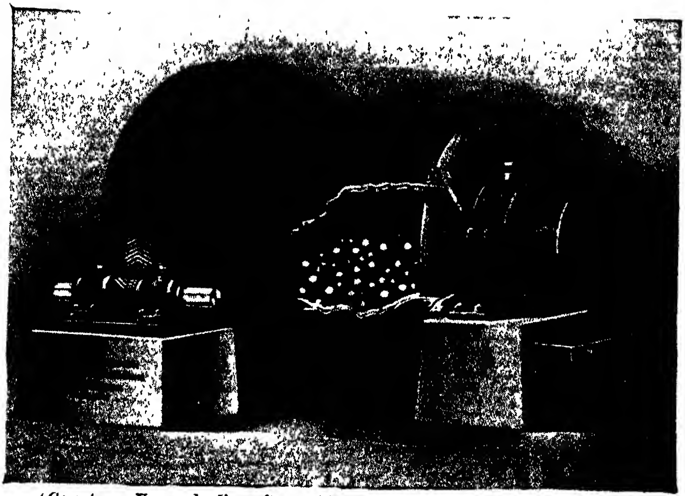
| Screen Aperture, Inch | Tons per 1400-pound Stamp per 24 Hours | Sizing Test of Product, Per Cent (a) | | | Tons of −90 Mesh per Stamp per 24 Hours |
|---|---|---|---|---|---|
| | | +60 Mesh | +90 Mesh | −90 Mesh | |
| 0.27 | 15 | 62 | 10 | 28 | 4.2 |
| 0.20 | 14 | 59 | 11 | 30 | 4.2 |
| 0.15 | 13 | 56 | 12 | 32 | 4.15 |
| 0.09 | 10 | 47 | 14 | 39 | 3.90 |
| 0.07 | 9 | 43 | 14 | 43 | 3.87 |
| 0.028 | 7 | 31 | 16 | 53 | 3.72 |
| 0.02 | 6 | 22 | 18 | 60 | 3.58 |

* Taggart, A. F.: Handbook of Ore Dressing; John Wiley & Sons, New York, 1927. Reprinted by permission.

(a) +60 mesh refers to the percentage of the material retained on a standard screen having 60 meshes to the linear inch (opening = 0.0097 inch); the notation −90 mesh refers to the percentage of the material which will pass through a 90-mesh screen (opening 0.0075 inch).

**Fine Grinding.**—Fine grinding is almost always done in a mill rotating on a horizontal axis and containing balls, rods, or pebbles (grinding media) which serve to grind the ore in the mill. The Hardinge mill has a short cylindrical section terminated by two conical sections (Fig. 8); most other mills have a cylindrical shape (Figs. 6 and 7). A mill containing steel or iron balls is a *ball mill;* if it contains steel rods it is called a *rod mill,* or if it contains flint pebbles, it is a *pebble mill.* Exceptionally long mills with relatively small diameters are designated *tube mills.*

When a ball mill is rotated about its horizontal axis, the balls are carried up the side by centrifugal force, and when they reach a certain height they "break" or fall away from the mill shell and drop back towards the center of the mill. This action results in a "cascading" action of the ball charge, and the resulting impact together with the abrasive action caused by the balls rolling upon one another grinds up the ore particles which are mixed with the ball



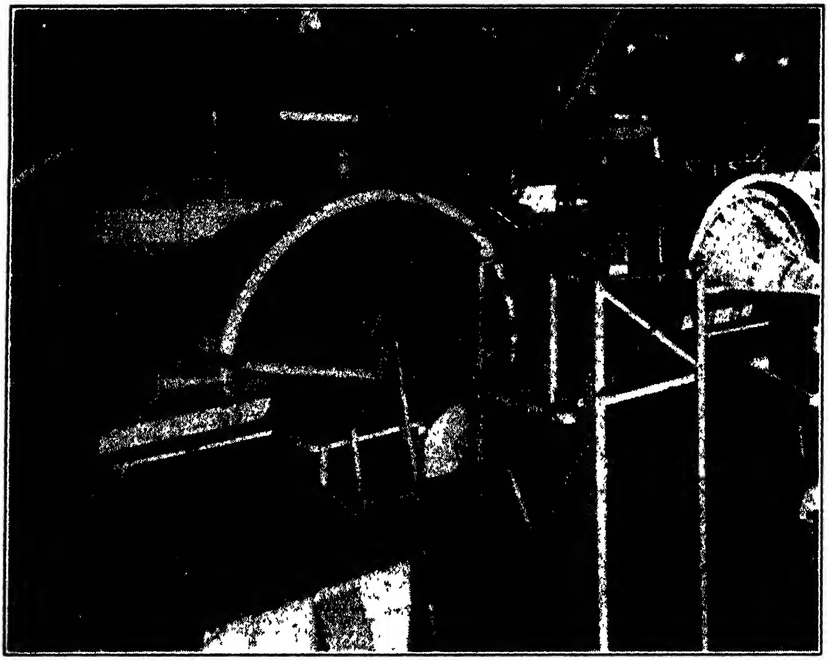
(*Courtesy Kennedy-Van Saun Mfg. and Eng. Corporation, New York*)

FIG. 6.—A Ball Mill. Side View.

(*Courtesy Kennedy-Van Saun Mfg. and Eng. Corporation, New York*)

FIG. 7.—A Rod Mill. End View.

charge. The faster the mill is rotated, the higher the balls will be lifted; and when the speed of rotation is great enough, the balls will be carried through a complete circle. When this happens, the charge is said to "centrifuge," and all grinding stops. The minimum speed at which a mill charge will centrifuge is known as the "critical speed" of the mill, and is given by the formula:



*(Courtesy Anaconda Copper Mining Company)*

Fig. 8.—Installation of Hardinge Ball Mills and Dorr Drag Classifiers at Anaconda.

$$N = \frac{54.19}{\sqrt{R}} \tag{1}$$

where $N$ is the critical speed in revolutions per minute and $R$ is the radius of the mill in feet. If the ball charge is to cascade properly, the mill must be operated below critical speed, and most commercial mills are operated at speeds ranging from 50 per cent to 80 per cent of the theoretical critical speed.

Ball mills consist of a steel shell lined with replaceable plates of manganese steel or other wear-resistant alloy. Soft rubber, however, may also be used as lining material. Metal liners may be smooth or corrugated—corrugated liners assist in lifting the grinding media and prevent their slipping back down the side of the mill. Most ball mills are mounted on trunnions; the feed enters the mill through one trunnion and is discharged through the other. Feeding is usually done by means of a spiral scoop which picks up the feed and delivers it to the mill. In some mills the discharge takes place simply by overflow of the pulp from the discharge trunnion; in other mills (quick-discharge mills), lifters or elevators remove the pulp at the discharge end.

Most ball mills used in ore-dressing operations perform wet grinding. Ball mills can be used for dry grinding; and such operations are common in cement mills, chemical plants, etc., but are rarely used for grinding ores. The pulp in a ball mill will contain from 20 to 50 per cent water by weight. The ore fed to the mill usually should not be coarser than ½ inch to ¾ inch, and the size of the discharge may be almost anything desired.

The average size of the ground ore discharged from the mill depends primarily upon how long the material has been in the mill. The longer the grinding action, the smaller the average particle size of the product. The length of time the ore is in the mill depends in turn upon the rate at which feed enters the mill, since the product must discharge at the same rate as the feed enters. Consequently, it is impossible to say that a ball mill of a given size has a certain capacity, for the mill will discharge material as rapidly or as slowly as it is fed in. Capacity is often expressed as the number of tons of material less than some specified size (− 100 mesh, for example) produced per hour.

In a brief discussion of this sort it is impossible to consider the effect of all the factors which influence the capacity of a rotating grinding mill. Some of the more important of these are:

1. Size of mill.
2. Shape of mill.
3. Nature of grinding media (balls, rods, pebbles).
4. Nature of mill lining.
5. Rate of feed.
6. Type of discharge.
7. Speed of rotation of mill.
8. Nature of feed.
9. Pulp density (amount of water used with ore).
10. Pulp level (amount of pulp in mill).
11. Size of balls or other grinding media.
12. Size of product desired.
13. Weight of ball load.
14. Whether open- or closed-circuit grinding is used.

All other variables being held constant, the capacity of a mill varies directly as the power consumption, the length of the mill (cylindrical mill), and the 2.6 power of the diameter (cylindrical mill). The capacity per unit volume varies as the 0.7 power of the diameter.[7] The capacity as referred to in this paragraph is given as the amount of new surface produced per unit of time—according to Rittinger's law, this is theoretically the correct way to express the capacity of any crusher or grinding machine.

The size of a ball mill is ordinarily given as its diameter. A 6-foot mill is 6 feet in diameter. If two dimensions are given, the first refers to the diameter, the second to the length; a 6′ × 4′ mill would be 6 feet in diameter and 4 feet long.

The steel consumption from balls and liners is from 2 to 4 pounds per ton, depending upon the type of ore, size of product, etc. New balls are usually added through the feed or discharge trunnion as they are needed. The balls gradually wear smaller and smaller until they disappear, and as a result the balls in an operating mill are of all sizes—from a maximum diameter equal to that of the new balls added, down to steel particles so small that they flow out with the pulp. When flint pebbles are used for grinding, the purpose is to avoid contamination of the pulp by iron abraded from steel balls; such mills may also use non-metallic liners (e.g., silex brick, rubber) for the same reason.

Data for some standard-size ball mills (cylindrical) are given in Table 8.

### TABLE 8 *

### Traylor Ball Mill Data (a)

### Wet Grinding, Closed Circuit, Diaphragm Discharge—Feed Minus 2 Inches

| Size of Mill, Feet | | R.P.M. | H.P. Motor | Usual Ball Charge, Pounds | Capacity in Tons per 24-hour to Size Given Below | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Mesh Size | | | | | | | | |
| Diameter | Length | | | | −8 | −14 | −20 | −30 | −35 | −48 | −60 | −100 | −200 |
| 3 | 2 | 35 | 10 | 1,000 | 20 | 18 | 16 | 13 | 12 | 10 | 8 | 4 | 1 |
| 4 | 4 | 31 | 30 | 2,800 | 66 | 50 | 52 | 44 | 40 | 32 | 27 | 15 | 4 |
| 5 | 6 | 29 | 60 | 7,500 | 185 | 165 | 143 | 127 | 125 | 98 | 67 | 37 | 9 |
| 6 | 5 | 25 | 125 | 10,000 | 330 | 290 | 250 | 220 | 200 | 165 | 125 | 67 | 17 |
| 7 | 6 | 23 | 175 | 21,500 | 800 | 690 | 580 | 500 | 465 | 390 | 300 | 156 | 42 |
| 9 | 9 | 19 | 400 | 56,000 | 1800 | 1540 | 1350 | 1150 | 1080 | 900 | 675 | 360 | 90 |

* Traylor Engineering Co. Bulletin 1103. Reprinted by permission.

(a) For dry grinding figure 60 per cent of capacities as shown. Capacities shown are approximate, as all materials vary in their resistance to grinding. The figures given are for Miami and Inspiration ores. For very hard quartz, capacity figures should be reduced 50 per cent; for soft porphyry like Ray Consolidated tonnage will increase from 80 per cent to 100 per cent.

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[7] Fahrenwald, A. W.: Some Fine Grinding Fundamentals; Transactions A.I.M.E., Vol. 112, page 88, 1934.

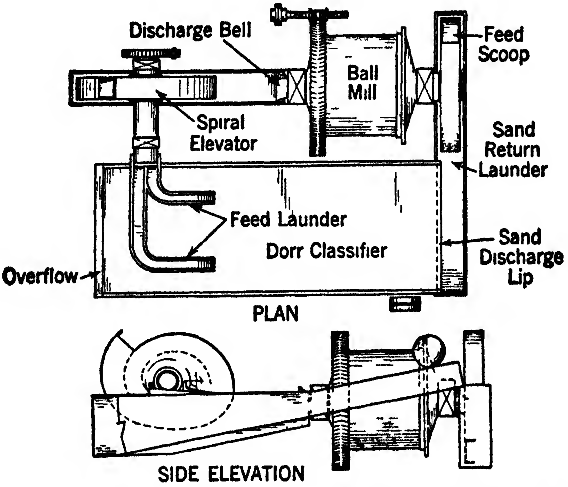
In some cases two and even three ball mills are used in series when particularly fine grinding is needed, and the successive stages are referred to as primary, secondary, and tertiary grinding.

**Comparison of Crushers and Grinders.**—The outstanding difference between crushers and grinding mills is that in crushers, the crushing elements are fixed with relation to one another, whereas in grinding mills the crushing elements are free and are held apart from one another only by the ore which is being ground between them. The stamp mill, according to this viewpoint, is intermediate between a crusher and a grinding machine. One important fact which follows from this distinction is that grinding mills and stamps require no adjustment for set, as do all crushers (including roll crushers).

**Closed-Circuit Grinding.**—We have noted that the capacity of a grinding mill is determined largely by the "time of residence" of the ore pulp in the mill. If we wished to grind ½-inch ore to −65 mesh, we could place a charge in a closed ball mill and allow it to grind until all the material would pass a 65-mesh screen. However, if we did this, we would find that much of the material was over-ground, so that a large part of the product would be much smaller than − 65 mesh. The ball mill does not confine its crushing action to the large particles only, but continues to act on particles which are already fine enough (− 65 mesh in this case), to grind them still smaller. Now the ideal form of comminution for concentration purposes is that which reduces the particle size sufficiently to liberate the ore minerals from the gangue with the minimum amount of over-grinding. If − 65 mesh represents the point at which liberation is complete, then our batch grinding would have two harmful effects: (1) there would be a large amount of over-ground mineral in the discharge which would be difficult to treat by concentration processes, and (2) a large amount of energy would have been consumed in doing this unnecessary and harmful over-grinding. If we should try to avoid over-grinding by using a continuous process (open-circuit grind) to let the ore discharge from the mill after it had been ground for a short time, we would find considerable oversize in the product.

To avoid having oversize in the product and to minimize the amount of over-grinding, most ball mills are operated in *closed circuit* with a classifier or a screen. The classifier is a device which takes the ball-mill discharge and separates it into two portions—the finished product, which is ground as fine as desired, and oversize material. The oversize is returned to the mill for further grinding, and this is called the *circulating load* of the system. In this way the ore can be passed through the ball mill rapidly enough to prevent serious over-grinding ("sliming"), but the classifier prevents the accompanying oversize material from escaping from the circuit.

The ball mill-classifier unit, then, gives a continuous operation which discharges a product of the required size but which tends to keep the ball mill working on coarse material as much as possible. The circulating load is commonly from 200 per cent to 1000 per cent of the amount of new feed entering the system. When stage ball milling is used, the primary ball mill is often used in open circuit, and only the secondary mill is in closed circuit. Rolls and other secondary crushers are often operated in closed circuit with a mechanical screening device.



*(Courtesy The Dorr Company, Inc., New York)*

Fig. 9.—Ball Mill-Classifier.

**Explosive Shattering.**—In the last few years considerable work has been done on the breaking of ores by explosive shattering rather than by mechanical crushing and grinding, but the process is still in the experimental stage. This method as described by Gross[8] consists in soaking the ore thoroughly in water and then heating to 180° C. under a pressure of 150 pounds per square inch. The pressure is then suddenly released, and the absorbed water is converted to steam which disrupts the ore. Explosive shattering is said to be more effective than ordinary crushing and grinding in liberating mineral particles without harmful overgrinding.

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[8] Gross, John: Progress in Explosive Shattering of Minerals; U. S. Bureau of Mines, R. I. 3223, 1934.

## SIZING; DE-WATERING

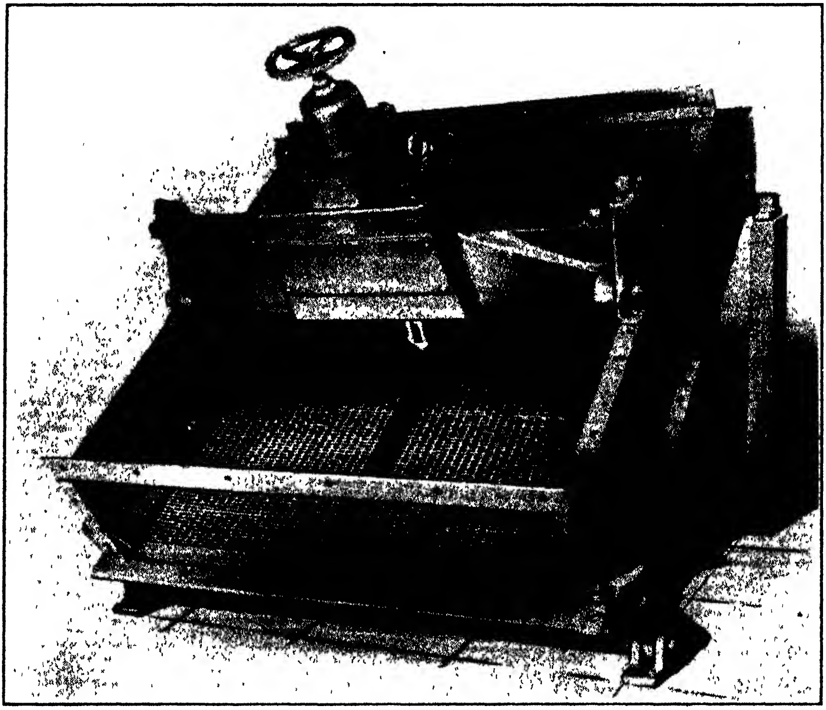
At various stages in milling operations it becomes necessary to separate crushed ore into two or more fractions with respect to the particle size of the material. For example, if − ½-inch feed is desired for a ball mill, a roll product may be sized on a screen having ½-inch openings. The undersize forms the ball mill feed, and the oversize is returned to the rolls for further crushing. The sizing of ore dressing products may be done either by screening or classification.

**Screening.**—Very coarse material is usually screened on a *grizzly*, which, in its simplest form, consists of a series of heavy parallel bars set in a frame. Some grizzlies employ chains instead of bars, and some are shaken or vibrated mechanically to help the sizing and to aid in the removal of the oversize from the top of the grizzly. The most common use of grizzlies in ore dressing is to size the feed for primary breakers—if a crusher produces a − 4-inch product, then the feed is usually passed over a 4-inch grizzly (one with a 4-inch spacing), and only the + 4-inch material is fed to the crusher, the undersize from the grizzly joining the crusher discharge. Grizzlies used with crushers are always set at an angle of 25° to 30° to facilitate the discharge of the oversize material. Grizzlies are used to screen dry material.

Revolving screens and trommels are used to some extent for sizing coarse material. They are still common in gravel-washing, coal-washing, and stone-treating plants, but are not very widely used in ore dressing. These screens consist of a cylindrical (sometimes conical) screening surface mounted on a revolving frame. Revolving screens rotate on rollers and have nothing on the interior of the screen, but trommels are supported from a shaft through the axis of the cylinder carrying two or more spiders to which the screen is attached. These cylindrical screens are commonly mounted with the axis inclined about 5° from the horizontal. The screening surface consists of punched steel plates or heavy woven wire screen. Revolving screens and trommels are made from 24 inches to 84 inches in diameter and from 6 feet to 30 feet in length.

These trommels and revolving screens are used principally in screening material between 2½ inches and ¼ inch in diameter; they may be used for wet or dry screening.

Although many types of punched-plate screens have been used for various purposes in ore dressing, the bulk of the screening at the present time is done with woven-wire vibrating screens. These screens are woven of steel wire and stretched tightly on a metal frame. Near the center of the screen is fastened the vibrating element of a high-speed vibrator, which produces a vibratory motion at right angles to the plane of the screen. The vibrator may be either a mechanical vibrator or a solenoid-buzzer type, and the screen usually vibrates at a frequency of about 1000 to 3600 vibrations per minute. The screens vary in size from about 36 inches × 36 inches to 72 inches × 60 inches, and they are set at an angle of 30° to 40°. The material to be screened is fed on at the top of the screen and travels down over the sloping surface. The tension in the screen wires and the amplitude of vibration should be adjusted so that the material hugs the screen closely but still is lively and in rapid motion. The rapid vibration of the screen surface tends to prevent "blinding" or clogging of the screen meshes with particles just slightly larger than the screen opening.



*(Courtesy the W. S. Tyler Company, Cleveland)*

FIG. 10.—The Hum-mer Electric Screen.

The opening or aperture of punched-plate screens and coarse woven-wire screens is commonly given by the diameter of the opening in inches or millimeters, and such a screen will pass any material smaller than the dimension given. In the finer woven screens, however, the aperture is given by means of a mesh number, and we use such designations as a 20-mesh screen or a 65-mesh screen. This gives the number of meshes to the linear inch; in order to know the actual aperture, the diameter of the wires must be known. In the Tyler standard screen scale, the sizes of the openings are regulated so that the aperture of any screen is 1.414, or $\sqrt{2}$, times the aperture of the next smaller screen. Table 9 gives the specifications of the screens in this series.

TABLE 9 [*]

TYLER STANDARD SCREEN SCALE

| Mesh | Opening, Inches | Opening, Millimeters | Diameter of Wire, Inches |
|---|---|---|---|
| .. | 1 050 | 26 67 | 0 148 |
| .. | 0 742 | 18.85 | 0.135 |
| .. | 0 525 | 13 33 | 0.105 |
| .. | 0.371 | 9.423 | 0.092 |
| 3 | 0.263 | 6.680 | 0.070 |
| 4 | 0 185 | 4 699 | 0.065 |
| 6 | 0 131 | 3.327 | 0 036 |
| 8 | 0 093 | 2.362 | 0.032 |
| 10 | 0.065 | 1.651 | 0.035 |
| 14 | 0.046 | 1.168 | 0.025 |
| 20 | 0.0328 | 0.833 | 0.0172 |
| 28 | 0.0232 | 0.589 | 0.0125 |
| 35 | 0.0164 | 0.417 | 0.0122 |
| 48 | 0.0116 | 0.295 | 0.0092 |
| 65 | 0.0082 | 0.208 | 0.0072 |
| 100 | 0.0058 | 0.147 | 0.0042 |
| 150 | 0.0041 | 0.104 | 0.0026 |
| 200 | 0.0029 | 0.074 | 0.0021 |

[*] W. S. Tyler Co., Cleveland, Ohio. Catalog 53. Reprinted by permission.

The Tyler standard screen scale is the most common in this country, and the notation "mesh" in metallurgical literature usually refers to this scale. By − 20 mesh is meant material that passes a 20-mesh screen; + 20 mesh would refer to material which would be retained on a 20-mesh screen. A product which passed a 20-mesh screen and was retained on a 35-mesh screen would be designated as − 20 + 35 mesh or 20/35 mesh. In the British nomenclature, the mesh number refers to the number of meshes per square inch.

Whatever the nature of a given screen is, the material passing it is limited by the opening of the screen and by that only. If a mixture of quartz and galena, for example, is sized into a number of fractions by means of screens, each fraction will contain quartz and galena particles of the same average diameter. This is not true of a product sized by a classifier, as we shall see presently.

In laboratory testing, screens as fine as 400 mesh may be used; but for tonnage screening in mills, the fine screens are too fragile and screen too slowly to be practical. Screens used in ore dressing plants will have apertures varying from 2 inches to about 0.008 inch (65 mesh).

**Classification.**—Classification or sorting may be defined as a method of separating mixtures of minerals into two or more products on the basis of the velocity at which the grains will fall through a liquid medium.

If a body falls freely in a vacuum, its velocity at any time is given by the expression

$$V = \tfrac{1}{2}gt^2 \tag{2}$$

where $g$ is a constant (the acceleration of gravity). The velocity is thus independent of the size and density of the body; and as time goes on, the velocity increases indefinitely. If the body falls in a viscous medium (air, water, or any other fluid), however, the frictional resistance opposes the force of gravity so that after a short time the body attains a certain *terminal velocity,* and from then on it settles at a uniform rate. The terminal velocity is a function of the size, shape, and density of the body and of the density and viscosity of the medium through which it is falling. For small solid spheres falling freely in a viscous medium, the terminal velocity $V$ is given by Stokes' law:

$$V = \frac{2}{9}a^2g\left(\frac{\rho - \sigma}{\mu}\right) \tag{3}$$

where $a$ = radius of particle in centimeters.
$\mu$ = coefficient of viscosity (c.g.s. units).
$g$ = acceleration of gravity (c.g.s. units).
$\rho$ = density of the sphere.
$\sigma$ = density of viscous medium.
$V$ = terminal velocity in centimeters per second.

The quantity $(\rho - \sigma)$ is the *effective density* of a body of density $\rho$ immersed in a liquid of density $\sigma$.

For spheres falling in water ($\sigma = 1$) at a definite temperature (since $\mu$ varies with temperature). Stokes' law reduces to

$$V = Ka^2(\rho - 1) \tag{4}$$

from which it follows that:

1. Large particles settle faster than small particles of the same density, and the terminal velocity varies directly as the square of the radius.
2. Particles of the same size but of different densities settle at different rates, and the heaviest body will settle most rapidly. The terminal velocity is directly proportional to the effective density of the particle.

Bodies of irregular shape will generally settle more slowly than spheres of the same size and density. For irregular grains (such as are always found in ore-dressing products) the constant in Stokes' formula must be multiplied by a "shape factor." For the common minerals, formulas of the type[9]

$$V = K_1a^2(\rho - 1) \tag{5}$$

are available, where $K_1$ is an experimentally determined constant, and is equal to the constant $K$ in equation (4) multiplied by the appropriate shape factor.

Stokes' law and related formulas give the *free-settling* velocity of a given particle, i.e., the velocity attained when only a few particles are settling in a large volume of liquid. When a large number of particles are allowed to settle in a comparatively small volume of liquid, *hindered-settling* conditions prevail. As each particle settles, it displaces an equal volume of liquid, and this gives rise to an upward current which opposes the fall of other grains. Under free-settling conditions the uprising current caused by displacement of liquid is too small to have any appreciable effect on the terminal velocity of the falling particles, but under the conditions of hindered settling the uprising current is sufficient to reduce materially the terminal velocity attained by a given particle.

Most *hydraulic classifiers* contain a number of vertical sorting columns in which a current of *hydraulic water* is rising. When an ore pulp is brought above one of these columns, those particles whose terminal velocity is greater than the upward velocity of the hydraulic water will settle through the sorting column and be discharged as a

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[9] Taggart, A. F.: Handbook of Ore Dressing; John Wiley & Sons, New York, 1927.

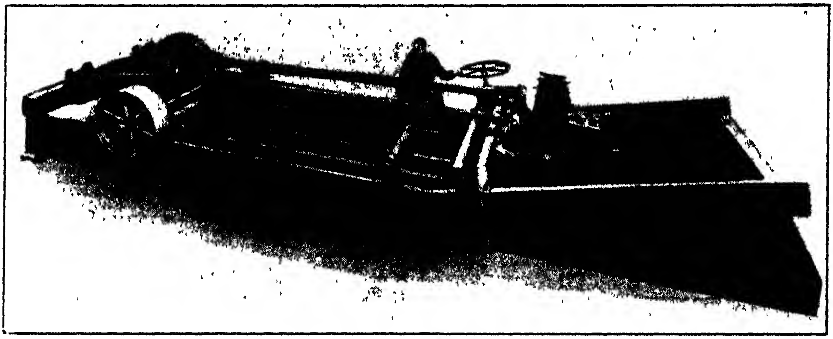
spigot product at the bottom of the column. By flowing pulp through a launder over a series of these sorting columns, which have successively smaller rising velocities of the current of hydraulic water, a series of spigot products can be made. The material which is too fine to settle in any of the sorting columns (slime) overflows at the end of the classifier. Each spigot product contains mineral particles which have the same settling rate in water; and if the classifier is working on a quartz-galena mixture, for example, each spigot product will contain galena grains of a definite size and quartz grains sufficiently larger to have the same terminal settling velocity according to the laws we have cited above. The *free-settling ratio* of quartz to galena is about 3.75; i.e., the quartz particles in a spigot product from a free-settling classifier will have a diameter 3.75 times the diameter of the galena particles in the same product. If hindered-settling conditions prevail in the sorting column, an even greater difference between the sizes of heavy and light minerals will exist. The *hindered-settling ratio* of quartz to galena is about 6.

Hydraulic classifiers have their principal use in preparing feed for shaking tables (gravity concentrators), since a table operates best on feed which has been classified. These classifiers are not so important in ore dressing as they used to be, because concentrating tables are no longer of major importance in milling operations. Hydraulic classifiers function efficiently only on relatively coarse sands (for example, ¼ inch down to 65 mesh) and are not applicable to the classification of fine material (for example, −100 mesh) or "slimes."

Many types of classifiers, washers, thickeners, etc., are used in milling operations; the number and variety are so great that it is difficult to present an orderly classification of these machines. We shall not have the space for an exhaustive discussion of this topic and shall consider only two important and widely used pieces of equipment—the mechanical classifier and the Dorr thickener.

*Mechanical classifiers* are used to make a sand-slime separation; i.e., they make only two products, an undersize ("overflow," "slime") and an oversize ("sand"). The Dorr classifier (Fig. 11) consists of an inclined rectangular tank containing one or more reciprocating rakes. Pulp to be classified is fed into the tank, and the liquid forms a pool in the lower end of the tank in which the classification proper takes place. As the pulp continues to feed into the tank, the liquid overflows a weir at the bottom end, carrying with it all the material which is too fine to settle against the uprising current in the pool of water. Particles coarse enough to settle to the bottom of the tank are carried up the sloping bottom by the action of the rakes and discharged at the upper end. The size of material carried away by the overflow depends upon a number of factors—the height of the weir, amount of feed entering the classifier, pulp density in the classifier, size of feed particles, etc. It is commonly reported that a classifier of this type will overflow, for example, −150- or −65-mesh material. This statement, of course, is not strictly true, because a classifier adjustment which permitted the overflow of a 65-mesh galena particle would result in the overflow of much larger quartz particles.

The Akins classifier is similar to the Dorr in principle, but it utilizes a semicylindrical tank; and the sands are carried up by means of a revolving spiral ribbon instead of reciprocating rakes.



(Courtesy The Dorr Company, Inc., New York)

FIG. 11.—Drag Classifier.

Mechanical classifiers are most commonly used to classify a ball mill or rod mill discharge into finished product and oversize to be returned for more grinding (closed circuit).

The *Dorr thickener* is widely used for thickening or partially de-watering pulps. In many instances it becomes necessary to remove some of the water from an ore-water pulp and thus increase the pulp density. Most pulps contain finely divided mineral particles of such size that they settle very slowly in water. The thickener is designed to aid this settling in such a way as to permit the continuous resolution of a pulp into two products—clear water (overflow) and a thickened pulp (spigot product).

A cross-section of a Dorr traction thickener is shown in Fig. 12. The thickener consists of a circular tank with a bottom sloping slightly toward the center where the pulp discharge or spigot is located. The pulp to be thickened is fed into the thickener near the top of the tank at the center; and, as the pulp slowly diffuses into the tank, the suspended solids settle to the bottom. The feed to the thickener is ad-

## TABLE 10 *

### PERFORMANCE OF DORR CLASSIFIERS

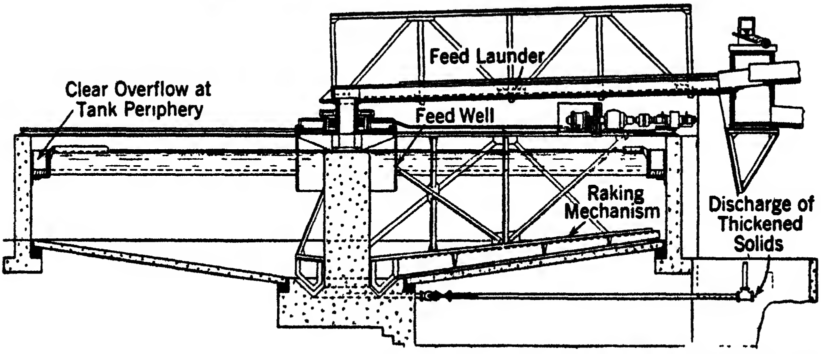
| Size and Type | C.D. | 4′6″ × 16′4″ | D.D. | S. 3′ × 15′9″ |
|---|---|---|---|---|
| Slope of bottom, inches per foot | 2.75 | 3 | 1.5 | 3 |
| Strokes per minute | 22.5 | 28 | 30 | 27 |
| Moisture %, feed | 78.3 | 25.4 | 55 | 48 |
| Moisture %, sand | 31.0 | 15.6 | 30 | 20 |
| Moisture %, overflow | 83.9 | 65.0 | 95 | 53 |
| Tons overflow, 24 hours | 134 | 150 | 400 | 280 |
| Tons sand, 24 hours | 270 | 560 | 2065 | 435 |
| Tons total feed, 24 hours | 404 | 710 | 2465 | 715 |
| Size at which separation is wanted, millimeters | 0.208 | 0.295 | 0.295 | 0.833 |
| Efficiency at separation size (*a*) | 73.6 | 35.5 | 53.5 | 69.6 |

* Taggart, A. F.: Handbook of Ore Dressing; John Wiley & Sons, New York, 1927. Reprinted by permission.

C. D. Standard duplex (2 rakes) 4′6″ × 16′ – 18′.

D. D. Heavy duplex 6′ × 18′. S. Simplex (simple rake).

(*a*) The efficiency is defined as the ratio expressed in percentage of the weight of classified material in the overflow to the weight of classifiable material in the feed.



(*Courtesy The Dorr Company, Inc., New York*)

FIG. 12.—Section Through a Dorr Thickener.

justed so that the pulp never builds up above a certain level. The surface liquid near the periphery of the tank is a layer of clear water (in most cases; *vide* Table 11), and this overflows into a circular launder surrounding the edge of the tank. A raking mechanism causes the rakes to sweep around slowly on the bottom of the tank. These rakes aid somewhat in the sedimentation of the solid material and sweep the thickened pulp toward the center of the tank bottom where it is removed. In many instances it is necessary to add a floc-

TABLE 11 *

PERFORMANCE OF DORR THICKENERS

| | Flotation Feed | Flotation Feed | Flotation Concentrate | Flotation Concentrate | Cyanide Pulp | Cyanide Pulp |
|---|---|---|---|---|---|---|
| Size, diameter × depth, feet...... | 20 × 9 | 200 × 17 | 30 × 6 | 40 × 10 | 28 × 10 | 33 × 10 |
| Power installed, horsepower..... | 2 | 2.5 | 2 | 5 | ..... | ..... |
| Speed of rakes, min. per. rev. . | 5.5 | ..... | 3 | 5 | 7 | 8 |
| Speed, peripheral feet per minute.. | 11.4 | 14 0 | 31.4 | 25 | ..... | ..... |
| Feed, tons solid per 24 hours....... | 300 | 3500 | 38–44 | 125 | ..... | ..... |
| Feed, % through 200 mesh....... | 61 | 89 | 64 | ..... | 72 | 64 |
| Feed, % solid..... | 12–25 | 16 | 40 | 15 | 20 | 9 |
| Spigot product, % solid........... | 20–34 | 24 | 60 | 60–65 | 50 | 67 |
| Overflow, % solid.. | 10 | clear | 0.2 | clear | clear | clear |
| Tank area, square feet per ton of solid feed per 24 hours.......... | 1.0 | 9.0 | 17.2 | 10.0 | 4.9 | 15.5 |
| Tank area, square feet per gallon of water overflowed per minute..... | 3.5 | 30.2 | 166 | 11.9 | 9 4 | 10 |
| Rising current, millimeters per second........... | 0.17 | ..... | 0.004 | 0.05 | 0.06 | 0.06 |
| Recovery of liquid, %............ | 52.3 | 39.7 | 41.7 | 89.7 | 75 | 95.2 |

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*** Taggart, A. F.: Handbook of Ore Dressing; John Wiley & Sons, New York, 1927. Reprinted by permission.**

culating agent (lime, for example) to promote the settling of fine slime. Such a substance causes the fine particles to agglomerate into flocs which settle more rapidly than the individual dispersed particles would.

*Filters* are used in many dressing and milling operations when (1) it is desired to obtain the solid material from a pulp in substantially dry form (dry enough to be shoveled, for instance) or (2) it is desired to separate the liquid as completely as possible from the solid in order that the liquid may be treated. An example of the first case would be the preparation of flotation concentrates for shipment, and an example of the second would be the recovery of gold-bearing solution from a cyanide pulp.

All metallurgical filters contain a canvas (or other fabric) diaphragm which serves as the filtering medium, and the pulp is forced through the filter either by suction or pressure. The clear liquid passes through the filter, and the suspended solids remain on the filter cloth in the form of a filter cake. Vacuum or suction filters may be continuous or intermittent in operation. Pressure filters (filter presses) are invariably of the intermittent type.

The *Oliver filter* is a continuous filter made in the form of a cylindrical drum with filter cloth stretched over the convex surface of the drum. The drum rotates slowly about a horizontal axis, and the lower part of the drum is immersed in a tank containing the pulp to be filtered. Arrangement of pressure and suction pipes on the interior of the drum permits the application of suction to the filtering surface which dips into the tank and to most of the surface outside of the tank. As the filter passes through the tank, it picks up a layer of solid material and emerges from the tank carrying a layer of filter cake. The exposed cake is still under suction as it emerges from the tank; and if necessary, it may be washed by playing a spray of water upon it. When the filter cake has made almost a complete revolution, it encounters a zone where air pressure instead of suction acts upon the inner surface of the filtering cloth. This pressure loosens the filter cake; the cake is dislodged on to a conveyor belt or into a bin; and the cleaned filter cloth enters the pulp tank to pick up another load. The *American filter* is a similar continuous vacuum filter, but the filtering cloths are mounted on both sides of disk-shaped filter leaves which revolve about a horizontal axis with the lower part of the disk dipping into a pulp tank.

Intermittent filters usually consist of a number of filtering leaves which are simply rectangular frames carrying filter cloth on the outer surface. A number of these leaves are mounted in a suitable tank, and pulp is either (1) pumped into the tank under pressure, or (2) drawn in by means of a suction in the interior of the leaves. In either case, the clear liquid passes through the filter cloth and out through pipes leading from the interior of each filter leaf. The solid material forms a cake on the outside of the leaf. Filters of this type must be dismantled whenever it is necessary to remove the filter cake.

Intermittent filters have greater filtering area for a given floor space than continuous filters, and they usually require less water and permit more thorough washing of the filter cake. Their great disadvantage is the fact that they are not continuous. When valuable material is being filtered, the intermittent filter may be kept locked at all times, except during the cleaning, and this prevents possible theft.

Filtering is a comparatively slow and expensive operation, and in most cases a pulp is thickened before it goes to the filter (*vide* Fig. 16) in order to take as much of the load as possible off the filter. The feed to filters ordinarily contains about 50 per cent moisture, and the moisture content of the filter cake varies from 6 per cent to 18 per cent.

## CONCENTRATION

With the exception of some magnetic separators and hand picking operations, all the common concentrating devices act upon a mineral-water pulp. This pulp is prepared by the various methods which we have mentioned in previous sections; crushing and grinding liberate the mineral particles, and screening, classification, thickening, etc., put the pulp in the condition best suited for a particular concentration process. The feed to a concentrating system is called the *heads,* and the concentrating machine produces one or more rich concentrates, a tailing or discard, and possibly a *middling* which requires further treatment before it can be resolved into a concentrate and a tailing. A *true middling* contains ore and gangue minerals which are still locked together; and when such a product is separated, it is returned to the grinding circuit for further comminution.

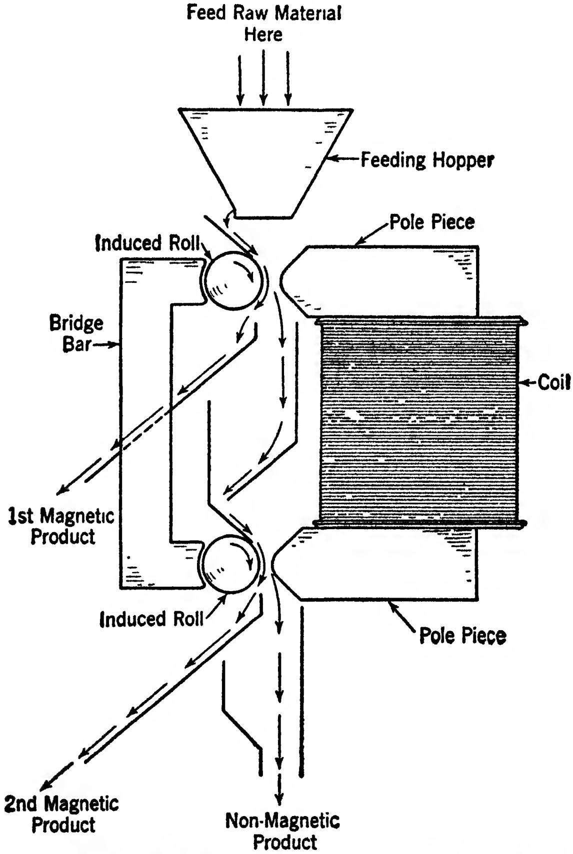
The separation of mineral mixtures into two or more products is possible because of the difference of certain properties of these minerals. The difference in color and luster is utilized in hand picking; difference in density permits separation by various methods of gravity concentration; differences in magnetic properties permit the use of magnetic separation; and the differences in surface properties of minerals account for the separations made by the froth-flotation process.

**Hand picking** is practiced in relatively few instances; but when conditions are suitable, it may prove to be a very economical process. The ore which is suited for hand picking must be such that the coarse ore shows marked segregation into high-grade pieces and/or large pieces of barren waste. The hand-picking operation usually follows the coarse crushing stage. The ore from the coarse crusher is passed over a slowly moving conveyor belt or table between rows of pickers, and these operators pick off either pieces which are high-grade ore or those which are obviously barren waste. Usually each picker selects only one type of material; and if two products are removed, there are two groups of pickers—one for each material. The ore is usually sprayed with water to wash off dust and make the recognition of minerals easier. The removal of waste in this manner raises the grade of the mill feed (material left on the belt or table by the pickers) and decreases the volume of mill feed. Removal of high-grade ore also decreases the volume of mill feed and may give a product which is rich enough to ship to a smelter without milling. The picker removes the pieces from the belt and throws them into bins located below the picking floor from which they may be removed when desired. In most mining operations, the miners sort ore from waste as completely as possible before the ore is brought to the surface. Satisfactory hand-sorting is possible only when the pieces to be picked out are larger than 3 or 4 inches in diameter, but still small enough to be lifted easily.

**Magnetic Separation.**—Figure 13 illustrates the action of one type of magnetic separator designed to separate a magnetic mineral from non-magnetic material. Magnetic separators are used for the removal of magnetite from other minerals, roasted pyrite from sphalerite, hematite from silica, etc. The magnetic separation method has never had wide application in the ordinary milling of non-ferrous ores, but it may eventually prove to be an important process in the beneficiation of iron ores. Magnetic separators have found considerable application in the processing of non-metallic minerals—monazite sand, garnet, rutile, zircon, etc. Most magnetic separators operate on dry materials, but a few have been developed to take a wet feed.

Heavy guard magnets are often used in mills to remove dangerous tramp iron from ore entering a crusher. Magnets have also been used to remove finely divided iron from pulp ground in a ball mill.

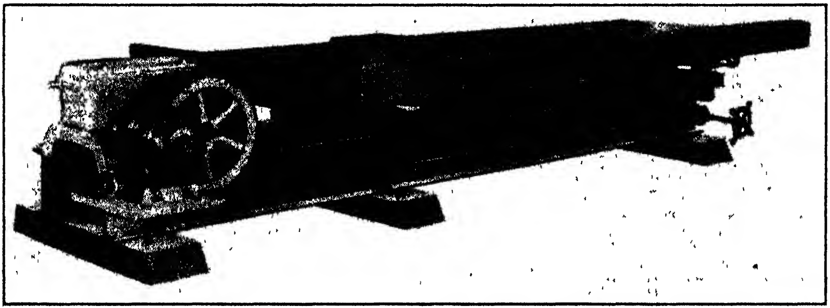
**Gravity Concentration.**—Before the advent of flotation, gravity concentration methods were the most important of all concentrating processes. During the period of extensive application of gravity separation, hundreds of different machines were designed to treat ores of various kinds, but we shall not have space to consider more than two or three typical gravity concentrators. The emphasis which is laid on flotation in modern milling practice should not lead to the belief that all gravity concentrators are necessarily obsolete—flotation is undoubtedly superior for most non-ferrous milling, but there are still many uses for which the gravity concentrator is best. Often flotation and gravity concentration can be used together to very good advantage.



*(Courtesy Dings Magnetic Separator Company, Milwaukee)*

FIG. 13.—Diagrammatic Sketch of a Magnetic Separator.

The miner's gold pan is the simplest of gravity concentrators, and it illustrates as well as any other the principle of *stratification* which is the basis of many gravity separators. The gold pan is a shallow steel pan having flaring sides; the usual size is 15 to 18 inches in diameter at the top and 2 to 2½ inches deep, with the side inclined from 30° to 80° to the bottom. In using the pan it is filled with the ore to be panned, the ore is covered with water, and the pan is shaken to allow the minerals to stratify. It is important to note that this stratification differs from the arrangement produced by free- or hindered-settling classification. When the mixture of minerals is shaken in the pan, the heavy minerals regardless of their size settle to the bottom of the pan and the lighter materials remain on top. Small particles of light mineral work their way into the interstices of the mass and progress toward the bottom, and the larger particles of light material work towards the top of the mass. Hence, the pan is most effective in separating small, heavy minerals from coarse, light minerals; the (hydraulic) classifier has the opposite effect, since a classifier tends to put small, heavy minerals and coarse, light minerals into the same product. This fact can be easily demonstrated by panning quartz-galena mixtures. A classified sample will pan more easily and give a cleaner concentrate than a screen-sized sample.



*(Courtesy Denver Equipment Company, Denver)*

FIG. 14.—A Wilfley Table, Rear View.

After the minerals have been stratified in the pan, the operator scrapes or washes the top material out of the pan, then shakes it again, washes more material off the top and continues until only a concentrate of heavy minerals remains in the pan. The gold pan is a very useful tool for testing purposes, both in the field and in the laboratory.

The *shaking table* is probably the most widely used gravity concentrator, and Fig. 14 shows the Wilfley table which is one of the common types. This table consists of a flat deck usually covered with linoleum and having on its surface a number of parallel wooden strips or riffles. These riffles are thickest (vertical dimension) near the head end of the table. They gradually become thinner until they disappear entirely before they reach the other end of the table (Fig. 14). The table is set so that the deck slopes slightly in a direction at right angles to the riffles. The motion of the table is a series of short reciprocations in the direction of the riffles; the forward stroke away from the head end is relatively slow, and the back stroke is more rapid. Feed enters a feed box in the corner (Fig. 14), and wash water enters all along the upper side of the table (the side nearest the observer in Fig. 14). A film of water is flowing across the riffles at all times.

The various factors which effect the separation of minerals in the table feed are as follows:

1. The shaking action of the table causes the bed of minerals in the riffles to stratify in the same way as they do in a gold pan. Thus, the heavy minerals remain in the bottom of the riffles where they are protected from the cross current of wash water. The light, coarse minerals, however, ride on top of the material in the riffles and are carried over by the wash water and flow off on the side of the table. The fact that the depth of the riffles gradually diminishes as the material moves away from the head end allows the removal of successively finer and finer light mineral.

2. The slow forward stroke of the table deck followed by the rapid return stroke causes the minerals to move parallel to the riffles and away from the head end of the table. The heavy minerals move faster and farther per stroke than the light minerals because (*a*) of their greater inertia, and (*b*) they are resting directly on the deck of the table while the light minerals are resting on a loose bed of heavier minerals.

3. The washing action of the stream of water across the riffles tends to carry the minerals off the side of the table. Light minerals are moved more readily than heavy minerals by water currents.

The net result of these various factors is that the heavy mineral concentrate tends to ride off the table near the "front" or concentrate end of the table, and an operating table will show a "streak" of concentrate roughly parallel to the line formed by the ends of the riffles. The light tailing flows off the side of the table near the head end, and somewhere between the tailing and concentrate cuts a middling is discharged. The fact that stratification in the riffles is an important factor in segregating heavy minerals from light minerals means that the table operates most efficiently on a classified feed.

Tables are sand concentrators; i.e., they work best on material from about 2.5 mm. in diameter down to about 65 to 100 mesh. They cannot successfully handle "slimes" or very finely divided material (for example, $-100$ mesh).

*Jigs* are gravity concentrators designed for handling material which is too coarse for table feed (1.5 inch in diameter down to 2 mm.). A jig consists essentially of a screen which supports a bed of ore (under water) and is provided with means of bringing the ore bed into partial suspension at regularly recurrent intervals. This may be accomplished by suddenly dropping the screen for a short distance (movable-screen jig) or by forcing a current of water up through the screen (fixed-screen jigs). After each pulsation the ore is allowed to settle back on the screen, and after a few repetitions of the pulsation-subsidence cycle, the minerals in the bed stratify with the light mineral (tailing) on top and the heavy mineral (concentrate) at the bottom. Jigs are operated by continually feeding material into the screen compartment and removing the light tailing from the top of the bed to permit the layer of concentrate to build up. After a sufficient quantity of concentrate has accumulated, it may be removed either manually or automatically. Theoretically, a jig will produce tailing and concentrate; but because of the coarse size of the material, either one of these may be really a middling which must undergo further grinding and concentration. A jig also makes a *hutch product* which consists of the fine, heavy minerals which pass through the meshes of the screen.

The use of jigs in base-metal milling is largely confined to cases where liberation is possible in coarse sizes. Jigs are used in the milling of some gold ores, and in many placer operations.

*Sluices* or *sluice boxes* are long inclined troughs or launders containing riffles in the bottom. These riffles may have one of a number of different forms, and their purpose is to provide a lodging place for heavy minerals. The material to be concentrated is carried down through the sluices on a current of water; coarse, light material is washed through the sluice and carried out the end, and small, heavy minerals lodge in the crevices formed by the riffles and are held in the bottom of the sluice. Most sluice boxes are intermittent in operation; when the time comes for the "clean-up," the feed is shut off, the riffles are removed, and the heavy concentrate is washed out of the sluice.

Sluice boxes are widely used in placer operations for concentrating such minerals as gold, platinum, and cassiterite from stream gravels. Sluice boxes for washing fine material often have blankets, corduroy cloth, or corrugated rubber in the bottom instead of riffles.

**Flotation.**—The importance of flotation in modern ore-dressing practice is due to a number of factors which have caused it to supplant gravity concentration in the great majority of cases. Some of the reasons for the switch to flotation concentration are listed below.

1. The necessity for mining and treating ores in which the ore minerals were finely disseminated required finer and finer grinding to liberate the values. The resulting "slimes" were difficult to handle by gravity methods, and before the advent of flotation, scores of elaborate and intricate devices were invented in a vain effort to concentrate finely divided mineral. In modern flotation practice, material as fine as a theoretical "2000 mesh" has been successfully treated.

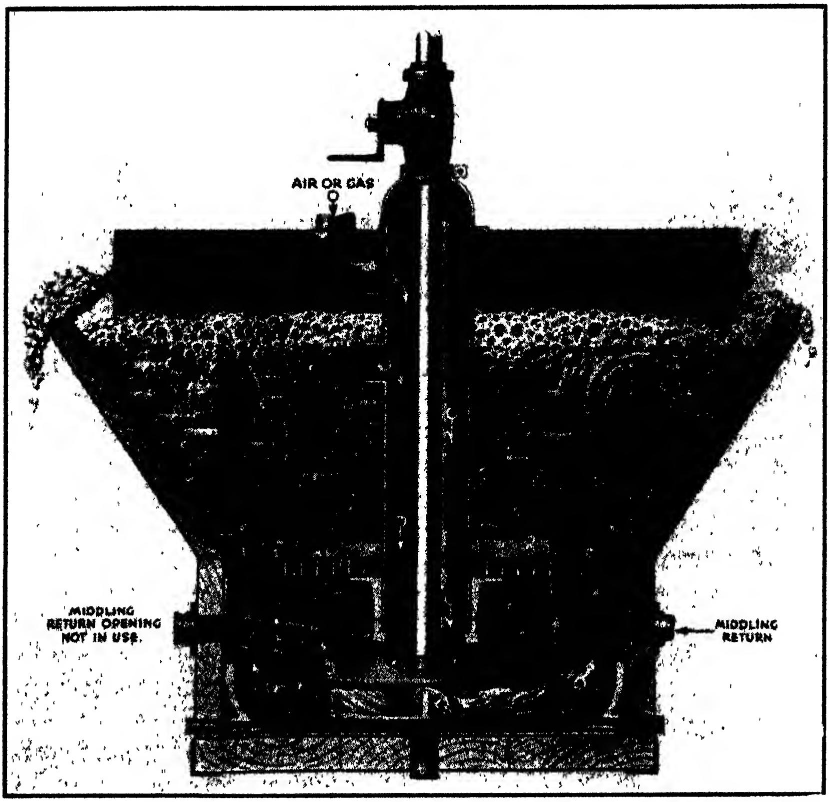
2. In many complex ores it was desirable to separate the valuable ore minerals into two or more separate concentrates to facilitate subsequent chemical treatment; galena-sphalerite, pyrite-sphalerite, and other mineral separations were desired; but the "spread" of specific gravity between these minerals was so small that gravity methods were unsatisfactory. Differential flotation has solved many of the milling problems connected with complex ores.

3. The natural tendency of finely ground sulfide minerals to float on the surface of water was a hindrance to such gravity operations as tabling, but this tendency was turned to good advantage in the flotation process.

4. In most cases ore minerals can be floated if they are ground below 48 or 65 mesh and are liberated from gangue minerals. Flotation concentration can be used successfully over a wide range of particle sizes, and flotation feed does not ordinarily require elaborate preliminary treatment (screening, hydraulic classification, etc.). This, together with the fact that flotation machines require less floor space and head room than gravity machines, has made it possible to build smaller, simpler, and more efficient mills.

5. Sulfide ores are by far the most important type of non-ferrous ores, and most sulfide minerals respond readily to flotation treatment.

Figure 15 is a cross-section of a mechanical flotation cell. The ore-water pulp feeds into the cell and is kept agitated and in circulation by means of the impeller mounted at the bottom of the vertical shaft. The rotating impeller creates vacuum enough to draw air down the standpipe surrounding the impeller shaft, and the impeller disperses the air throughout the pulp in the form of small bubbles. The flotable minerals are carried upward by the bubbles and eventually collect in the froth above the pulp in the machine. Non-flotable minerals remain in the body of the pulp, since they have no tendency to adhere to the rising bubbles. Automatic scrapers remove the mineral-laden froth which contains the concentrate, and after the values have been removed, the barren pulp containing the tailing flows out of the cell. Flotation cells are usually operated in series, with the pulp flowing continuously from one cell to the next, giving up some flotable mineral in each cell. The size and number of cells and the rate of pulp feed are adjusted so that the last cell in the series makes a finished tailing; i.e., practically all the flotable minerals are removed from the pulp before it discharges from the last cell.



*(Courtesy Denver Equipment Company, Denver)*

FIG. 15.—Section of a Sub-Aerated, Mechanical Flotation Cell.

Many types of flotation machines are in use. Other mechanical machines differ from the one illustrated in certain details, and often they require that the air be blown in under pressure. Pneumatic machines consist of a cell containing a porous bottom—air is forced through the bottom of the cell, and the rising bubbles serve to agitate the pulp as well as to aerate it.

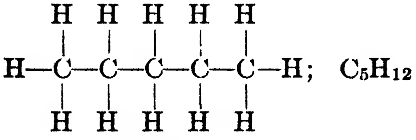
The questions of the action of various flotation reagents upon minerals, the different reagents used, the flotation of non-sulfide minerals, etc., are far too lengthy for a detailed discussion here. We shall merely consider some of the principal types of reagents used for sulfide flotation and illustrate their use in one or two simple cases.

1. *Frothers.* If air is bubbled through water, the bubbles break up as soon as they reach the surface and do not form a stable froth. In order to cause a layer of froth to form on the surface of a pulp, it is necessary to add a reagent which serves to stabilize the froth and hold the minerals until the froth can be scraped off into the concentrate launder. The most common frothers or frothing agents are pine oil and cresylic acid. Small amounts of these substances in a pulp lower the surface tension of the liquid and cause bubbles to form a stable froth—the frothers perform only this one function. They have practically no effect on the flotability of the minerals in the pulp.

2. *Collectors* (collecting agents, promoters, "oilers"). Some minerals, such as galena, will float quite readily without the addition of any collecting agent to the pulp; others, such as sphalerite, ordinarily cannot be floated without first adding a collector which alters the mineral surface in such a way as to cause it to adhere to an air bubble. Many investigators doubt that even galena is naturally flotable if absolutely clean and unaltered at the surface; but whether a sulfide mineral has any "natural" flotability or not, the practice of using collecting reagents is universal.

The exact mechanism of the action of collectors is still obscure, but it appears to be fairly well established that if a mineral is to float it must have an air-avid or water-repellent surface; if it is not to float, it must have a water-avid surface. Clean glass has a water-avid surface and is easily wetted by water. If a drop of water is placed on a clean glass plate, it immediately spreads out and completely wets the glass surface. A drop of water placed on the surface of solid paraffin, however, remains as a coherent drop with as little surface as possible in contact with the paraffin. We say, then, that the paraffin has an air-avid or water-repellent surface; such a surface seems to prefer contact with air to contact with water, and a particle with a surface of this sort would adhere to an air bubble and float out of a flotation pulp. The object of all reagent additions in flotation is to form a water-repellent (paraffin-like) surface on the minerals to be floated, and a water-avid surface (like that of clean glass) on the minerals which are not to float.

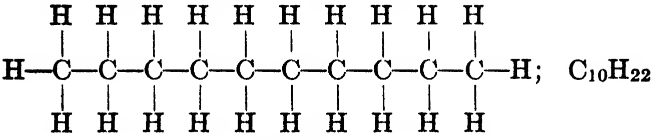
Ordinary paraffin wax consists of a mixture of solid hydrocarbons of the paraffin or methane series. These compounds consist of carbon and hydrogen atoms linked in a straight chain (branched-chain isomers exhibit similar properties, but for simplicity we shall discuss only the straight-chain compounds) as, for instance:



$$\begin{matrix} & H & H & H & H & H & \\ & | & | & | & | & | & \\ H- & C- & C- & C- & C- & C & -H;\quad C_5H_{12} \\ & | & | & | & | & | & \\ & H & H & H & H & H & \end{matrix}$$

Pentane

or

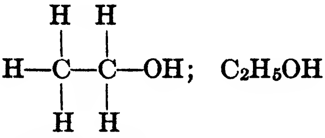


$$\begin{matrix} & H & H & H & H & H & H & H & H & H & H & \\ & | & | & | & | & | & | & | & | & | & | & \\ H- & C- & C- & C- & C- & C- & C- & C- & C- & C- & C & -H;\quad C_{10}H_{22} \\ & | & | & | & | & | & | & | & | & | & | & \\ & H & H & H & H & H & H & H & H & H & H & \end{matrix}$$

Decane

Other molecules have even longer chains, and all these hydrocarbon-chain molecules are strongly water-repellent.

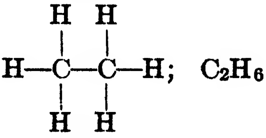
Now, an alcohol may be formed from one of the paraffin hydrocarbons by replacing one of the hydrogens by the hydroxyl group (OH) so that we have, for example,



$$\begin{matrix} & H & H & \\ & | & | & \\ H- & C- & C & -OH;\quad C_2H_5OH \\ & | & | & \\ & H & H & \end{matrix}$$

Ethyl alcohol

corresponding to the hydrocarbon



$$\begin{matrix} & H & H & \\ & | & | & \\ H- & C- & C & -H;\quad C_2H_6 \\ & | & | & \\ & H & H & \end{matrix}$$

Ethane

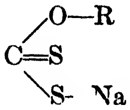
The monovalent radical formed by removing one hydrogen atom from a paraffin hydrocarbon is called an alkyl group or radical; and if we represent the alkyl group by the symbol R, we may designate any of the monohydroxy, primary saturated alcohols by the notation

$$ROH$$

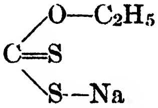
Now these alcohols react with $CS_2$ and NaOH to form *xanthates*, which are the most widely used collecting agents. The reaction is:

$$ROH + CS_2 + NaOH \rightarrow H_2O + ROCSSNa$$

where the structural formula of the xanthate is



If R represents the ethyl group, we have sodium ethyl xanthate



or we may have higher xanthates such as butyl xanthate, amyl xanthate, etc., in which the alkyl radical has a longer chain of carbon atoms.

These (solid) sodium xanthates dissolve and ionize in water into $Na^+$ ions and singly charged, negative xanthate ions. When PbS, for instance, is immersed in a water solution containing dissolved xanthate, it appears that insoluble lead xanthate is formed on the surface owing to attachment of xanthate ions to the lead atoms on the surface of the particle. This coating of lead xanthate is oriented so that the long hydrocarbon chains point outward, giving a water-repellent surface which is effectively the same as a paraffin surface. When such a coating has been formed, the particle is said to be "oiled" or treated so that it is ready to be floated.

Many other reagents have been used for collectors, although xanthates are the most common. All collector molecules (or ions), however, have the same type of structure; a reactive end which can attach to the mineral particle, and a water-repellent end which produces the "oily" coating. Collectors of this type do not ordinarily attach themselves to gangue particles, and so the gangue particles do not float. The discussion above presents a simplified version of the action of collectors, but the problem is by no means definitely settled, nor is there any detailed, comprehensive theory that explains the action of collectors in all cases. The same statement applies with even more force to the theories developed to explain the action of depressing and activating agents.

3. *Depressing agents* are those substances (usually inorganic) whose presence in the pulp prevents the anchoring of the collector

molecules on a mineral surface and thus inhibits flotation of the mineral. Activating agents are those reagents which have the opposite effect; they affect the surface of minerals in such a way that it is easy for the collector atoms to become attached. Differential flotation, or the removal of two or more minerals as separate concentrates, is made possible by the use of suitable depressing and activating agents. One of the most common applications of differential flotation is the treatment of lead-zinc (galena-sphalerite) ores. NaCN is a depressant for sphalerite but not for galena, so that if NaCN and xanthate are added to a flotation pulp, the galena floats and the sphalerite remains in the tailing. If the tailing from the lead cells is treated by adding $CuSO_4$ (an activating agent for ZnS) in the presence of more xanthate, the ZnS becomes flotable and can be collected as a zinc concentrate substantially free from lead. NaCN and CaO are also depressing agents for pyrite ($FeS_2$).

4. *Conditioning agents* are those substances added to the pulp to maintain the proper pH (measure of acidity or alkalinity of the pulp) to "protect" such salts as NaCN which would decompose in an acid circuit, etc. $Na_2CO_3$ and CaO are the most common conditioning agents, since most flotation pulps should be alkaline.

The amount of reagent used in flotation practice is usually very small in comparison with the amount of ore treated. Reagent consumption is commonly given as pounds of reagent per ton of ore treated, and the reagents consumed in floating typical lead-zinc ore are about as follows:

| | |
|---|---|
| Frothers (pine oil, cresylic acid) | 0.1 –0.2 lb./ton |
| Depressant (NaCN) | 0.1 –0.3 lb./ton |
| Activator ($CuSO_4$) | 0.8 –1.2 lb./ton |
| Conditioner ($Na_2CO_3$) | 1.0 –2.0 lb./ton |
| Conditioner (CaO) | 2.0 –4.0 lb./ton |
| Collector (xanthate) | 0.01–0.2 lb./ton |

Flotation pulps must undergo a certain conditioning period before the froth is removed in order to allow the reagents to act on the mineral surfaces. Usually the pulp is agitated for 10 to 20 minutes in a conditioning tank before it enters the flotation cells.

The importance of flotation as an ore dressing method may be seen from the fact that, in 1929,[10] 268 plants treated more than 65,000,000 tons of ore by flotation in the United States.

Figure 16 is a schematic flow sheet which illustrates nicely the flow of material in a small mill treating lead-zinc ore. A brief study

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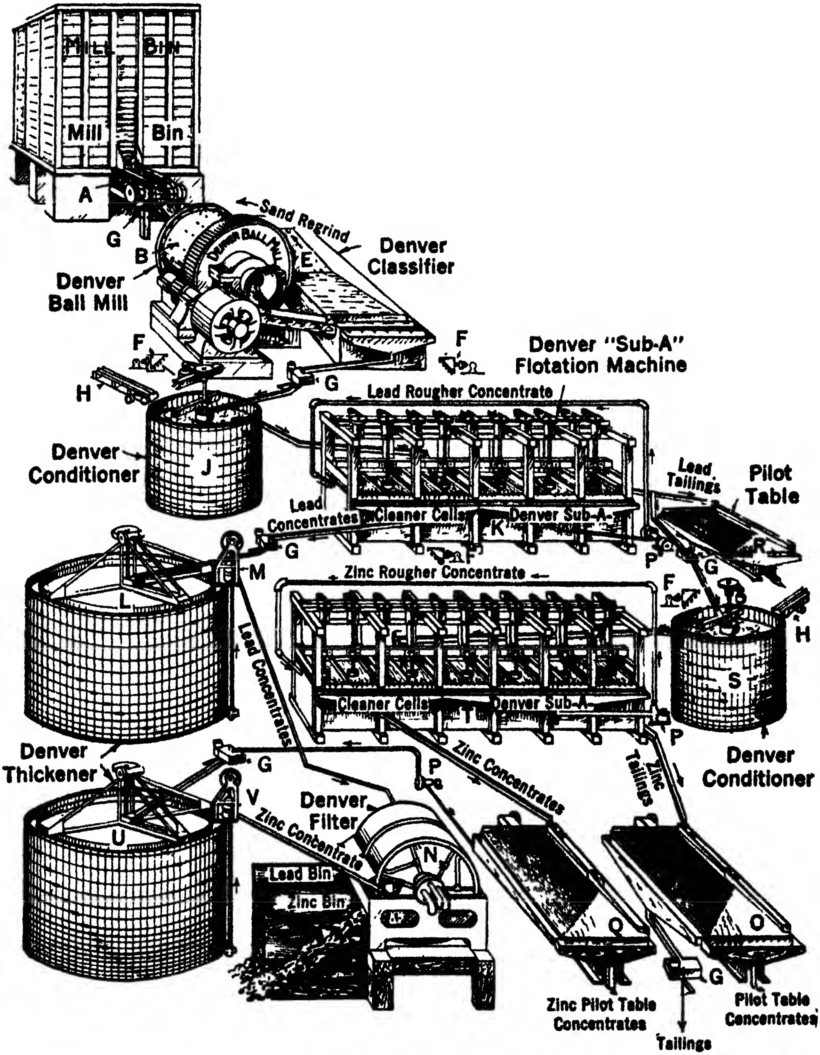
[10] Gaudin, A. M.: Flotation, McGraw-Hill Book Co., New York, 1932.

of this figure will show some of the applications of the equipment we have been considering.



*(Courtesy Denver Equipment Company, Denver)*

FIG. 16.—Schematic Flowsheet Showing the Flow of Material in Lead-Zinc Differential Flotation.

The mill bin holds ore which has passed through the primary and secondary grinding stages and which is ready for fine grinding. An automatic feeder (*A*) feeds the ore to the ball mill-classifier unit, and the classifier overflow enters the conditioning tank (*J*). Here the necessary reagents for depressing sphalerite and floating galena are added, and after conditioning, the pulp enters the bank of lead flotation cells (*K*). There are ten cells in this bank, and the pulp flows through the cells from left to right with the tailing discharging from the last cell on the right. As the pulp proceeds from left to right, it becomes leaner in valuable mineral; and the "grade" of the concentrate becomes lower. Consequently, only the concentrate from the first four cells (*cleaner cells*) is taken as a finished product. The concentrate from the last six *rougher cells* enters the first cleaner cell. The purpose of the rougher cells is to produce a low-grade (finished) tailing, even though considerable gangue may be carried into the concentrate; the purpose of the cleaner cells is to make a high-grade (finished) concentrate. Although the tails from the cleaner cells are high in lead, this lead is recovered in the roughers. The "cleaner tails" and "rougher concentrate" are really middlings as far as this operation goes. Note that the conditioner discharge enters the last of the cleaner cells.

The lead tailings (still carrying the zinc, of course) pass over the pilot table (*R*) and then into the conditioning tank (*S*) where the activator for ZnS and more collector are added. The pilot table is used principally as a check on the grinding and flotation performance—the appearance of the concentrate streak on the table warns the operator at once if excessive amounts of lead begin to pass through the lead circuit.

After conditioning (*S*) the zinc pulp enters the last cleaner cell in a bank of twelve zinc flotation machines (*T*). The zinc cleaner concentrates pass over a pilot table (*Q*), and the zinc rougher tailings pass over another pilot table (*O*) and out to the discard. Lead and zinc concentrates each go to a thickener (*L*, *U*), and the spigot products from this thickener go to a two-compartment filter (*N*) which produces the two finished concentrates ready for shipping.

Other important features shown on this diagram are the sand pumps (*P*), reagent feeders (*F*, *H*), and automatic samplers (*G*).

**Some Common Ore-Dressing Nomenclature.**—The ratio of the weight of the heads to the weight of concentrate produced is the *ratio of concentration*; thus, if 100 tons of concentrate are obtained from 2000 tons of feed, the ratio of concentration is 20 to 1. The *recovery* is the percentage of the valuable metal in the heads that is recovered in the concentrate. From the weights and assays of tailing and concentrate it is possible to compute the *theoretical* or *calculated* head assay. If this does not check the actual head assay, there must be a discrepancy in either the weights or assays of some of the material.

## BENEFICIATION OF IRON ORES

The various treatments given iron ores to prepare them for the blast furnace differ in many respects from non-ferrous milling methods. In non-ferrous milling the principal problem is to produce a high-grade concentrate from low-grade ore, but in dressing iron ores the problem of concentration may not be the most important consideration. Beneficiation of iron ores may be used for either or both of the following purposes:

1. To improve the analysis of the ore; i.e., build up the iron content and remove such impurities as silica, sulfur, and phosphorus.
2. To improve the physical properties of the ore to suit the demands of the iron blast furnace.

In non-ferrous milling the problem of concentration has been the main item, and the question of the physical shape (especially particle size) of the concentrate has been a secondary consideration. Flotation concentrate, for example, is ordinarily too fine for blast-furnace smelting; but the tendency has been to alter roasting and smelting practices to take care of the flotation concentrate. In ferrous metallurgy, however, the tendency is to adapt the beneficiation processes to the existing iron blast furnace, and it is doubtful that there will be much change in the smelting of iron ores to accommodate iron ore concentrates which are not adapted to the present furnaces—at least not for some time.

Iron ore is relatively high-grade and cheap as compared with non-ferrous ores. There are still available large amounts of direct-smelting iron ore which require no preliminary treatment. The dressing operations, therefore, must be quite cheap and simple if the beneficiated product is to compete with direct-smelting ores. As the richer ores are exhausted, however, it seems inevitable that beneficiation must become of greater and greater importance.

Ideal ore for the iron blast furnace should be high in iron and as low as possible in silica, sulfur, and phosphorus. It also should be of fairly uniform size—free of lumps much greater than 6 inches in diameter and also free of fine material. The question of proper physical condition is as important as chemical composition, and both items must be considered in any projected method of beneficiating ores.

During the ten years preceding 1934, about 25 per cent[11] of the ores shipped from the Lake Superior district had been beneficiated. About half of this had been merely crushed and screened; the other half was concentrate.

**Crushing and screening** constitute the simplest of the beneficiation processes, the purpose being simply to reduce the size of the ore to minus 6 inches. Ore of this sort is better than run-of-mine ore, which may contain lumps up to 3 feet in diameter. Several million tons of ore are crushed and screened annually in the Lake Superior district.

**Washing.**—Wash ore which is suitable for treatment by a washing operation is ore in which the coarse lumps consist of fairly pure iron oxide, and the fine material is low-grade and sandy. The fine material is washed away from the coarse high-grade by means of log washers, washing trommels, Dorr washers, bowl classifiers, etc. Normally about 5 million tons[11] of wash-ore concentrate are produced annually in the Lake Superior region.

**Jigging and magnetic concentration** are also used for treating certain iron ores to yield enriched concentrates. Both are very satisfactory in many cases, but the cost of treatment has prevented widespread application.

Finely divided ore or concentrate cannot be charged into the blast furnace unless it constitutes only part of an ore containing larger particles. If fine ore is to be used in any quantity, it must be *sintered* into the form of fairly coarse lumps. Sintering is an important step in many beneficiation processes—we shall consider it at greater length in the discussion of pyrometallurgy.

## TREATMENT OF PLACER DEPOSITS

Placer or alluvial deposits of ore minerals are formed by the weathering of rocks containing these minerals, and subsequent concentration by the action of running water. Minerals found in placers are those which are resistant to chemical attack and which have high specific gravities. The important ore minerals in placers are native gold and platinum, cassiterite ("tin-stone"), and occasionally cinnabar. Other heavy minerals often found in placers are magnetite, ilmenite, rutile, garnet, zircon, etc. ("black sand"), and monazite sand.

As we have mentioned, a placer deposit may often be profitably exploited even when the average tenor is far below the grade required

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[11] **Davis, E. W.: Iron-ore Beneficiation in the Lake Superior District; Transactions A.I.M.E., Vol. 112, page 824, 1934.**

for a commercial ore of the same metal. The reason for this is simply that much of the necessary "mining" and "ore dressing" has already been done by natural forces. Weathering and erosion liberate the ore minerals from the gangue so that comminution (the most expensive operation in milling) is unnecessary, and the action of running water results in a partial concentration of the valuable minerals.

The metallurgical processes involved in the exploitation of placers usually apply simple gravity concentrating devices such as sluice boxes and occasionally jigs and tables; flotation may eventually prove to be valuable in the recovery of very fine placer gold ("flour" gold). The most important factor in the treatment of low-grade placers is the problem of economically handling large tonnages of gravel and disposing of the washed tailing.

## EXERCISES

1. In a laboratory flotation test the following data were obtained:

| | Weight | Assay |
|---|---|---|
| Head | 2000 grams | 2.1% Pb |
| Tailing | . | 0.1% Pb |
| Concentrate | 70 grams | 55.1% Pb |

Calculate the ratio of concentration and recovery. Assuming that the weight of the tailing may be found by difference, calculate the theoretical head assay. To what might the discrepancy be due?

2. From Stokes' law calculate the terminal velocity of a piece of galena 1 mm. in diameter falling in water. Find the diameter of a piece of quartz that would have the same terminal velocity, and hence calculate the free settling ratio of quartz and galena, which in this case is the ratio of the diameter of the quartz particle to that of the galena particle.

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# CHAPTER X

## HYDROMETALLURGY

The first of the chemical extraction processes which we shall consider is hydrometallurgy, or the extraction of metals by leaching with an aqueous solvent. Hydrometallurgy is more closely related to ore dressing than any other extraction method, since the leaching cycle is often intimately associated with such operations as grinding, flotation, classification, thickening, and filtering. Particularly in the leaching of gold and silver are the ore dressing and hydrometallurgical operations so closely interrelated as to defy separate classification—the term "gold milling" usually refers to both ore dressing and hydrometallurgy.

In hydrometallurgical operations an ore or concentrate is brought in contact with a liquid (invariably an aqueous solution) which will dissolve the valuable metal without attacking the gangue. After the metal is in solution, it may be recovered by chemical precipitation, electrolytic precipitation, or evaporation of the solvent. The dissolution of the valuable metal is called leaching or lixiviation. In order that an ore may be treated by leaching, it must have the following characteristics:

1. The metal to be recovered must be soluble in the solvent used.
2. The gangue minerals must be insoluble in the solvent.
3. The dissolved metal must be readily recoverable from the solution.

Hydrometallurgy is the large-scale application of the process which is known in the chemical laboratory as *extraction*—the separation of a soluble substance from an insoluble one by means of a solvent.

Hydrometallurgy has many features to recommend it. It usually shows high extraction of the valuable metal. It requires very little fuel except when preliminary roasting is necessary. The equipment needed is relatively simple and inexpensive as compared with the equipment required for pyrometallurgical operations; and the principal expense is the cost of the necessary chemical reagents. In some processes the solvent is regenerated by the precipitation operation;

such a process is to be preferred to one in which the solvent must be constantly replenished from new material.

Hydrometallurgical methods have been making considerable progress in recent years owing both to the improvement in practice and to the fact that hydrometallurgy is particularly adapted to the treatment of many low-grade ores. At the present time about one-tenth of the copper, one-fourth of the zinc, one-half of the gold, and three-fourths of the cadmium produced in the United States are recovered by hydrometallurgical methods; and it is entirely possible that these figures will increase in the future. Likewise, hydrometallurgical processes for the recovery of other metals may be developed.

To offset the many obvious advantages of hydrometallurgy, there is that fact that many materials will not respond to treatment by leaching methods. Unless new solvents and a new technique can be developed, it is not likely that hydrometallurgy will ever displace some pyrometallurgical processes.

**Materials Suitable for Leaching.**—The types of material which are amenable to leaching may be roughly divided into two classes:

1. Low-grade ores.
2. Other materials.
    (*a*) Concentrate.
    (*b*) Calcine (oxidized material formed by roasting sulfide concentrates).
    (*c*) Matte (artificial sulfides of metals).
    (*d*) Speiss (artificial arsenides or antimonides).
    (*e*) Alloys.

The leaching of low-grade ore is done on a very large scale. The great bulk of ore treated requires a large amount of solvent. If the process is to be profitable, the solvent must be cheap. If possible it should be regenerated by the precipitation process. As a rule, the materials in the second group contain large amounts of valuable metal concentrated in a small bulk, and the cost of reagents required for leaching is not such an important factor.

Gold and silver ores, oxidized copper ores, and sulfide zinc ores are the most important types of ores which may be treated by leaching. The zinc ore requires preliminary treatment, but the other ores can often be leached directly. The important feature in ores of this type is mineralogical composition, for the metallic minerals must be soluble in the reagent used, and the gangue must be substantially insoluble. Native gold and silver can be dissolved, as can native copper. Other copper minerals which are quite readily soluble are cuprite, $Cu_2O$; malachite, $CuCO_3 \cdot Cu(OH)_2$; azurite, $2CuCO_3 \cdot Cu(OH)_2$; brochantite, $CuSO_4 \cdot 3Cu(OH)_2$; chalcanthite, $CuSO_4 \cdot 5H_2O$; and atacamite,

$CuCl_2 \cdot 3Cu(OH)_2$. As a general rule, the sulfides, tellurides, and selenides cannot be leached but must first be converted into other compounds.

Because of the small amount of metal in low-grade ores, the leaching cost must be kept down, and this means that the reagent must be cheap and effective when used in dilute solution. Although most leaching processes could be accelerated by heating the solvent, heating is seldom practicable in large-scale leaching.

Higher-grade material can be treated with more concentrated reagents; more efficient agitation can be employed, and the leach solution can be heated if necessary. The leaching of alloys is usually called *parting*.

**Crushing and Grinding.**—Ore to be leached must be crushed and ground to such a size that the solvent can readily act on the soluble minerals. For porous, oxidized ores, grinding is usually unnecessary; and material from a secondary crusher is often fine enough for leaching. Some ores, such as gold ores, may require very fine grinding before the minerals are exposed to the solvent.

For leaching purposes, ore products are divided into two classes—*sands* and *slimes*; and a rough distinction may be made as follows. Slimes are ore products which are so finely ground that they tend to pack into a vat or tank and prevent the free circulation of liquid through the interstices of the bed of ore. Sands are products which are coarse enough to permit circulation of the solvent through the void spaces between the ore particles. These two materials require different methods of attack. Sand leaching is done by allowing the solvent to percolate through the ore to be treated; slime leaching must be carried out by agitating the slime and solvent together in a suitable agitating tank.

**Water Supply.**—The fact that an adequate supply of water is necessary for leaching is obvious enough, but it is sometimes overlooked. Not only for hydrometallurgy, but also for ore dressing and pyrometallurgy, a reliable supply of water must be available. Often this is the most important factor to be considered in locating a metallurgical plant.

**Preliminary Treatment.**—For some materials preliminary treatment is unnecessary, and the material can be leached directly. Oxidized copper ores and certain gold ores can be leached directly, and alloys which are to be parted usually require no preliminary treatment.

Sometimes the ore is concentrated previous to leaching. This has the advantage of concentrating the valuable metal in a smaller bulk so that less solution is required and better leaching conditions are possible. Likewise, certain harmful minerals may be rejected in the tailing. Some gold ores are concentrated by flotation, and the gold is then leached from the concentrate. Sulfide zinc ores are also concentrated, but the concentrate cannot be leached directly but must first be roasted.

Roasting (heating in contact with air to oxidize sulfides to oxides or sulfates) is used on material to be leached for one or more of the following reasons: (1) to convert the metal into a soluble form, (2) to volatilize certain soluble impurities which would contaminate the solution, and (3) to render the metallic compounds porous so that they are readily attacked by the solvent. Roasting is a relatively expensive operation and can be used only on high-grade ore, concentrate, matte, or speiss. Roasting of low-grade sulfide ores is not practicable, but in a few cases the same effect is obtained by the natural *weathering* of the ore which results in the oxidation of sulfide minerals.

Most roasting is either an oxidizing or sulfatizing roast and is carried out in a multiple-hearth roaster, since the finely divided porous calcine is best suited for leaching operations. The compact sinter produced in Dwight-Lloyd roasting would be unsuitable for leaching. Weathering, or the slow oxidation of sulfides by the action of the atmosphere, is most commonly carried out by piling broken ore in heaps and allowing it to stand until the oxidation has converted the metal to a soluble form. The most important application has been to certain sulfide copper ores. Weathering is slow and inefficient, and ties up a large amount of metal for a long time. For these reasons it is seldom used at the present time. Two advantages of weathering in the treatment of copper ores are that it is cheap and that it converts most of the copper into the sulfate which can be dissolved in water.

Chloridizing roasting (roasting with NaCl or other chloridizing agent) has had considerable use in the past in the treatment of gold and silver ores, since such a roast converts these metals into soluble chlorides. The decline of this method in recent years is due primarily to the fact that cyanidation has proved to be more efficient than chloride leaching.

Some of the common applications of roasting previous to leaching are:

1. Zinc concentrates containing sphalerite are roasted in multiple-hearth furnaces, and the following reactions take place:

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$$

$$ZnS + 2O_2 \rightarrow ZnSO_4$$

The roasting temperature is low in order to have as much $ZnSO_4$ ("water-soluble zinc") as possible and also to prevent the formation of zinc ferrite, $ZnFe_2O_4$. The ferrites are practically insoluble in the solvents used ($H_2O + H_2SO_4$), so that any zinc in this form is not recovered. When the zinc mineral is *marmatite*, (Zn, Fe)S, it is very difficult to prevent the formation of a certain amount of zinc ferrite.

2. Gold tellurides are insoluble in cyanide, and ores or concentrates which contain tellurides are given an oxidizing roast which drives off the volatile $TeO_2$, leaving metallic gold.

3. Copper sulfides in low-grade ores may be oxidized by weathering and leached, but high-grade ores and concentrates are usually not treated by hydrometallurgical methods.

4. Speiss and mattes are usually crushed and given a dead roast (completely converted to oxide) before leaching. Probably the most extensive application of leaching to the treatment of mattes is in the various processes for refining nickel and nickel-copper mattes.

**Solvents.**—Any solvent to be used for leaching must possess the following qualifications:

1. The solvent must dissolve the ore minerals rapidly enough to make commercial extraction possible, and the solvent should not attack the gangue minerals. If the gangue is attacked, an excessive amount of the solvent will be consumed and the solution will be fouled with impurities.
2. The solvent must be cheap and readily obtainable in large quantities.
3. If possible, the solvent should be such that it can be regenerated in the precipitation process.

Many different solvents have been used for leaching purposes. Some have been very successful; others have not. The following list includes the most important solvents that have had commercial application.

1. *Water.* Water can be used for leaching such minerals as $CuSO_4$ and $ZnSO_4$. This is the solvent used when leaching in place or in heaps, and sometimes rainwater or natural mine waters are employed as solvents for copper sulfate. $ZnSO_4$ is leached in agitating tanks.

2. *Acids.* Dilute sulfuric acid is used in the dissolution of oxidized copper and zinc according to such reactions as

$$CuO + H_2SO_4 \rightarrow CuSO_4 + H_2O$$

$$ZnO + H_2SO_4 \rightarrow ZnSO_4 + H_2O$$

Concentrated sulfuric acid is used in parting gold-silver alloys (Doré bullion), and concentrated nitric acid may also be used for this purpose.

Hydrochloric acid has been used in the dissolution of zinc oxide, but is no longer used to any extent.

3. *Bases.* Ammonium hydroxide + oxygen, or ammonium carbonate + ammonium hydroxide are suitable for leaching native copper and copper carbonates. One advantage of this method is that it can be used on ores with a carbonate gangue which would consume too much acid in an acid leach. The copper in ammoniacal solution is precipitated as CuO by heat, and this drives off the $NH_3$ which can be recovered.

Sodium hydroxide is used in the Bayer process for the purification of bauxite. The calcined bauxite is digested with strong NaOH solution in an autoclave under about 60 pounds pressure, and the $Al_2O_3$ dissolves to form sodium aluminate:

$$2NaOH + Al_2O_3 \rightarrow 2NaAlO_2 + H_2O$$

4. *Salts.* In the presence of oxygen, NaCN or KCN dissolves gold and silver

$$4Au + 8NaCN + O_2 + H_2O \rightarrow 4NaAu(CN)_2 + 4NaOH$$

$$4Ag + 8NaCN + O_2 + H_2O \rightarrow 4NaAg(CN)_2 + 4NaOH$$

Other salts which are useful as solvents are $Na_2S_2O_3$ for dissolving silver chlorides; NaCl solution (brine) for the dissolution of silver and lead chlorides; and ferric salts for the dissolution of copper minerals. The use of ferric salts as solvents depends upon the fact that they are reduced to ferrous salts, as shown by the following reactions. Note that copper sulfides may be dissolved in this way

$$CuS + 2FeCl_3 \rightarrow CuCl_2 + 2FeCl_2 + S$$

$$Cu_2S + 2FeCl_3 \rightarrow 2CuCl + 2FeCl_2 + S$$

$$3CuO + Fe_2(SO_4)_3 \rightarrow 3CuSO_4 + Fe_2O_3$$

$$Cu_2S + Fe_2(SO_4)_3 \rightarrow CuS + CuSO_4 + 2FeSO_4$$

$$CuS + Fe_2(SO_4)_3 \rightarrow CuSO_4 + 2FeSO_4 + S$$

**Leaching Methods.**—Copper ores are sometimes leached *in place*; i.e., mine water is circulated through oxidized zones so that it may dissolve $CuSO_4$. In some cases the ore is broken and allowed to weather or oxidize in the stopes, and in the Butte mines considerable copper has been extracted from water pumped through the fire stopes.

At the present time the leaching of ore in place is unimportant, except for the incidental recovery of copper from certain mine waters.

*Heap leaching* has also been practiced on copper ores. The broken ore is heaped up and oxidized either by weathering or by heap roasting, and water is then applied to dissolve the copper sulfate. Heap leaching is also practically obsolete, because of the wastefulness of the method and the length of time required for leaching. Because of the unavoidable loss of the solvent in heap leaching, the only practicable solvent is water—sometimes water is pumped onto the heaps and sometimes rainfall alone supplies the solvent.

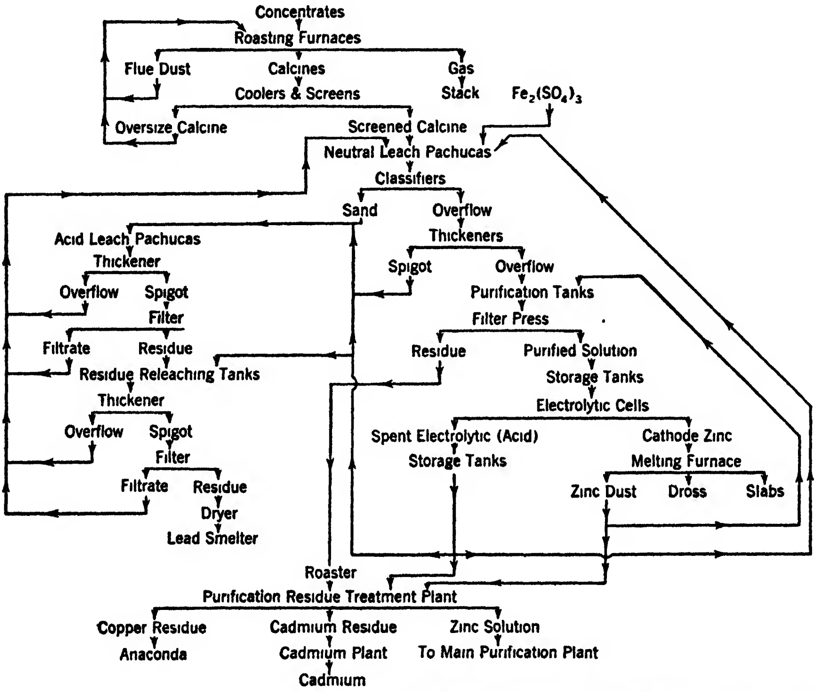
*Sand leaching* or *percolation* may be practiced wherever the ore is coarse enough to permit free passage of the solvent through the voids. The ore is loaded into large vats or tanks which are then filled with leaching solution. After the solution has been in contact with the ore for a certain time, it is withdrawn and fresh solution is added. Ordinarily several stages of leaching are required, and these are designed to obey the countercurrent principle—the first leach is usually made with a weak (spent) solution of the solvent, and the final leach is made with the strongest solution used. After the leaching cycle is complete, the ore is washed with water once or more times, and then the leached ore (tailing) is removed from the leaching tank.

Sand leaching vats are usually made of wood or concrete and may be lined with some material (asphalt, lead) which will not be corroded by the solvent. To facilitate the addition and withdrawal of the leach solutions and wash water, these vats are made with filter bottoms through which the solution will pass freely. Sometimes the bottom is made of wooden openwork and the ore packs in such a way as to form its own filter bottom; sometimes material such as coco matting is used. With coco-matting bottoms, a false bottom of wood is often built above the filter bottom to protect it from mechanical injury.

Liquid may be added to these tanks from the top (downward percolation) or from the bottom (upward percolation). The large volumes of solutions and wash water are distributed by means of a series of pumps.

Sand leaching is essentially a batch process rather than a continuous process, for the ore must be charged and the tailing removed while the tank is not in operation. However, in spite of this disadvantage, this system is the most efficient that has been discovered for the leaching of large quantities of low-grade ore. In large operations, the ore is charged and the tailing removed by steam shovels or similar devices.

*Slime leaching* is done by agitation. The slime and the leach solution are agitated in one or more agitators until the ore minerals have been dissolved. Some agitators have mechanically driven paddles or elevators inside an agitation tank which serve to keep the pulp in circulation until dissolution is complete. *Pachuca tanks* are also very widely used in slime leaching. A Pachuca is a cylindrical tank with a conical bottom and contains a pipe which is co-axial with the leaching tank and is open at both ends. Compressed air is introduced at the lower end of this pipe which behaves as an air-lift. The density of the pulp within the pipe is less than that of the pulp surrounding it, because of the column of air bubbles contained in the pipe, and the pressure of the denser pulp causes the pulp in the central pipe to rise and overflow, thus circulating the entire charge. The Pachuca tank is extremely simple in design and has no moving parts to get out of order. Slime leaching operations may be either continuous or intermittent.

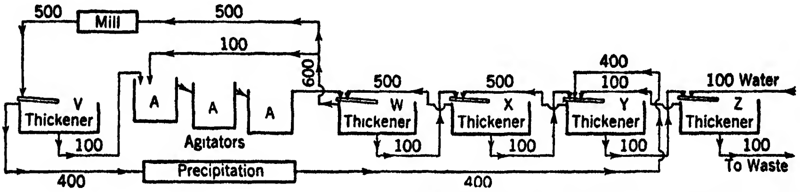


(*Courtesy Anaconda Copper Mining Company*)

FIG. 1.—Flowsheet of the Zinc Plant at Great Falls.

**Separation of Solution and Residue.**—When the dissolution has been completed, the next problem is to separate the liquid from the solid material so that the metal may be precipitated and the tailing discarded. Complete removal of the liquid is never practicable, so that the tailing losses in hydrometallurgical work are (1) chemical losses due to incomplete dissolution of the metal, and (2) mechanical losses due to entrained solution left in the tailings. The amount of mechanical loss is governed by the cost of washing the material and depends entirely upon the value of the metal concerned. The rule is to continue to wash the tailings until the value of the metal remaining is less than it would cost to remove it. Sand tailings are washed by simply allowing wash water to percolate through the leached ore.

Tailing from a slime leach is washed by decantation followed by filtration, and the decantation or thickening is done in a machine such as the Dorr thickener. In washing slimes, several thickeners are often used in series in the continuous countercurrent decantation (C. C. D.) process. The ore flows in one direction, and the wash water in the opposite direction (Fig. 2). The spigot product from the last thickener is discarded, if it has been washed sufficiently. If not, it is sent to a filter.



(*Courtesy The Dorr Company, Inc., New York*)

FIG. 2.—Flowsheet of a C. C. D. Washing System.

Figures refer to solution tonnages.

The following example will illustrate the principles involved in countercurrent decantation as well as some details common to all hydrometallurgical processes.

### EXAMPLE 1[1]

This example is concerned with the process shown by the flow sheet in Fig. 2. The lines indicate the flow of the pulp, and all figures refer to solution tonnages per day. This mill treats 100 tons of gold ore per day, and $10 in gold is dissolved from each ton of ore. Dissolution takes place in the ball mill and in the three agitators (*A*). The ball-mill discharge goes to thickener *V*, and the overflow from *V* goes to precipitation. The underflow from *V* is then agitated in

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[1] The Dorr Co. Bulletin 15. Reprinted by permission.

the agitators and washed in the C. C. D. system (thickeners $W$, $X$, $Y$, and $Z$). The discharge from $Z$ goes to waste. The conditions are summarized as follows:

(*a*) 100 tons of ore ground per day in cyanide solution.

(*b*) The discharge from all thickeners contains 50 per cent moisture.

(*c*) \$10.00 dissolved per ton of ore; 50 per cent in mill and 50 per cent in agitators.

(*d*) 400 tons of solution from thickener $V$ precipitated to \$0.02 per ton.

(*e*) Pulp in the agitator contains 2 parts of solution to 1 of solids.

(*f*) The cyanide solution contains 1.0 pound per ton, and the consumption of cyanide in the solution may be neglected.

Required: (1) the percentage of the dissolved metal recovered; (2) the mechanical loss of cyanide per ton of ore.

Solution: (1) Let $V$, $W$, $X$, $Y$, and $Z$ represent the value in dollars per ton of the solution discharged from each thickener. The solution overflow and the solution in the spigot product must have the same assay value in any given thickener, and the value entering must be the same as the value leaving. Therefore, the following equalities may be set up by equating in and out of each of the five thickeners:

$$100V + 400V = 500W + \frac{(\$10.00 \times 100)}{2}$$

$$100W + 600W = 500X + 100V + 100W + \frac{(\$10.00 \times 100)}{2}$$

$$\begin{aligned}
100X + 500X &= 100W + 500Y\\
100Y + 500Y &= 100X + 100Z + 400\ (\$0.02)\\
100Z + 100Z &= 100Y + 100\ (\$0.00)
\end{aligned}$$

Simplifying:

$$\begin{aligned}
V - W &= \$1.00\\
W - X &= \$1.20\\
X - Y &= \$0.24\\
Y - 0.2Z &= \$0.064\\
2Z &= Y
\end{aligned}$$

Solving:

$$\begin{aligned}
V &= \$2.51111\\
W &= \$1.51111\\
X &= \$0.31111\\
Y &= \$0.07111\\
Z &= \$0.03556
\end{aligned}$$

Since the only gold lost from the system is in the discarded tailing, and since 100 tons of solution are discarded for each 100 tons of ore treated, the value recovered per ton is \$10.00000 — \$0.03556 = \$9.96445, and the percentage recovery equals

$$\frac{9.96445}{10.00000} \times 100 = 99.64 \text{ per cent recovered} \quad (1)$$

(2) In the second case let $V$, $W$, $X$, $Y$, and $Z$ represent the cyanide content in pounds per ton in the solution discharged from each of the five thickeners. Cyanide is added so that the solution has its maximum strength of 1 pound per

ton in the dissolution circuit, i.e., in the ball mill, thickener $V$, and the agitators. Equating in and out of each thickener:

$$\begin{aligned} V &= 1.0 \\ 100W + 600W &= 100V + 100W + 500X \\ 100X + 500X &= 100W + 500Y \\ 100Y + 500Y &= 100Z + 400V + 100X \\ 100Z + 100Z &= 100Y + 100\ (0.00) \end{aligned}$$

Simplifying:

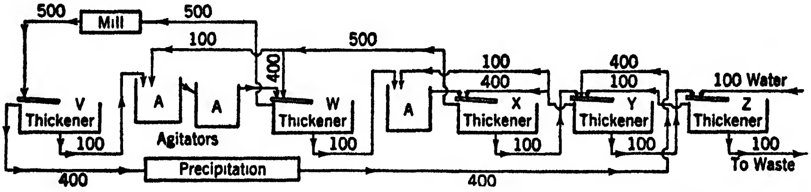
$$\begin{aligned} V &= 1.0 \\ 6W &= 5X + 1.0 \\ 6X &= W + 5Y \\ 6Y &= Z + X + 4 \\ 2Z &= Y \end{aligned}$$

Solving:

$$\begin{aligned} V &= 1.0 \\ W &= 0.9109 \\ X &= 0.8932 \\ Y &= 0.8898 \\ Z &= 0.4449 \end{aligned}$$

$0.4449 \times \frac{100}{100} = 0.4449$ pound of cyanide, the mechanical loss per ton of ore treated. (2)

Filtration is used to remove more solution from the tailings if the discharge from the last thickener still carries too many dissolved values. The spigot product from a thickener will contain from 70 to 50 per cent moisture—rarely less than 50 per cent. The cake from a filter, however, usually contains only about 15 to 20 per cent moisture, and may be as low as 7 per cent. Filtration is slow and expensive as compared with thickening, and whenever a filter is used on large tonnages of tailing or concentrate, it operates on the spigot product of a thickener so that as much de-watering as possible is done by the thickener. Filters are also used to remove liquid from the metallic precipitates produced by some of the common precipitation methods which will be discussed in the next section.



*(Courtesy The Dorr Company, Inc., New York)*

FIG. 3.—Flowsheet of a C. C. D. Washing System.

Figures refer to solution tonnages.

**Precipitation.**—The dissolved metal from a leaching cycle may be precipitated in one of two ways: (1) by chemical precipitation, or (2) by electrolytic deposition using insoluble anodes. Chemical precipitation is usually much cheaper, but electrolytic deposition gives a very pure deposit of metal and may regenerate the solvent. The precipitate produced by the chemical methods is usually quite impure. Electrical precipitation will be discussed in the chapter on electrometallurgy.

Chemical precipitation is of two types: (1) *cementation,* where a metal is displaced from solution by a less noble element; and (2) other chemical reactions. Fe, Cu, Zn, Al, and C are commonly used for cementing, and $Na_2S$, CaS, $SO_2$, and $Al(OH)_3$ are other chemical precipitants. $Al(OH)_3$ is used in precipitating $Al(OH)_3$ from the $NaAlO_2$ solution in the Bayer process of refining bauxite according to the reaction

$$NaAlO_2 + 2H_2O \rightarrow Al(OH)_3 + NaOH$$

This reaction is the reverse of the solution reaction and is brought about by diluting the solution and releasing the pressure. The added $Al(OH)_3$ acts as "seed" to start the precipitation but does not enter into the chemical reaction. Note that the solvent, NaOH, is regenerated by this process. The action of other precipitating agents is illustrated by the following equations:

Cementation:

$$CuSO_4 + Fe \rightarrow FeSO_4 + Cu$$

$$Ag_2SO_4 + Cu \rightarrow 2Ag + CuSO_4$$

$$NaAu(CN)_2 + 2NaCN + Zn + H_2O \rightarrow Na_2Zn(CN)_4 + Au + H + NaOH$$

$$NaAg(CN)_2 + 2NaCN + Zn + H_2O \rightarrow Na_2Zn(CN)_4 + Ag + H + NaOH$$

$$2NaAu(CN)_2 + 4NaOH + 2Al \rightarrow 4NaCN + 2Au + Na_2Al_2O_4 + 2H_2$$

Others:

$$CuSO_4 + SO_2 + 2H_2O \rightarrow Cu + 2H_2SO_4$$

$$2Na_2S_2O_3 \cdot Ag_2S_2O_3 + Na_2S \rightarrow Ag_2S + 3Na_2S_2O_3$$

$$2AuCl_3 + 6FeSO_4 \rightarrow 2Au + 2FeCl_3 + 2Fe_2(SO_4)_3$$

Cementation is by far the most common chemical method of precipitation, and it is usually carried out by simply bringing the solution in contact with the metal in question. Copper is usually precipitated as cement copper, by allowing the copper-bearing solution to flow over scrap iron in launders or towers. Gold and silver are precipitated either by flowing the solution over zinc shavings or by agitating with aluminum or zinc powder in a special precipitation chamber. The precipitates of the precious metals are filtered in a press and then melted down into bricks. Cement copper is very impure (it may contain less than 70 per cent copper) and must be melted and fire refined.

Much of the copper and all the zinc produced by hydrometallurgical methods are recovered by electrolytic precipitation.

**Treatment of the Pregnant Solution.**—The metal-bearing solution which has been clarified (by thickening and filtering) must often be subjected to further treatment before it is ready for the precipitation process. This treatment is particularly important in closed circuit operations where the reagent is regenerated in the precipitation process and the solution is used again as a leaching agent. The impurities in the leach solution in zinc plants are cemented out on powdered zinc before the solution enters the electrolytic cells. This method removes all the metals more noble than zinc, and gives a very pure solution of zinc sulfate. In copper circuits certain impurities often build up to the point where they begin to precipitate in the electrolytic cells, and in this case it is necessary to "bleed" a certain amount of electrolyte from the circuit and replace it by fresh acid solution; usually the copper is cemented from the fouled electrolyte removed in this manner.

## CYANIDATION AND AMALGAMATION

The importance of these two methods in the metallurgy of gold and silver is sufficient to warrant a short discussion in addition to what has been said about hydrometallurgy in general.

**Cyanidation.**—As has been mentioned in the previous discussion, cyanidation is an important method in the treatment of gold and silver ores. Of the two, the cyanidation of gold ores is the more important. With the exception of telluride gold ores, the metal always occurs native; and this metal is dissolved by cyanide according to the equation given in preceding sections. Native silver is dissolved in the same way, and the silver chloride and sulfide are also soluble:

$$AgCl + 2NaCN \rightarrow NaAg(CN)_2 + NaCl$$

$$Ag_2S + 4NaCN \rightarrow 2NaAg(CN)_2 + Na_2S$$

the $Na_2S$ then oxidizing:

$$2Na_2S + 2O_2 + H_2O \rightarrow Na_2S_2O_3 + 2NaOH$$

**Preliminary Tests.**—A great many factors must be considered in determining whether or not a given ore can be economically treated by the cyanidation process, and the determination is made by running a series of laboratory tests on a representative sample of the ore. These tests are made by agitating samples of the ore in a cyanide solution for a given time, filtering off the liquid, and assaying the tailings to determine the extraction. The strength of solution and other variables is changed from test to test in order to determine the optimum conditions. Information on the following points will suffice to determine whether or not the ore is amenable to cyanidation, and will also be of great help in drawing up a flow sheet.

1. *Cyanide consumption.* In gold ores, the theoretical requirement of cyanide (NaCN or KCN) as calculated from the chemical equation is almost negligible, and most of the chemical loss of cyanide is due to other reactions such as the following:

$$(a)\quad NaCN + CO_2 + H_2O \rightarrow HCN + NaHCO_3$$

$$(b)\quad Fe + 6NaCN + 2H_2O \rightarrow Na_4Fe(CN)_6 + 2NaOH + H_2$$

$$(c)\quad 2Cu + 4NaCN + 2H_2O \rightarrow Na_2Cu_2(CN)_4 + 2NaOH + H_2$$

$$(d)\quad Fe(OH)_2 + 6NaCN \rightarrow Na_4Fe(CN)_6 + 2NaOH$$

Reaction (*a*) is typical of a series of reactions which take place whenever NaCN or KCN is exposed to an acid solution; it means that the cyanide is hydrolyzed to give volatile HCN which is lost. Free acids, acid salts, and dissolved $CO_2$ gas will cause cyanide loss by reactions similar to this one, and therefore cyanidation is always done in an alkaline circuit. The necessary *protective alkalinity* is obtained by adding lime to the circuit. The strength of cyanide solution with respect to cyanide and lime content is given in pounds of reagent per ton of solution.

Reactions (*b*), (*c*), and (*d*) are typical reactions showing how cyanide is consumed by *cyanicides.* Metallic iron from grinding, copper and most copper compounds, ferrous hydroxide, and certain antimony and bismuth minerals are the most common cyanicides. Sometimes cyanicides can be removed by preliminary treatment, but usually the presence of such substances makes the cyanide consumption so great that cyanidation is not feasible. Note that, in the examples illustrated, the NaCN is converted into double cyanides, and these have no solvent power for gold and silver.

Native metals (Fe, Cu) graphite, and organic material are harmful in cyanide circuits because they cause premature precipitation of the dissolved gold and silver.

2. *Extraction.* Laboratory tests show the extraction or the amount of metal dissolved by the cyanide solution, and by making a series of

tests it is possible to determine the time required for extraction, the amount of NaCN or the strength of the solution required for best extraction, and the amount of lime required. All these factors are more or less interrelated; and if cyanidation is to be used, the following conditions must be satisfied.

(*a*) Sufficient extraction must be made in a reasonably short time.

(*b*) The cyanide and lime consumption must be low. It is impossible to give an exact figure as to percentage extraction, time required, and reagent consumption, because many other factors must be considered, such as the grade of the ore being treated, and the possibility of combining cyanidation with flotation, gravity concentration, amalgamation, or a combination of these.

Gold and silver particles must be very fine or dissolution will be too slow to be practicable. The rule for free gold ores is that particles visible to the naked eye are probably too large for cyanidation.

3. *Solution Strength.* As a rule, low-grade gold ores require cyanide solutions containing 0.1 to 1.0 pound of NaCN per ton when slime leaching is used. Silver ores require stronger solutions because of the larger amount of metal to be dissolved; generally from 2 to 4 pounds per ton are needed. Sand leaching for both gold and silver ores requires stronger solutions—4 to 6 pounds per ton.

NaCN is the only material used for cyaniding. It is cheaper than KCN (pound for pound) and is more efficient since a pound of NaCN contains more CN than a pound of KCN.

4. *Size of Ore Particles.* Proper laboratory experiments will also determine the amount of grinding required for best extraction of the values.

**Amalgamation.**—This method for the recovery of relatively coarse, free gold is classed as a hydrometallurgical process, although it does not resemble the leaching operations that have been considered so far. Clean gold, when brought in contact with metallic mercury, will *amalgamate;* i.e., the liquid mercury will alloy with the surface gold to form a mercury-coated particle which has surface properties similar to those of pure mercury. Such amalgamated particles will coalesce or cling together much as drops of pure mercury will collect into a single puddle. When mercury has amalgamated as much gold as possible, the result is a gray plastic mass of *amalgam.* If this is retorted (heated), the mercury is distilled off, leaving metallic gold in the retort.

Amalgamation plates are most commonly used for recovering gold by this method. These are copper plates heavily coated with mercury (copper will also amalgamate with mercury), and the crushed gold ore is washed over this plate as a thin pulp. The heavy gold particles sink to the bottom and amalgamate with the mercury. When the plate is covered with gold amalgam, the amalgam is scraped off, and the plate dressed with fresh mercury. The excess liquid mercury is removed from the amalgam by squeezing through canvas or chamois skin, and the dry amalgam is then retorted. Amalgamation of high-grade ores or concentrates may be done by agitating in a revolving barrel with mercury ("barrel amalgamation").

Mercury for amalgamation must be "quick" and "charged." Mercury that is not "quick" is said to be "sickened"; i.e., impurities are present which contaminate the surface and prevent contact between mercury and gold particles. Grease or oil, and some compounds of mercury, will sicken the mercury and cause it to "flour," or break up into a number of small drops. After mercury has been used for amalgamation, a small amount of gold is dissolved in the liquid mercury, and this "charged" mercury is much more effective in amalgamation than chemically pure mercury. Native silver will amalgamate, and platinum will amalgamate with liquid sodium amalgam, but not with pure mercury.

The following example illustrates further some of the principles of hydrometallurgy as applied to the treatment of a silver ore. Note the difference in details of the practice in this case as compared with Example 1.

### EXAMPLE 2

Silver ore containing 14.03 ounces of silver with no gold is given a single leach with strong cyanide solution (5 pounds per ton), and then washed with water. The total amount of solution obtained (pregnant solution plus wash water) is 7.36 tons per ton of ore treated. The extraction (dissolution) of silver by the solvent is 93 per cent. The solution and washings are precipitated down to 0.13 ounce per ton in zinc boxes, and the solution is then discarded. The leaching consumes 3.0 pounds of NaCN per ton of ore treated, and 1.38 pounds of zinc per ton of ore are consumed in the precipitating boxes. Solution entering the zinc boxes carries 0.88 pound of NaCN per ton.

Required: (1) the recovery of silver; (2) the amounts of leaching solution and wash water used; (3) the percentage of NaCN and Zn consumed that is theoretically required by the solution and precipitation equations respectively.

Solution: The solution (Elsner's) equation is:

$$4Ag + 8NaCN + O_2 + 2H_2O \rightarrow 4NaAg(CN)_2 + 4NaOH$$

and the precipitation equation is:

$$2NaAg(CN)_2 + 4NaCN + 2Zn + 2H_2O \rightarrow 2Ag + 2Na_2Zn(CN)_4 + H_2 + 2NaOH$$

Ag in solution entering zinc boxes = 14.03 × 0.93 = 13.04 oz.
Ag in solution leaving zinc boxes = 0.13 × 7.36 = 0.956 oz.
Ag recovered = 13.04 − 0.956 = 12.084 oz.

$$\frac{12.084}{14.03} = 0.857 = 85.7\% \text{ recovery} \qquad (1)$$

NaCN consumed in leaching = 3.00 pounds
NaCN left in solution = 0.88 pounds
Total NaCN used = 3.88 pounds

But since each ton of strong solution contains 5 pounds of NaCN, there are required

$$\frac{3.88}{5.00} = 0.776 \text{ ton of strong solution per ton of ore} \qquad (2)$$

$$7.36 - 0.776 = 6.584 \text{ tons of wash water} \qquad (2)$$

From the solution equation: 432 parts of Ag requires 392 parts of NaCN and 13.04 oz. requires

$$13.04 \times \frac{392}{432} = 11.82 \text{ oz. (troy) NaCN}$$

$$\frac{11.82}{14.58} = 0.812 \text{ pound of NaCN}$$

$$\frac{0.812}{3.00} \times 100 = 27.1\% \text{ of the NaCN used that is consumed in dissolving Ag} \qquad (3)$$

or:

$$\frac{0.812}{3.88} \times 100 = 20.9\% \text{ of total NaCN that is consumed in dissolving Ag} \qquad (3)$$

From the precipitation equation, 65 parts of zinc will precipitate 108 parts of Ag.

$$12.084 \times \frac{65}{108} \times \frac{1}{14.58} = 0.497 \text{ pound of Zn}$$

$$\frac{0.497}{1.38} \times 100 = 36.0\% \text{ of Zn consumed that is used in precipitating Ag} \qquad (3)$$

Note the meaning of "extraction" and "recovery" as applied to hydrometallurgical problems.

## EXERCISES

1. Electrolyte obtained from the leaching of roasted zinc concentrates is purified by agitating with zinc dust to remove metallic impurities and neutralize free $H_2SO_4$. What common metals would be removed by this method? Write equations. Write the equation for the neutralization reaction.

2. From the flowsheet in Fig. 3 calculate the recovery and the mechanical loss of cyanide. Figures in the flowsheet refer to solution tonnages, and the necessary data are as follows:

(*a*) 100 tons of ore ground in cyanide solution per day.

(*b*) Discharge from all thickeners at 50 per cent moisture.

(*c*) $12 value extracted per ton of ore.

(*d*) Extraction 50 per cent in mill, 40 per cent in first two agitators, and 10 per cent in last agitator.

(*e*) 400 tons of solution from thickener *V* precipitated to $0.02.

(*f*) Agitation with a dilution of 2 of solution to 1 of solids.

(*g*) Cyanide content of solution = 1 lb. per ton in ball mill.

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# CHAPTER XI

## PYROMETALLURGY—1. CHEMICAL PRINCIPLES

Ever since the first metal was reduced from an ore by the action of a wood fire, the operations of *pyro* or *fire metallurgy* have been of the greatest importance in the extraction of metals from their ores. Pyrometallurgy is by far the most important of the extractive processes—all iron and steel, nickel, and tin; most copper; a large proportion of zinc, gold, and silver; as well as many of the minor metals are won from their ores or concentrates by pyrometallurgical means.

Pyrometallurgy deals with chemical reactions at high temperatures, and the necessary heat for the processes is provided by the burning of fuel. High-temperature processes in which heat is supplied by electric currents are classed under electrometallurgy. It will be convenient to break the subject into three parts: (1) a study of certain chemical principles underlying pyrometallurgical operations; (2) a study of heat, including fuels, combustion, and pyrometry; and (3) a brief discussion of the important processes of pyrometallurgy.

### CHEMICAL AFFINITY

If we consider a simple chemical reaction such as:

$$C + O_2 \rightarrow CO_2 \qquad (a)$$

taking place at constant pressure and constant temperature, we find that a certain amount of heat is generated. A reaction such as the one given by equation (*a*) may be regarded as a transformation from one system to another. We start with a system containing solid carbon and gaseous oxygen at 20° C., and we end with a system composed of the single gaseous phase $CO_2$ also at 20° C. Now the system $C + O_2$ at 20° C. contains a certain amount of energy in the form of heat stored as motion of vibration, translation, and rotation of the $O_2$ molecules and the C atoms. Likewise, the system $CO_2$ contains a certain amount of energy at 20° C. stored as energy of motion of the $CO_2$ molecules. The heat content of the $CO_2$ is less than the heat content of the $C + O_2$ system, and as a result, when the transformation (reaction) from one system to the other takes place, this difference in energy content appears in the form of heat which is given up to the surroundings. Actually, the effect, as we well know, is that the heat evolved goes to heat up the $CO_2$ formed; but if we collect all the $CO_2$ formed and cool it back to 20° C., we can measure the heat generated by the reaction. The *heat of reaction* (in this case), $\Delta H$, is defined as the number of calories of heat absorbed when 1 gram-atomic weight (12 grams) of carbon reacts with 1 gram-molecular weight of oxygen (32 grams) to form 1 gram-molecular weight of $CO_2$ (44 grams). Since the heat is evolved in this case and not absorbed, $\Delta H$ is negative, and we may write this in an equation

$$C + O_2 \rightarrow CO_2;\ \Delta H = -97{,}200 \text{ calories} \qquad (b)$$

In reactions of this type, $\Delta H$ represents the number of calories absorbed when the indicated reaction takes place from left to right, with each chemical symbol representing 1 gram-atomic weight. Thus, we might write equations such as:

$$\begin{aligned}
2C + 2O_2 &\rightarrow 2CO_2; & \Delta H &= -\ 194{,}400 \text{ calories}\\
2C + O_2 &\rightarrow 2CO; & \Delta H &= -\ 58{,}320 \text{ calories}\\
C + \tfrac{1}{2}O_2 &\rightarrow CO; & \Delta H &= -\ 29{,}160 \text{ calories}\\
Cu_2S + O_2 &\rightarrow 2Cu + SO_2; & \Delta H &= -\ 51{,}980 \text{ calories}\\
2Cu + SO_2 &\rightarrow Cu_2S + O_2; & \Delta H &= +\ 51{,}980 \text{ calories}
\end{aligned}$$

When $\Delta H$ is positive, the indicated reaction is *endothermic* and absorbs heat. When $\Delta H$ is negative, heat is evolved, and the reaction is *exothermic*.

Early experimenters observed that, whenever a simple reaction occurred in which a compound was formed from its elements, the highly stable compounds were formed with the evolution of large amounts of heat, and the less stable compounds were formed with the evolution of smaller amounts of heat. Hence, they proposed that the heat evolved (heat of reaction) should be a measure of the *chemical affinity* of the combining elements for one another. If we have reactions such as:

$$Ca + \tfrac{1}{2}O_2 \rightarrow CaO;\ \Delta H = -\ 151{,}600 \text{ calories}$$

and

$$Ca + S \rightarrow CaS;\ \Delta H = -\ 113{,}500 \text{ calories}$$

we should say that at 20° C. (the temperature of these reactions) calcium had a greater affinity for oxygen than for sulfur, or that CaO was more stable than CaS. In line with this hypothesis, we would expect oxygen to displace sulfur from CaS under proper conditions.

When attempts were made to quantify this hypothesis, it was discovered that $\Delta H$ or the heat of reaction was not the true measure of chemical affinity or the driving force behind a chemical reaction, and that the true measure of chemical affinity for reactions occurring at constant pressure and temperature was the *free energy change*, $\Delta F$ (ordinarily measured in calories).

The heat content of a substance at any temperature $T$ ($T$ will be used to refer to Kelvin or absolute Centigrade temperatures) depends upon its specific heat at constant pressure $C_p$, and the temperature $T$. The heat content $H$ of any substance at temperature $T$ is:

$$H = T\int_0^T \frac{C_p dT}{T} \tag{1}$$

Now suppose we have the reaction

$$a + b \rightarrow c + d \tag{c}$$

with a heat of reaction = $\Delta H$.

Here the two substances $a$ and $b$ react to form the new substances $c$ and $d$ at a temperature of $T°$. The *sensible heat content* of the reagents at $T°$ is:

$$H_r = T\int_0^T \frac{C_{p_a} dT}{T} + T\int_0^T \frac{C_{p_b} dT}{T}$$

or

$$H_r = T\int_0^T \frac{(C_{p_a} + C_{p_b})}{T}\,dT \tag{2}$$

and the sensible heat content of the products is

$$H_p = T\int_0^T \frac{(C_{p_c} + C_{p_d})}{T}\,dT \tag{3}$$

The difference between these is

$$H_p - H_r = T\int_0^T \frac{(C_{p_c} + C_{p_d} - C_{p_a} - C_{p_b})}{T}\,dT \tag{4}$$

which we may write

$$H_p - H_r = T\int_0^T \frac{\Delta C_p}{T}\,dT \tag{5}$$

where $\Delta C_p$ is used to represent the quantity in parentheses in equation (4). Now the quantity $H_p - H_r$ represents the difference in sensible heat content between the system $c + d$, and the system $a + b$ at $T°$ K. The intrinsic energy change $\Delta F$ which accompanies equation (*c*) is the same as $\Delta H$ *if, and only* if, $H_p = H_r$. If $H_p$ is greater than $H_r$, then $\Delta F > \Delta H$ since, besides the heat energy intrinsically absorbed by the reaction, some additional heat is absorbed because the products have a greater heat capacity than the reagents. Hence we may write the relation between $\Delta H$ and $\Delta F$ as:

$$\Delta F = \Delta H + (H_p - H_r)$$

or

$$\Delta F = \Delta H + T\int_0^T \frac{\Delta C_p dT}{T} \tag{6}$$

or

$$\Delta F = \Delta H + T\Delta S \tag{7}$$

where $\Delta S$, the *change in entropy*, is used for the equivalent expression

$$\int_0^T \frac{\Delta C_p}{T}\,dT\cdot$$

The change in free energy or the intrinsic energy change in any chemical reaction is the true measure of the driving force or potential of the reaction or of the affinity of the reagents for one another. This fact can be deduced from the laws of thermodynamics.

Equations analogous to equation (*b*) may be written such as:

$$C + O_2 \rightarrow CO_2; \quad \Delta F = -\ 94{,}260 \text{ calories}$$
$$C + \tfrac{1}{2}O_2 \rightarrow CO; \quad \Delta F = -\ 32{,}510 \text{ calories}$$

(compare with the corresponding equations involving $\Delta H$ as given previously), and such equations may be added, thus:

$$\begin{array}{lll} & C + O_2 \rightarrow CO_2; & \Delta F = -\ 94{,}260 \text{ calories} \\ + & CO \rightarrow C + \tfrac{1}{2}O_2; & \Delta F = +\ 32{,}510 \text{ calories} \\ \hline & CO + \tfrac{1}{2}O_2 \rightarrow CO_2; & \Delta F = -\ 61{,}750 \text{ calories} \end{array}$$

When $\Delta F$ is negative, the indicated reaction can take place; when $\Delta F = 0$ the indicated reaction is at equilibrium; and when $\Delta F$ is positive, it is impossible for the indicated reaction to proceed spontaneously.

The actual heat absorbed by a reaction ($\Delta H$) can be determined experimentally by means of a calorimeter. In order to calculate the value of $\Delta F$ for a given reaction, it is necessary to have data on either (1) the specific heats of all substances concerned from $T°$ K. to 0° K. (to determine $\Delta Cp$, and use equation 6) or (2) the entropy change of the reaction (to make use of equation 7). It is not our purpose to discuss the quantitative use of free energy equations, but merely to indicate the meaning of chemical affinity and to present some qualitative rules concerning it. For a more detailed treatment of the subject, the reader is referred to standard works on chemical thermodynamics.[1, 2] Let us summarize some of the important facts relating to the free energy change of a chemical reaction.

1. $\Delta F$ is negative for all spontaneous reactions. If $\Delta F$ comes out to have a positive value for some hypothetical reaction, then it is impossible for that reaction to take place spontaneously. This rule may be used to predict which reactions cannot take place and which reactions may take place. The fact that calculation shows a reaction to have a large negative value for $\Delta F$ does not necessarily mean that the reaction will occur. For example, the reaction of $H_2$ and $O_2$ at 25° C. is

$$H_2 + O \rightarrow H_2O; \quad \Delta F = - 56{,}560 \text{ calories}$$

but a mixture of $H_2$ and $O_2$ gases will remain indefinitely at 25° C. without forming $H_2O$—at least, not enough to be detected analytically. The value of $\Delta F$ indicates the direction of a reaction, the free energy change, and, as we shall see presently, the extent of the reaction. It gives no information, however, about the velocity of the reaction.

2. Any chemical system endeavors to change spontaneously in such a way as to make its free energy content a minimum. This means that, if several reactions are possible, the reaction which produces the maximum negative change in free energy content $(- \Delta F)$ is the most likely to occur.

3. Equation (6) shows that $\Delta F$ may be expressed as a function of $\Delta H$, $T$, and $\Delta C_p$. Since all these quantities change as the reaction temperature changes, it follows that $\Delta F$ is a function of the temperature at which the reaction occurs. As the reaction temperature changes, the value of $\Delta F$ may change considerably in magnitude and even may change sign (Tables 1 and 2); consequently, the affinity of one element for another will change as the temperature changes. It is well known, for example, that, in purifying iron containing phosphorus and carbon by oxidizing the impurities, carbon will oxidize ahead of phosphorus at high temperatures, but at low temperatures phosphorus will oxidize before the carbon. This means that the af-

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[1] Lewis, G. N., and Randall, Merle: Thermodynamics, McGraw-Hill Book Co., New York, 1923.

[2] Butts, Allison: A Textbook of Metallurgical Problems, McGraw-Hill Book Co., New York, 1932.

finities of oxygen for carbon and phosphorus change with the temperature—at low temperature phosphorus has a greater affinity for oxygen than carbon; at higher temperatures the reverse is true.

4. In some cases $\Delta H$ may be almost equal to $\Delta F$ in magnitude and sign, and then the heat of reaction is a fair approximation of the chemical affinity. In other cases, however, there may be considerable difference in magnitude and even a difference in sign, especially when $\Delta H$ and $\Delta F$ are small.

5. A large negative value for $\Delta F$ indicates the possibility of a vigorous chemical action. As we have mentioned before, however, the value of $\Delta F$ does not predict the velocity of the reaction, and accordingly the reaction may be very slow even with large values for $-\Delta F$. In any case, however, the large value of $-\Delta F$ indicates a potentially vigorous reaction. Often a suitable catalyst will speed the reaction up remarkably. It is futile, however, to search for a catalyst to promote a reaction which has a positive $\Delta F$ and hence is thermodynamically impossible.

## CHEMICAL EQUILIBRIUM

Let us consider the reaction

$$Cu_2O + CO \rightleftharpoons 2Cu + CO_2 \qquad (d)$$

assuming that the reagents and products are confined to a closed chamber, and that we start with only $Cu_2O$ and CO present. The reaction will begin in the direction of the upper arrow; but as soon as appreciable amounts of Cu and $CO_2$ are formed, the reverse reaction will begin. Eventually the two reactions will attain the same velocity, and then the four substances ($CO_2$, CO, Cu, and $Cu_2O$) will be present *in equilibrium,* and the effective reaction will stop since the two reactions balance each other. Now the law of mass action states that the velocity of any reaction is proportional to the product of the activities[3] of the reacting substances. We cannot enter into an extended discussion of the meaning of the thermodynamic term *activity;* for our present purpose the following approximate rules will suffice:

1. For gaseous substances the activity is equal to the partial pressure of the gas concerned.
2. For solid substances the activity is a constant at any given temperature, and independent of the amount of solid present.

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[3] Lewis, G. N., and Randall, Merle: Thermodynamics, McGraw-Hill Book Co., New York, 1923.

3. For pure liquid substances the activity is equal to the vapor pressure, and hence is constant at a given temperature and independent of the amount of liquid present.
4. For substances in solution the activity is equal to the concentration (molality) of the substance in question.

Now, in our example, the $Cu_2O$ and Cu are assumed to be in the solid state, and CO and $CO_2$ in the gaseous state. If we let $K_{Cu}$ and $K_{CuO}$ be the activities of the Cu and $Cu_2O$ respectively, and $P_{CO}$ and $P_{CO_2}$ be the partial pressures (activities) of CO and $CO_2$, we may write for $V_1$ the velocity of the reaction in the direction of the upper arrow:

$$V_1 = K_1 K_{Cu_2O} P_{CO} \tag{8}$$

and for the opposing reaction:

$$V_2 = K_2 K_{Cu} P_{CO_2} \tag{9}$$

Now at equilibrium $V_1 = V_2$, or

$$K_1 K_{Cu_2O} P_{CO} = K_2 K_{Cu} P_{CO_2}$$

or

$$\frac{P_{CO_2}}{P_{CO}} = K \tag{10}$$

where $K$ is the *equilibrium constant* of the reaction. Conventionally, the equilibrium constant of a given reaction is expressed as the product of the activities of the substances on the right-hand side divided by the product of the activities of the substances on the left-hand side. In our example, since the ratio of $\frac{P_{CO_2}}{P_{CO}}$ must remain constant at any given temperature (equation 10) if we add $CO_2$ to the system and hence increase its partial pressure, the reaction will go in the direction of the lower arrow until the partial pressure of $CO_2$ has decreased to the point where equation (10) again holds. Addition of more CO to the system would promote the reaction in the direction of the upper arrow. The value of $K$ for a given reaction indicates how nearly the reaction approaches completion. For example, we may consider the reaction of $H_2$ and $O_2$ to form water vapor at 1397° K.[4] The reaction is:

$$H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O; \quad K = 2.05 \times 10^6$$

or

$$\frac{P_{H_2O}}{P_{H_2} P_{O_2}^{1/2}} = 2{,}050{,}000$$

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[4] Lewis, G. N., and Randall, Merle: Thermodynamics, McGraw-Hill Book Co., New York, 1923.

indicating that the partial pressure of water vapor is much greater than the product of the pressure of $H_2$ by the square root of the pressure of $O_2$. In other words, only 0.0078 per cent of the water vapor is dissociated into $H_2$ and $O_2$ when equilibrium is reached at 1397° K.

Large values for $K$ indicate that the reaction from left to right goes practically to completion; very small values for $K$ indicate that the reverse reaction is substantially complete.

When a reaction takes place in a confined space, the reaction will not go to completion unless $K$ is so large that the amount of uncombined reagents is negligible. If, however, some or all of the products are removed as soon as they are formed, a reaction which would otherwise be incomplete may be brought to completion. Thus, for example, the right-to-left reaction in equation (*d*) is caused by the partial pressure (activity) of the $CO_2$ formed. We can completely reduce $Cu_2O$ to Cu by passing a stream of CO gas over the solid $Cu_2O$, because the current of gas sweeps the $CO_2$ away as fast as it is formed and does not permit the $CO_2$ pressure to build up to the point where the reverse reaction takes place. Similarly, solid Cu could be completely oxidized to $Cu_2O$ in a current of $CO_2$ gas.

**Relation of $\Delta F$ to $K$.**—Both $\Delta F$ and $K$ are measures of chemical affinity and are functionally related. When all reagents and products are in their standard states, the notation $\Delta F°$ is used to represent the free energy change, and

$$\Delta F° = -RT \ln K \tag{11}$$

where $K$ is the equilibrium constant, $R$ is the gas constant equal to 1.9885 calories per degree, $T$ is the temperature of the reaction, and ln means logarithm to the base *e*, or natural logarithm. If the reacting substances and products are not in their standard states, $\Delta F$ for the reaction may be calculated from the relation

$$\Delta F - \Delta F° = RT \ln A_q \tag{12}$$

where $A_q$ is the *activity quotient* which must be determined from the actual activities of the substances and their activities in their standard states. We shall not pursue this question further because we merely intend to indicate the nature of the relationship between $\Delta F$ and $K$. Equation (11) shows that, in general, when $\Delta F°$ is negative, ln $K$ is positive and $K$ therefore $> 1$ (since $\ln 1 = 0$). The larger the value of $-\Delta F°$, the greater is $K$; and the more nearly the left-right reaction goes to completion. When $\Delta F°$ is positive, ln $K$ is negative, and $K$ is a positive fraction less than 1. When $\Delta F°$ has a large positive value, $K$ is a very small fraction; the right-left reaction goes nearly to completion, and the left-right reaction is substantially impossible. Either $\Delta F$ or $\Delta F^\circ$ measures the free energy change under certain standard and often highly artificial conditions; for example, the equation[5]

$$H_2O\text{ (gas)} + CO \rightarrow CO_2 + H_2; \quad \Delta F^\circ_{298} = -7240$$

means that if 1 mol of CO reacts with 1 mol of $H_2O$ to form 1 mol of $CO_2$ and 1 mol of $H_2$, the free energy of the system decreases by 7240 calories, provided that all four gases are in their standard states, which, for practical purposes, means that the partial pressure of each gas is 1 atmosphere. This equation holds true if, and only if, the partial pressure of each gas remains constant throughout the reaction, which means that the reaction must take place in the presence of such large amounts of the four gases that the interaction of 1 mol of $H_2O$ and 1 mol of CO will not appreciably alter the concentration of any of the gases. If we had conditions as represented by this equation and could maintain the partial pressures of each gas at 1 atmosphere, the reaction would continue indefinitely and 7240 calories of free energy would be lost each time 1 mol of gas reacted. If, however, we have finite amounts of these gases sealed in a container, we find that as the reaction proceeds the activity of the $H_2O$ and CO (partial pressure) decreases and the activity of $H_2$ and $CO_2$ increases. As this change continues, we find that the free energy decrease ($\Delta F$) per mol of $H_2O$ reacting soon becomes less than 7240 calories and decreases steadily until it becomes zero at the equilibrium point. We can calculate the relative concentrations (partial pressures) of the four gases at the equilibrium point by the use of equation (11), thus:

$$\ln\left(\frac{P_{CO_2}\cdot P_{H_2}}{P_{H_2O}\cdot P_{CO}}\right) = \frac{-7240}{-1.9885 \times 298}$$

$$\ln\left(\frac{P_{CO_2}\cdot P_{H_2}}{P_{H_2O}\cdot P_{CO}}\right) = 12.218$$

$$\log\left(\frac{P_{CO_2}\cdot P_{H_2}}{P_{H_2O}\cdot P_{CO}}\right) = 5.304$$

$$P_{CO_2}\cdot P_{H_2} = 202{,}000\ (P_{CO}\cdot P_{H_2O})$$

Hence, these gases would be in equilibrium at 298° K. when the product of the partial pressures of $CO_2$ and $H_2$ was 202,000 times the

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[5] Lewis, G. N., and Randall, Merle: Thermodynamics, McGraw-Hill Book Co., New York, 1923.

product of the partial pressures of CO and $H_2O$. Under these conditions no change could occur which would decrease the free energy of the system and $\Delta F$ would be zero. In other words, the standard free energy changes, $\Delta F$ and $\Delta F^\circ$, as found in tables, do not give the actual free energy change under all conditions, but only under certain restricted conditions. These values, however, do give us a measure of the "affinity" or "potential" of the reaction and permit us to calculate how far it will go and in what direction.

The equilibrium constant $K$ varies with the temperature just as does $\Delta F$. The values of $K$ and $\Delta F^\circ$ for two important reactions are given in Tables 1 and 2.

TABLE 1 *

FREE ENERGIES AND EQUILIBRIUM CONSTANTS FOR THE REACTION

$ZnO + CO \rightarrow Zn\ (gas) + CO_2$

| Temp °C. | $\Delta F^\circ$ | Log $K$ | $K$ (atmospheres) |
|---|---|---|---|
| 427 | +25,174 | −7.8543 | $1.339 \times 10^{-8}$ |
| 527 | +22,260 | −6.0769 | $8.377 \times 10^{-7}$ |
| 627 | +19,391 | −4.7056 | $1.970 \times 10^{-5}$ |
| 727 | +16,561 | −3.6169 | $2.416 \times 10^{-4}$ |
| 827 | +13,766 | −2.7331 | $1.849 \times 10^{-3}$ |
| 927 | +11,003 | −2.0025 | $9.943 \times 10^{-3}$ |
| 1027 | + 8,265 | −1.3885 | $4.088 \times 10^{-2}$ |
| 1127 | + 5,550 | −0.8658 | $1.362 \times 10^{-1}$ |
| 1227 | + 2,851 | −0.4151 | $3.845 \times 10^{-1}$ |
| 1327 | + 168 | −0.0229 | $9.487 \times 10^{-1}$ |
| 1427 | − 2,506 | +0.3219 | 2.099 |
| 1527 | − 5,175 | +0.6279 | 4.245 |

$$K = \frac{P_{Zn} \cdot P_{CO_2}}{P_{CO}}$$

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* Maier, C. G.: Zinc Smelting from a Chemical and Thermodynamic Viewpoint; U. S. Bureau of Mines Bulletin 324, 1930.

Other laws and rules have been evolved to determine the equilibrium conditions of chemical reactions, and we shall briefly consider a few of them. All these can be derived from the basic law of the free energy change, and some involve a certain amount of approximation.

**Le Chatelier's Principle.**—The principle of Le Chatelier is a very important generalization in predicting the direction of a chemical reaction. It may be stated as follows: If a system in equilibrium be subjected to an external influence, a change will take place in such

### TABLE 2*

FREE ENERGIES AND EQUILIBRIUM CONSTANTS FOR THE PRODUCER-GAS REACTION $C + CO_2 \rightarrow 2CO$

| Temp. ° C. | Δ F° | Log K | K (atmospheres) |
|---|---|---|---|
| 527 | + 7,702 | −2.1026 | $7.896 \times 10^{-3}$ |
| 627 | + 3,473 | −0.8428 | $1.436 \times 10^{-1}$ |
| 727 | − 730 | +0.1594 | 1.443 |
| 827 | − 4,908 | +0.9745 | 9.435 |
| 927 | − 9,062 | +1.6493 | 44.60 |
| 1027 | −13,196 | +2.2169 | 164.78 |
| 1127 | −17,308 | +2.7000 | 501.2 |
| 1227 | −21,395 | +3.1151 | 1,303.5 |
| 1327 | −25,462 | +3.4756 | 2,989.5 |
| 1427 | −29,506 | +3.7906 | 6,174.5 |
| 1527 | −33,524 | +4.0676 | 11,684 |
| 1627 | −37,511 | +4.3118 | 20,502 |
|  | $K = \frac{(P_{CO})^2}{P_{CO_2}}$ |  |  |

* Maier, C. G.: Zinc Smelting from a Chemical and Thermodynamic Viewpoint; U. S. Bureau of Mines Bulletin 324, 1930.

a way as to oppose this influence and tend to restore the original conditions. The simplest way to explain the meaning of this is by a few examples.

1. Consider the effect of a change of temperature on the equilibrium of the reaction considered in the previous section.

$$Cu_2O + CO \rightleftarrows 2Cu + CO_2$$

The reaction in the direction of the upper arrow is exothermic, i.e., it is accompanied by the liberation of heat; and the reverse reaction is endothermic, or is accompanied by the absorption of heat. If we raise the temperature of the system, we must perforce increase its heat content. In opposition to this external influence, the reaction will go more nearly to completion in the direction of the lower arrow, since this reaction absorbs heat. The same reasoning will show that a lowering of the temperature should promote the reaction in the direction of the upper arrow. This particular application of the Le Chatelier principle is known as *Van't Hoff's principle.*

2. Consider the effect of external pressure on the equilibrium of these gases:

$$3H_2 + N_2 \rightleftarrows 2NH_3$$

*From Avogadro's hypothesis, it follows that the reaction in the direction of the upper arrow is accompanied by a 50 per cent reduction in* volume at constant pressure, or a 50 per cent reduction in pressure at constant volume. If the external pressure on the system is increased, the reaction will go in the direction of the upper arrow, since this will tend to lower the pressure. Similarly, a decrease in external pressure will promote the dissociation of $NH_3$.

**The CO-$CO_2$ Equilibrium.**—The equilibrium points of the reaction

$$CO_2 + C \rightleftarrows 2CO$$

at various temperatures are of great importance in any operation where CO is used as a reducing agent, particularly in the smelting of iron ore. Since the reaction in the direction of the upper arrow is endothermic, an increase in temperature means an increase in the concentration of CO. Figure 1 shows the various concentrations of CO and $CO_2$ that can exist in equilibrium at different temperatures (cf. Table 2). Note that $CO_2$ cannot exist above 1000° C. in the presence of carbon, and consequently CO is not a reducing agent above 1000° C., because $CO_2$ cannot form; and in order for CO to reduce anything, it itself must be oxidized to $CO_2$.

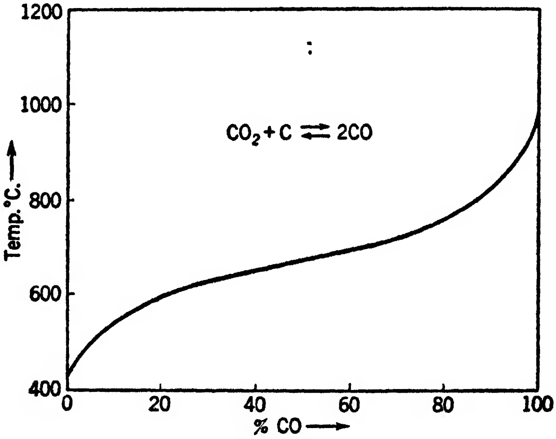

FIG. 1.—The CO-$CO_2$ Equilibrium.

The reaction for the reduction of iron oxide in the iron blast furnace may be written:

$$FeO + CO \rightarrow Fe + CO_2$$

If, however, the temperature is high enough and the concentration of $CO_2$ great enough, the reverse reaction takes place:

$$Fe + CO_2 \rightarrow FeO + CO$$

and the Fe is re-oxidized by the $CO_2$. In order to prevent this, an excess of carbon is burnt in the blast furnace so that an excess of CO will always be present. The general equation for the reduction of iron ore is of the type:

$$FeO + 4CO \rightarrow Fe + CO_2 + 3CO \qquad (e)$$

and this accounts for the high percentage of CO in the gases discharged at the top of the blast furnace. Thermodynamic considerations show that the reduction of iron oxides by CO is a limited reaction; it attains equilibrium before all the oxide is reduced, and it is impossible to reduce the iron oxide completely without having an excess of CO present as indicated by equation (*e*). Before blast-furnace men were acquainted with this principle, they thought that the CO in the stack gases was due to insufficient contact with the oxides, and tried to remedy the defect by building higher furnaces.

**Dissociation Tension.**—If we let M represent any metal, the equation

$$M + O_2 \rightleftarrows MO_2$$

represents the general oxidation reaction which is reversible. Associated with every oxide is a property called its *dissociation tension* (a *pressure* measured in millimeters of mercury), which is a measure of the stability of the oxide; and the dissociation tension increases rapidly as the temperature rises. The quantitative definition of dissociation tension may be given most easily by reference to the equation above. When equilibrium has been established at a given temperature, then the dissociation tension of the oxide is numerically equal to the partial pressure of the surrounding oxygen. To fix the ideas about this important property, let us take a numerical example. Consider what happens when metallic palladium is heated in air. The normal pressure of the atmosphere is 760 mm.; and since air contains 21 per cent $O_2$ by volume, the partial pressure of the oxygen is $760 \times 0.21 = 160$ mm., and as the metal is to be heated in air, the circulation of the atmosphere will keep the pressure of oxygen constant at this figure. Table 3 gives the dissociation tension of PdO at various temperatures. At any temperature below 756° C., the dissociation tension is less than 67 mm., which is less than 160 mm.; and consequently the reaction

$$2PdO \rightleftarrows 2Pd + O_2$$

will proceed in the direction of the lower arrow as long as the partial pressure of $O_2$ (160 mm.) is greater than the dissociation tension of

PdO. If we continue to heat above 756° C., the dissociation tension of PdO will increase, and at about 794° will equal 160 mm. At this point the reaction will stop (attain equilibrium); and if we heat above 794°, the reaction will proceed in the direction of the upper arrow, since now the dissociation tension of PdO is greater than the pressure of $O_2$. In other words, metallic palladium will oxidize in air at temperatures below 794°, and palladium oxide will dissociate if heated above 794° C. in air.

The noble metals such as Pd, Pt, Au, Ag, and Hg have oxides which possess high dissociation tensions at relatively low temperatures. Consequently, their oxides are easily reduced. Often heating alone will suffice to reduce the oxide to the metal. The oxides of metals high in the electromotive series, however, have low dissociation tensions even at high temperatures, and consequently are difficult to reduce.

Dissociation tensions are characteristic of all compounds which can dissociate to yield a gaseous product. Thus the reactions

$$CaCO_3 \rightleftarrows CaO + CO_2$$

$$Fe_2(SO_4)_3 \rightleftarrows Fe_2O_3 + 3SO_3$$

will proceed in the direction of the upper arrows only when the dissociation tensions of $CaCO_3$ and $Fe_2(SO_4)_3$ are greater than the opposing partial pressures of $CO_2$ and $SO_3$ respectively.

TABLE 3 *

DISSOCIATION TENSION OF CERTAIN METALLIC OXIDES

| $2BaO_2 \rightleftarrows 2BaO + O_2$ | | $2PdO \rightleftarrows 2Pd + O_2$ | | $4CuO \rightleftarrows 2Cu_2O + O_2$ | |
|---|---|---|---|---|---|
| Temperature, Degrees C. | $O_2$ Tension, Millimeters | Temperature, Degrees C. | $O_2$ Tension, Millimeters | Temperature, Degrees C. | $O_2$ Tension, Millimeters |
| 525 | 20 | 756 | 67 | 960 | 50 |
| 555 | 25 | 808 | 212 | 1000 | 118 |
| 650 | 65 | 812 | 230 | 1010 | 142 |
| 670 | 80 | 840 | 414 | 1020 | 174 |
| 720 | 210 | 850 | 510 | 1030 | 212 |
| 735 | 260 | 864 | 634 | 1040 | 258 |
| 750 | 340 | ... | ... | 1050 | 314 |
| 775 | 510 | | . | 1060 | 380 |
| 785 | 620 | | | 1070 | 458 |
| 790 | 670 | | | | |

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* Fulton, C. H.: Principles of Metallurgy; McGraw-Hill Book Co., New York, 1910. Reprinted by permission.

TABLE 4*

TEMPERATURES AT WHICH METALLIC OXIDES DISSOCIATE IN AIR

(Dissociation Tension = 160 mm.)

| Reaction | Temperature, Degrees Centigrade |
|---|---|
| $2Ag_2O \rightleftarrows 4Ag + O_2$ | 130 |
| $4CuO \rightleftarrows 2Cu_2O + O_2$ | 1020 |
| $2Cu_2O \rightleftarrows 4Cu + O_2$ | 1662 |
| $2CuO \rightleftarrows 2Cu + O_2$ | 1502 |
| $2PbO \rightleftarrows 2Pb + O_2$ | 2075 |
| $2NiO \rightleftarrows 2Ni + O_2$ | 2478 |
| $2ZnO \rightleftarrows 2Zn + O_2$ | 3554 |
| $6Fe_2O_3 \rightleftarrows 4Fe_3O_4 + O_2$ | 1375 |

* Fulton, C. H.: Principles of Metallurgy; McGraw-Hill Book Co., New York, 1910. Reprinted by permission.

## REACTION VELOCITY

The thermodynamic laws which we have mentioned in the previous sections are useful in predicting the direction and extent of a given reaction, but they give no information about the speed of the reaction. Thermodynamic laws in general consider only the initial and final states of a system and are not concerned with the steps by which the system progresses from one state to another. If a chemical reaction is to be useful in a technical process, however, it must proceed with a reasonable velocity.

The velocity of a chemical reaction depends upon (1) the number of contacts made per unit of time by the atoms or molecules which are to react, and (2) a certain inherent resistance to reaction which is characteristic of each particular chemical system, and which is roughly analogous to friction in mechanical processes.

**Surface.**—When a reaction takes place between two phases, the reaction can occur only at the contact surface between the two phases; and the greater this surface, the more rapidly the reaction will proceed. *Wenzel's law* applies to the dissolution (reaction) of a solid in a liquid and states that the rate of dissolution is proportional to the surface area of the solid exposed to the action of the solvent. In general, any reaction will increase in velocity in direct proportion to the amount of contact surface between the reacting phases. For example, in dissolving gold in a cyanide solution, the gold will dissolve more rapidly from a rich ore than from a lean ore in a solution of the same cyanide content. This is not because the mass of gold present makes any difference (the activity of a solid substance is independent of its mass), but simply because there is a greater surface area of gold exposed to the cyanide solution in the rich ore.

**Temperature.**—Entirely apart from the effect of temperature on the equilibrium point of a reaction, there is the fact that heating a reaction mixture usually increases the velocity of the reaction. In some cases a rise of 10° C. will double or triple the reaction velocity. This effect may be due entirely to the larger number of molecular contacts caused by the increased thermal agitation of the molecules or atoms concerned, but it is questionable that this increased mobility alone accounts for the large increase in reaction velocity.

Many important reactions do not take place rapidly enough at low temperatures to be of any practical use. A piece of coal will remain in cold air for a long time without any appreciable oxidation taking place; but if the coal is heated to a red heat, the reaction

$$C + O_2 \rightarrow CO_2$$

will take place so rapidly that all the carbon will be consumed in a short time. If a reaction (such as this one) is exothermic, the heat generated by the reaction may be sufficient to keep the reagents above the reaction temperature. Once the reaction is started, it becomes self-supporting. For endothermic reactions or those exothermic reactions which do not generate much heat, it is necessary to supply heat continuously in order to keep the reaction going. The temperature at which various combustible materials (fuels, sulfides) begin to oxidize rapidly enough to support their own combustion is called the *kindling point*.

Proper temperature control is essential in all pyrometallurgical operations, both to promote desirable reactions and to inhibit those which are undesirable.

**Catalyzers.**—By forcing our analogy of the chemical resistance to friction, we may liken a catalytic agent or catalyzer to a lubricant. A catalyzer is some substance which speeds up a chemical reaction without being consumed itself. Whether the catalyzer actually participates in intermediate reactions or not is undecided—in some cases it apparently does; in others it apparently does not. Whatever the mechanism, however, catalysts have the power of remarkably accelerating certain chemical reactions. For instance, the reaction between hydrogen and oxygen gases at room temperatures is so slow as to be practically non-existent, but the addition of a small amount of sponge platinum to the mixture of gases causes a vigorous reaction. Let it be emphasized again, however, that a catalyzer is powerless to promote a chemical reaction which is thermodynamically impossible.

We have said that the magnitude of $\Delta F$ or $K$ tells nothing about the velocity of a reaction. This is true in the sense that we cannot predict the speed of a reaction from the thermal constants. It must be remembered, however, that for any given reaction the velocity is proportional to the activities of the reagents. The farther the system is away from equilibrium, the faster will be the reaction. It would be more accurate to say that the velocity of any reaction is proportional to the product of the activities of the reagents (law of mass action), but thermodynamic data alone cannot determine the value for the proportionality constant.

### THE COUNTERCURRENT PRINCIPLE

In many metallurgical and industrial chemical processes it is necessary that two substances react with one another. When the process is continuous, the substances usually flow through the reaction chamber in opposite directions (countercurrent). An example to illustrate this principle will show the reasons for its use.

In the ordinary multiple-hearth roaster, the material to be roasted enters the top of a furnace which contains a series of horizontal hearths. The ore moves down from one hearth to the next until it discharges at the bottom. Roasting is essentially a reaction between oxygen from the air and the solid particles of ore. The air enters the roasting furnace at the bottom and passes upward over the ore on the hearths. The waste gases discharge at the top of the furnace.

Let us assume that we are to roast a zinc concentrate consisting primarily of ZnS. The principal reaction is

$$2ZnS + 3O_2 \rightleftarrows 2ZnO + 2SO_2$$

The velocity of the reaction in the direction of the upper arrow is affected (1) by the concentration (activity, partial pressure) of $O_2$ in the gases, and (2) by the amount of ZnS present, since the reaction velocity depends upon the amount of surface exposed to the action of the gases. The reverse reaction is promoted by the concentration of $SO_2$ and the amount of ZnO exposed. The ZnO forms as a porous crust on the ZnS particles; and the deeper this layer becomes, the more difficult it is for the oxygen to get at the ZnS. Now, the $O_2$ concentration is greatest in the gases near the bottom of the furnace, and the $SO_2$ concentration is greatest in the gases near the top. The ore near the top of the furnace contains large amounts of unaltered ZnS which is easily attacked by $O_2$, even in the partially depleted atmosphere and in the presence of large amounts of $SO_2$. The ore near the bottom of the furnace contains much less ZnS, and it is covered by a layer of ZnO which increases the difficulty of oxidizing it.

However, the air at this point has the maximum $O_2$ content and minimum $SO_2$ content, so that it has the maximum oxidizing action. The use of the countercurrent system in this case insures that the material which is easiest to oxidize is acted upon by the weakest oxidizing gases, and the strongest oxidizing gases act upon the material which is most difficult to oxidize.

Two other illustrations of the application of the countercurrent principle are:

1. In leaching operations, the strong leaching solution comes in contact with ore which is almost completely leached; the fresh ore first comes in contact with spent leach solution.
2. In drying ore in a current of hot gas, the moist ore comes in contact with the gases which contain the most water vapor. The ore which is almost completely dried is acted upon by the driest gases.

The countercurrent principle insures the most uniform and complete reaction possible between two substances. It is easy to illustrate but difficult to define. Probably the best definition is the statement that it is a means of maintaining the chemical potential at a uniform level during a reaction.

## STOICHIOMETRY; THE GAS LAWS

**The Chemical Equation.**—A properly balanced chemical equation gives quantitative information on the following points:

1. The composition of the reagents.
2. The composition of the products.
3. The relative weights of all reagents and products.
4. The relative volumes of all gaseous reagents and products.
5. The heat balance of the equation.

The meaning and application of 1, 2, and 3 follow directly from the law of conservation of matter; 4 is based on Avogadro's hypothesis that equal volumes of all gases at the same conditions of temperature and pressure contain the same number of molecules; item 5 will be discussed in a later section. The following equations illustrate the law of relative volumes; Roman numerals refer to relative volumes.

$$\overset{\text{II}}{2H_2} + \overset{\text{I}}{O_2} \rightarrow \overset{\text{II}}{2H_2O}$$

$$\overset{\text{I}}{CH_4} + \overset{\text{II}}{2O_2} \rightarrow \overset{\text{I}}{CO_2} + \overset{\text{II}}{2H_2O}$$

$$\overset{\text{II}}{2C_6H_6} + \overset{\text{XV}}{15O_2} \rightarrow \overset{\text{XII}}{12CO_2} + \overset{\text{VI}}{6H_2O}$$

If the $C_6H_6$ or $H_2O$ are in the liquid state, the laws of relative volumes do not apply to them.

Relative volumes may be converted into actual volumes by the following rules:

1. One gram-mol of any gas at 0° C. and 760 mm. (standard conditions) occupies 22.4 liters.
2. One kilogram-mol of any gas at standard conditions occupies 22.4 cubic meters.
3. One ounce (avoirdupois)-mol of any gas at standard conditions occupies 22.4 cubic feet.

Kilograms and cubic meters are more commonly used in metallurgical calculations than grams and liters. The occurrence of the number 22.4 in rule 3 is due to certain fortuitous relations between English and metric units. One pound-mol of a gas at standard conditions occupies 359 cubic feet and

$$\frac{359}{16} = 22.4$$

The accuracy of this approximation is well within the limits usually required in metallurgical calculations, as may be seen by the relations:

1 cubic foot = 0.02832 cubic meter
1 ounce (avoirdupois) = 0.02835 kilogram

### Example 1

A copper converter contains 8000 kg. of $Cu_2S$. Air is blown in to oxidize the $Cu_2S$:

$$Cu_2S + O_2 \rightarrow 2Cu + SO_2$$

Required: the volume of air necessary.

32 kg. of S require 22.4 cu. m. of $O_2$, or 1 kg. of S requires $\frac{22.4}{32}$ cu. m. of $O_2$

The weight of S in the converter is

$$\frac{32}{2(64) + 32} \times 8000 = 1600 \text{ kg.}$$

$$1600 \times \frac{22.4}{32} = 1120 \text{ cu. m. of } O_2 \text{ required}$$

Air is 21.0% $O_2$ by volume and

$$\frac{1120}{0.21} = 5330 \text{ cu. m. of air required}$$

Note that the temperature and pressure of the gas are not specified. In cases like this, the gases are generally assumed to be at standard conditions, and the fact that furnace gases may be at a temperature of 1000° C. does not prevent us from expressing their quantity as a volume referred to standard conditions. The relative volumes of all gases remain the same, regardless of temperature and pressure changes. In solving problems, it will usually be advantageous to express volumes of gases as cubic meters or cubic feet at standard conditions, and to convert these to cubic meters or cubic feet at actual conditions only when this is specifically required.

**Balancing Equations.**—All equations involved in chemical problems should be written out in full and balanced. The correct molecular formula for all gases must be used. Equations such as

$$H_2 + O \rightarrow H_2O$$

are incorrect, although they are used quite frequently. Such an equation gives the correct weight relationships between reagents and products, but does not give the correct volume relations because oxygen is *not* a monatomic gas. The correct equation is

$$2H_2 + O_2 \rightarrow 2H_2O$$

**The Gas Laws.**—For most metallurgical problems the simple gas laws are sufficiently accurate. These state that the volume of a gas is inversely proportional to the pressure, and directly proportional to the absolute temperature. Example 2 illustrates a simple method of applying these gas laws to numerical problems.

### Example 2

A certain amount of nitrogen (or any other gas) occupies 10 cu. m. at 55° C. and 720 mm. What will be its volume at 300° C. and 950 mm.?

Solution: Consider the two corrections separately: 55° + 273° = 328° K. 300° + 273° = 573° K. Now if the gas is to be heated from 328° K. to 573° K, it will expand, and consequently the 10 cu. m. must be multiplied by the factor $\frac{573}{328}$. As the pressure rises from 720 mm. to 950 mm., the volume will decrease so that the multiplying factor for the pressure correction is $\frac{720}{950}$. Applying these two corrections, we have:

$$10 \times \frac{573}{328} \times \frac{720}{950} = 13.2 \text{ cu. m. at } 300^\circ \text{ C. and } 950 \text{ mm.}$$

## THERMOCHEMISTRY

**Heats of Formation.**—Item 5 in the information given by a chemical equation deals with heat balances or thermochemistry. Before proceeding with a definition of heat of formation, let us summarize the essential facts about units for measuring quantities of heat.

The most common heat unit is the small calorie or gram calorie (cal.), which is the amount of heat required to raise 1 gram of water

1° C. For accurate work the temperature range must be specified, for the specific heat of water varies between 0° C. and 100° C. The normal calorie is defined as the amount of heat required to raise 1 gram of water from 14.5° C. to 15.5° C. The mean calorie is the hundredth part of the heat required to raise 1 gram of water from 0° C. to 100° C. Practically, there is little difference between these units, and we shall use the term "calorie" as defined in the first sentence of this paragraph.

Since the calorie is a very small unit. the large calorie or kilogram calorie (Cal.) is commonly used in metallurgical work. This is the amount of heat required to raise 1 kilogram of water 1° C., and is equal to 1000 calories. The fundamental heat unit of the English system is the British thermal unit (B.t.u.) which is the amount of heat required to raise 1 pound of water 1° F. The pound calorie is a hybrid between English and metric units and is the amount of heat required to raise 1 pound of water 1° C.

The *heat of formation* of a compound is *the number of calories liberated or absorbed when 1 gram-molecular weight of a compound is formed from its elements.* If heat is evolved in the formation of a compound, the compound is exothermic and its heat of formation is written with a plus sign. If heat is absorbed, the compound is endothermic and a minus sign precedes the heat of formation. In tables the plus sign is sometimes omitted, the minus sign never. The heat of formation of elements is assumed to be zero. Since the elements themselves are not formed in ordinary chemical reactions, this restriction will not affect our calculations. Some representative heats of formation are as follows:

| | | | | | |
|---|---|---|---|---|---|
| $CO_2$ | 97,200 cal. | FeS | 23,050 | $Cu_2S$ | 18,950 |
| CO | 29,160 | FeO | 64,100 | $CuSO_4$ | 178,700 |
| $CH_4$ | 19,100 | $Fe_2O_3$ | 191,600 | ZnO | 83,260 |
| $C_2H_4$ | —9,560 | $FeSO_4$ | 217,200 | $SO_2$ | 70,940 |
| $C_2H_2$ | —54,340 | PbS | 22,200 | $SO_3$ | 91,600 |
| | | $PbSO_4$ | 214,500 | $H_2O$ | 57,840 |
| | | PbO | 52,500 | CaO | 151,600 |
| | | $Al_2O_3$ | 389,500 | $CaCO_3$ | 285,900 |

The student may have observed that some of these heats of formation are the same as the values of $\Delta H$ we have mentioned before, except that they have the opposite sign. In most books on physical chemistry and thermodynamics, the convention is to call the quantity of heat liberated negative, and we write such a reaction as:

$$C + O_2 \rightarrow CO_2; \quad \Delta H = -97,200 \text{ cal.}$$

In metallurgical and engineering textbooks the opposite convention is used. When heat is liberated it is called positive, and the reaction above would be written:

$$C + O_2 \rightarrow CO_2 + 97{,}200 \text{ cal.}$$

We shall use the latter convention for the balance of our work in thermochemistry. It is unfortunate that this difference in notation exists; but since it does, it is necessary to recognize it.

**Rules of Thermochemistry.**—Following are the three most important rules of thermochemistry:

I. The heat of decomposition of a compound is equal to its heat of formation but is of opposite sign.

II. In the formation of any compound, the same amount of heat is required, regardless of the number of intermediate steps in the process.

III. Of two possible chemical reactions, that one is more likely to occur which evolves the greater amount of heat. What amounts to practically the same thing is that stable compounds have high heats of formation and are exothermic (see list above).

Rules I and II are laws based on the principle of conservation of energy. Rule III is a generalization which applies only when the heat evolved is nearly the same as the decrease in free energy.

**Heat of Reaction.**—Let us see how the heats of formation may be applied to calculate the heat of a reaction.

$$C + O_2 \rightarrow CO_2 + 97{,}200 \text{ cal.} \qquad (f)$$

In this instance the *heat of reaction* is the same as the heat of formation of $CO_2$. The quantity of heat is always written on the right-hand side. When preceded by a plus sign, it means that heat is evolved; such a reaction is exothermic. The equation above reads: "When 12 grams of carbon are burnt with 32 grams of oxygen to form 44 grams of $CO_2$, 97,200 calories of heat are liberated." The *heat of combustion* of carbon or the heat liberated when 1 gram of carbon is completely burned $= \frac{97{,}200}{12} = 8100$ cal.

$$4FeS + 7O_2 \rightarrow 2Fe_2O_3 + 4SO_2 \qquad (g)$$

In this reaction 2 gram mols of $Fe_2O_3$ and 4 gram mols of $SO_2$ are formed. These contribute respectively $2(191{,}600) = 383{,}200$ cal.; and $4(70{,}940) = 283{,}760$ cal. Four gram mols of FeS are decomposed (i.e., the FeS disappears and its constituent atoms appear in other compounds); hence, to the heats of formation of $2Fe_2O_3$ and $4SO_2$

we must add the heat of decomposition of 4FeS, which is the same as subtracting its heat of formation. There is no heat of formation for the $O_2$, and consequently the heat of the reaction is:

$$(383{,}200 + 283{,}760) - 4(23{,}050) = 666{,}960 - 92{,}200 = 574{,}760 \text{ cal.}$$

and the complete reaction is:

$$4FeS + 7O_2 \rightarrow 2Fe_2O_3 + 4SO_2 + 574{,}760 \text{ cal.}$$

The heat evolved per gram of FeS burnt is

$$\frac{574{,}760}{352} = 1633 \text{ cal.}$$

The heat evolved per liter of $SO_2$ formed is:

$$\frac{574{,}760}{89.6} = 6415 \text{ cal.}$$

From this illustration we may derive a rule for finding the heat of reaction in any reaction which proceeds from left to right. From the sum of the heats of formation of the compounds shown on the right, subtract (*algebraically*) the sum of the heats of formation on the left. The difference is the heat of the reaction. If weights are given in pounds, heats of formation and reaction are in pound calories. If weights are in kilograms, heats are in kilogram calories.

Careful study of the following examples will illustrate further the application of the above rule.

$$\underset{2(-54{,}340)}{2C_2H_2} + 5O_2 \rightarrow \underset{4(97{,}200)}{4CO_2} + \underset{2(57{,}840)}{2H_2O} + 613{,}160 \text{ cal.} \qquad (h)$$

$$388{,}800 + 115{,}680 - (-108{,}680) = 504{,}480 + 108{,}680 = 613{,}160 \text{ cal.}$$

The heat of combustion of acetylene is $\frac{613{,}160}{44.8} = 13{,}686$ calories per liter or 13,686 Calories per cubic meter.

$$\underset{(285{,}900)}{CaCO_3} \rightarrow \underset{(151{,}600)}{CaO} + \underset{(97{,}200)}{CO_2} - 37{,}100 \text{ cal.} \qquad (i)$$

$$(151{,}600 + 97{,}200) - 285{,}900 = 248{,}800 - 285{,}900 = -37{,}100 \text{ cal.}$$

This is an example of an endothermic reaction.

Calculation of the heat of formation of $FeSO_4$ by an indirect method to illustrate Rule II.

$$2Fe + 2S \rightarrow \underset{2(23{,}050)}{2FeS} + 46{,}100 \text{ calories}$$

$$\underset{2(23{,}050)}{2FeS} + 3O_2 \rightarrow \underset{2(64{,}100)}{2FeO} + \underset{2(70{,}940)}{2SO_2} + 223{,}980 \text{ cal.}$$

$$\underset{2(70,940)}{2SO_2} + O_2 \rightarrow \underset{2(91,600)}{2SO_3} + 41{,}320 \text{ cal.}$$

$$\underline{\underset{2(64,100)}{2FeO} + \underset{2(91,600)}{2SO_3} \rightarrow \underset{2(217,200)}{2FeSO_4} + 123{,}000 \text{ cal.}}$$

Adding

$$2Fe + 2S + 4O_2 \rightarrow 2FeSO_4 + 434{,}400 \text{ cal.} \qquad (j)$$

$$\frac{434{,}400}{2} = 217{,}200 \quad \text{Q.E.D.}$$

In tables of heats of formation of compounds we frequently find notations such as

$$(Ag_2, S, O_4) = 166{,}000 \text{ cal.}$$

and

$$(Ag_2O, SO_3) = 67{,}450 \text{ cal.}$$

The first refers to the heat of formation of the compound $Ag_2SO_4$ from its elements as we have defined it. The second refers to the heat of formation of $Ag_2SO_4$ from the constituent oxides $Ag_2O$ and $SO_3$ and is equivalent to the heat of reaction:

$$\underset{6,950}{Ag_2O} + \underset{91,600}{SO_3} \rightarrow \underset{166,000}{Ag_2SO_4} + 67{,}450 \text{ cal.}$$

since 166,000 − (91,600 + 6950) = 67,450.

## REACTION TYPES

By far the most important of pyrometallurgical reactions are *oxidation* and *reduction*; together with *metathesis* (double decomposition) they account for all the important operations of pyrometallurgy. As a general rule, the chemical equations studied in pyrometallurgy are relatively simple.

**Reagents.**—The common reagents in pyrometallurgical reactions are ores, concentrates, fluxes, oxidizing agents, and reducing agents. Ores and concentrates may be thought of as primary reagents, since they contain the metal to be extracted; by the reaction between the ore minerals and the fluxes and oxidizing and reducing agents, the metal is changed from its chemically combined forms to the metallic or elemental state. The result is seldom attained in one operation, often two or three pyrometallurgical processes being necessary before the metal can be obtained as the element.

The composition of ores and concentrates has been discussed in previous chapters; the question of types and composition of fluxes will be taken up as the need arises. Many of the problems in pyrometallurgy arise from the fact that ores, concentrates, and fluxes are almost never pure. The best lead concentrate that can be produced commercially is never mineralogically pure galena, but contains impurities such as $SiO_2$, $FeCO_3$, $CaCO_3$, and ZnS; and the problem of dealing with these impurities in lead smelting may overshadow in importance the primary aim of the process which is the extraction of metallic lead from the lead-bearing minerals.

As to oxidizing and reducing agents, only a few are used to any extent. By far the most important oxidizing agent is air (21 per cent $O_2$ by volume). Metallic oxides such as FeO, $Fe_2O_3$, and $Cu_2O$, and steam are used as oxidizing agents in some processes. Reducing agents include carbon in the form of coal, coke, or charcoal; CO, carbon monoxide; and various reducing gases such as hydrogen and the hydrocarbons.

The types of chemical reactions which are of importance in pyrometallurgy are listed below together with some examples of their application.

1. Reactions between a solid and a gas.
    - Roasting.
    - Smelting (primary reduction of oxides).
2. Reactions between a liquid and a gas.
    - Fire refining.
    - Converting.
3. Reactions between two liquids or within a single liquid.
    - Reduction smelting (last stages).
    - Matte smelting.
    - Fire refining (open hearth).
4. Reactions between a liquid and a solid.
    - Recarburization of steel.

**Metathesis: Acids and Bases.**—Reactions such as

$$Cu_2O + FeS \rightarrow Cu_2S + FeO$$

may appear unfamiliar at first sight, since all the reagents and products are insoluble in water, and double decomposition reactions are usually thought of as taking place in aqueous solution. In pyrometallurgy, however, reactions such as this are very common. They take place in a molten furnace charge or igneous fusion.

The reaction between sulfuric acid and sodium hydroxide in aqueous solution may be written (assuming that both hydrogen atoms are replaced):

$$2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O$$

Note that the salt $Na_2SO_4$ contains no water and that the same reaction may be written:

$$Na_2O + SO_3 \rightarrow Na_2SO_4$$

since

$$Na_2O + H_2O \rightarrow 2NaOH$$

and

$$SO_3 + H_2O \rightarrow H_2SO_4$$

$Na_2O$ is a *basic oxide*, and $SO_3$ is an *acid anhydride*.

In pyrometallurgical reactions, combination takes place between basic oxides and acid anhydrides in igneous fusions and not in water solutions. In pyrometallurgy, acid anhydrides are called *acids*, and the basic oxides are called *bases*. By far the most common acid is silica, $SiO_2$. Other acids are $B_2O_3$, $P_2O_5$, $Cr_2O_3$, $SO_3$, and $Al_2O_3$. After reaction with a base, these acids form metallic silicates, borates, phosphates, chromates, sulfates, and aluminates, respectively. Practically all the metallic oxides are bases. FeO, ZnO, $Al_2O_3$, CaO, MgO, MnO, and $Na_2O$ are among the most common. Note that acids are usually oxides of the non-metals, and that the oxide of an amphoteric element such as aluminum may be either an acid or a base. The following equations illustrate some simple neutralization reactions:

$$CaO + SiO_2 \rightarrow CaSiO_3 \text{ calcium silicate} \quad (k)$$

$$ZnO + Al_2O_3 \rightarrow ZnAl_2O_4 \text{ zinc aluminate (a zinc spinel)} \quad (l)$$

$$FeO + SiO_2 \rightarrow FeSiO_3 \quad (m)$$

$$2FeO + SiO_2 \rightarrow Fe_2SiO_4 \quad (n)$$

$$FeO + 2SiO_2 \rightarrow FeSi_2O_5 \quad (o)$$

An acid slag means a slag which is high in silica (or other acid), and an acid refractory is a siliceous refractory. Similarly, the terms basic slag and basic refractory refer to materials which contain an excess of one or more of the metallic oxides. A *slag* is essentially a molten solution of one or more salts such as those given in the preceding equations. The slag formed in reaction (*n*) is more basic than that of reaction (*m*); reaction (*o*) produces a more acid slag than reaction (*m*). In order to form a slag it is not necessary that the acid and base shall be present in exactly equivalent amounts, for the liquid $FeSiO_3$ formed in reaction (*m*), for example, can dissolve an excess of either $SiO_2$ or FeO.

**Oxidation and Reduction.**—When an element enters into a reaction in such a way that its valence is increased (i.e., it loses one or more electrons), it is said to be oxidized. When the valence of an element is decreased, or it gains electrons, it is reduced. From consideration of the electronic theory of the structure of atoms, it follows that oxidation and reduction must go together; and whenever an element is oxidized, some other element must be reduced. The following reactions illustrate some typical oxidation-reduction reactions (the valence of an uncombined element is zero):

$$C + O_2 \rightarrow CO_2 \qquad (p)$$

Here the carbon is oxidized and the oxygen is reduced; oxygen is the oxidizing agent and carbon is the reducing agent.

$$2C + O_2 \rightarrow 2CO \qquad (q)$$

$$2CO + O_2 \rightarrow 2CO_2 \qquad (r)$$

In these equations the carbon is partially oxidized in the first reaction, and the CO is completely oxidized in the second.

$$Fe_2O_3 + CO \rightarrow 2FeO + CO_2 \qquad (s)$$

$$FeO + CO \rightarrow Fe + CO_2 \qquad (t)$$

These equations represent the reduction of $Fe_2O_3$ in two stages; the iron in $Fe_2O_3$ is more highly oxidized than the iron in FeO.

$$PbS + 2PbO \rightarrow 3Pb + SO_2 \qquad (u)$$

In this reaction the lead is reduced from both compounds. The valence of the oxygen remains the same, but the atom of sulfur goes from a valence of $-2$ to a valence of $+4$, supplying 6 electrons to neutralize (reduce) the lead atoms. Sulfur is the reducing agent, and the sulfur is oxidized.

Note that oxidation usually (but not necessarily) means the combination of an element with oxygen.

## METALLIC COMPOUNDS

In this section we shall consider the important chemical properties of the common metallic compounds met with in pyrometallurgical operations.

**Oxides.**—All metals can be made to combine with oxygen, although the oxides of Au, Pt, Pd and other noble metals are unstable and easily decomposed into the metal and oxygen. Many metals form two or more oxides. Most of the lower oxides are bases; i.e., they react with $SiO_2$ or other acids to form salts; other metallic oxides are amphoteric and may behave either as an acid or as a base.

All metallic oxides are solids, and generally show no luster. They are non-conductors of electricity at ordinary temperatures, although a few oxides become fair conductors at high temperatures. All these oxides are insoluble in water. The melting points of the oxides vary over a wide range of temperature, as shown by Table 5. $As_2O_3$ and $Sb_2O_3$ tend to volatilize or sublime when heated at atmospheric pressure.

TABLE 5

MELTING POINTS OF SOME METALLIC OXIDES

| Oxide | M.P., °C. | Oxide | M.P., °C. |
|---|---|---|---|
| $HgO$ | 100 (*d*) | $Fe_3O_4$ | 1538 (*d*) |
| $As_2O_3$ | 193 (*s*) | $Fe_2O_3$ | 1565 |
| $Ag_2O$ | 300 (*d*) | $MnO$ | 1650 |
| $As_2O_5$ | 315 (*d*) | $ZnO$ | 1800 |
| $PbO_2$ | 370 (*d*) | $BaO$ | 1923 |
| $Sb_2O_3$ | 656 | $Cr_2O_3$ | 1990 |
| $Bi_2O_3$ | 820 | $Al_2O_3$ | 2050 |
| $PbO$ | 888 | $BeO$ | 2570 |
| $CuO$ | 1026 (*d*) | $CaO$ | 2572 |
| $SnO_2$ | 1127 (*d*) | $ZrO_2$ | 2700 |
| $Cu_2O$ | 1235 | $MgO$ | 2800 |
| $FeO$ | 1420 | $TiO_2$ | 2930 |
| $CdO$ | 1426 | | |

(*d*) Decomposes.
(*s*) Sublimes.

With the principal exception of $Cu_2O$, which is soluble in molten copper, the metallic oxides are in general not soluble in molten metals or molten sulfides. They are usually very soluble, however, in molten slags or salts formed by the reaction of acid and basic oxides. These facts are very important in smelting operations, because they permit oxidized material (slag) and reduced metal or metallic sulfides to separate into two liquid layers.

Many oxides decompose when heated: $Au_2O_3$, $Ag_2O$, $PtO$, $HgO$ lose all their oxygen and yield the metallic element; $MnO_2$ loses part of its oxygen to form $MnO$. Other oxides take on more oxygen when heated; e.g.,

$$2Cu_2O + O_2 \rightarrow 4CuO$$

$$4Fe_3O_4 + O_2 \rightarrow 6Fe_2O_3$$

$$2PbO + O_2 \rightarrow 2PbO_2$$

Metallic oxides are common in nature and form important ore minerals of many metals. Practically all iron ore minerals, and all aluminum, manganese, and tin ore minerals, are oxides.

Oxides may be formed in metallurgical operations in the following ways:

1. By heating solid metal or solid metallic compounds (notably sulfides) in contact with air (roasting).

$$3Fe + 2O_2 \rightarrow 2Fe_3O_4$$

$$4FeS + 7O_2 \rightarrow 2Fe_2O_3 + 4SO_2$$

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$$

2. By blowing air or steam through molten metal (fire refining) or air through molten sulfides (converting). Steam is an efficient oxidizer for those metals whose affinity for oxygen is greater than that of hydrogen.

$$2FeS + 3O_2 \rightarrow 2FeO + 2SO_2$$

$$Zn + H_2O \rightarrow ZnO + H_2$$

$$Cd + H_2O \rightarrow CdO + H_2$$

$$4Sb + 5O_2 \rightarrow 2Sb_2O_5$$

$$2Mn + O_2 \rightarrow 2MnO$$

3. By heating metallic carbonates (calcining) or sulfates.

$$CaCO_3 \rightarrow CaO + CO_2$$

$$FeCO_3 \rightarrow FeO + CO_2$$

$$ZnSO_4 \rightarrow ZnO + SO_3$$

4. By treating a molten metal with an oxidizing flux (fire refining).

$$3Mn + Fe_2O_3 \rightarrow 3MnO + 2Fe$$

$$3Si + 2Fe_2O_3 \rightarrow 3SiO_2 + 4Fe$$

$$2Sb + 5PbO \rightarrow Sb_2O_5 + 5Pb$$

$$2As + 2NaNO_3 \rightarrow As_2O_3 + Na_2O + 2NO$$

Metallic oxides may be decomposed in one of the following ways:

1. By treating the oxide with an aqueous solvent to convert it to a soluble salt (hydrometallurgy).

$$ZnO + H_2SO_4 \rightarrow ZnSO_4 + H_2O$$

$$Al_2O_3 + 2NaOH \rightarrow 2NaAlO_2 + H_2O$$

2. By exposing the solid oxide to the action of reducing gases such as CO, $H_2$, or hydrocarbons (reduction smelting).

$$FeO + CO \rightarrow Fe + CO_2$$

$$PbO + CO \rightarrow Pb + CO_2$$

3. By the " roast-reaction " between oxides and sulfides (copper converting, lead smelting).

$$2Cu_2O + Cu_2S \rightarrow 6Cu + SO_2$$

$$2PbO + PbS \rightarrow 3Pb + SO_2$$

4. By electrolyzing an ionized oxide dissolved in a bath of molten salts (electrometallurgy).

$$2Al_2O_3 \rightarrow 4Al + 3O_2$$

(electrolysis of $Al_2O_3$ dissolved in a bath of molten cryolite)

Method 4 is used for recovering metals from oxides which are not reducible by carbon or its compounds.

5. By converting into other compounds by metathesis in an igneous fusion (matte smelting).

$$FeS + Cu_2O \rightarrow Cu_2S + FeO$$

**Sulfides.**—Metallic sulfides are usually fairly heavy substances with metallic luster. They are common in nature, and sulfides compose the principal ore minerals of copper, lead, zinc, nickel, and cobalt. Natural sulfides often contain arsenic or antimony in combination with sulfur to give such minerals as arsenopyrite, FeAsS; pyrargyrite, $Ag_3SbS_3$; and tetrahedrite, $Cu_3SbS_3 + x(Fe, Zn)_6Sb_2S_9$.

Most sulfides have fairly low melting points, and the sulfides of all the heavy metals burn to give the metallic oxide and $SO_2$ when heated in air. The artificial sulfides produced in smelting operations are called *mattes*, and ordinary copper matte consists principally of $Cu_2S$ and FeS. Mattes produced in lead smelting contain PbS in addition to the copper and iron sulfides; and nickel mattes contain $Ni_3S_2$ in addition to $Cu_2S$ and FeS. These sulfides are soluble in one another in the liquid state, and the mattes form as homogeneous liquid solutions.

Liquid sulfides are soluble in one another, but the liquid sulfides are not miscible with liquid slags; this permits the separation of matte and slag into two distinct layers. Molten copper, however, dissolves small amounts of $Cu_2S$; FeS is quite soluble in molten iron; and $Ni_3S_2$ and liquid nickel are miscible in all proportions. PbS and other sulfides are not soluble to any extent in molten lead.

Sulfides may be prepared by one of the following methods:

1. By adding elemental sulfur to molten metal, e.g.

$$2Cu + S \rightarrow 2Cu_2S$$

This method is sometimes used to remove dissolved copper from lead bullion.

2. By metathesis in igneous fusion (matte smelting, iron smelting).

$$Cu_2O + FeS \rightarrow Cu_2S + FeO$$

$$FeS + CaO + C \rightarrow CaS + Fe + CO$$

3. By heating metallic sulfates with a reducing agent, e.g.

$$PbSO_4 + 4C \rightarrow PbS + 4CO$$

Metallic sulfides may be decomposed by one of the following methods.

1. By dissolution in an aqueous solution (hydrometallurgy).

$$Cu_2S + 4FeCl_3 \rightarrow 2CuCl_2 + 4FeCl_2 + S$$

$$Ag_2S + 4KCN \rightarrow 2KAg\,(CN)_2 + K_2S$$

2. By heating solid sulfides in a current of air (roasting) to form either oxides or sulfates.

$$ZnS + 2O_2 \rightarrow ZnSO_4$$

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$$

$$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$$

3. By blowing air through molten sulfides (converting)

$$2FeS + 3O_2 \rightarrow 2FeO + 2SO_2$$

4. Simple heating will decompose pyrite and cause it to give up one atom of sulfur

$$FeS_2 \rightarrow FeS + S$$

5. By heating the sulfide with a metal or other element that has a stronger affinity for S

$$PbS + Fe \rightarrow FeS + Pb$$

Metallic sulfides are not appreciably affected by heating with carbonaceous reducing agents (C, CO, hydrocarbons, etc.), and hence most metals cannot be produced directly from a sulfide ore by reduction smelting.

**Silicates.**—Silicate minerals are very common in nature, but they are not important as ore minerals. The silicates which are of most interest to the metallurgist are the artificial silicates, or slags, formed in smelting operations. The silicates of all metals except Na and K are insoluble in water, and they have a vitreous luster and a nonmetallic appearance.

Most silicates are very stable compounds and have high heats of formation from their elements. The heats of formation of silicates from their constituent oxides, however, are usually smaller and are sometimes negative. This indicates that some silicates may be decomposed into their constituent oxides without great difficulty. Most silicates are miscible with one another in all proportions in the liquid states.

Although silicates of definite chemical composition have definite melting points, it is necessary to consider also the melting point of those silicates which do not correspond to any simple compound. We do this by the use of equilibrium diagrams exactly as we did for alloys. We may plot the equilibrium diagram between the oxides CaO and $SiO_2$ in the same way as we plotted the Pb-Sb diagram. Definite compounds, such as $CaSiO_3$, will show themselves in the same way as did the intermetallic compounds in our alloy diagrams. For the system CaO—FeO—$SiO_2$ we should use a ternary diagram. In general, these silicate melts, when cooled, show combinations exactly analogous to the constituents found in alloys. We have compounds, solid solutions, pure oxides (such as $SiO_2$, FeO, $Fe_3O_4$, etc.), or eutectic mixtures. All crystallized silicates contain only definitely known silicate minerals. These solid silicates differ from alloys, however, in that they may solidify partially or completely as a glass or amorphous solid.

Silicates are formed in pyrometallurgy by the reaction of basic oxides with $SiO_2$ in furnace charges.

In most cases no attempt is made to decompose metallic silicates in pyrometallurgy. The silicate slags formed in smelting are intended to be rejected, as they contain only those metals in the charge which are not to be recovered. In iron smelting, for instance, the desired slag is a calcium-aluminum silicate. Any iron oxide which is not reduced will dissolve in the slag and be lost; but since metallic iron is not soluble in slag, every effort is made to reduce the iron oxides to metallic iron before they have an opportunity to enter the slag. In some cases silicates of valuable metals may be decomposed by more active bases, e.g.,

$$Pb_2SiO_4 + CaO + FeO \rightarrow CaFeSiO_4 + 2PbO$$

setting the PbO free to be reduced by CO or other reducing agents.

The important silicates in smelting operations are, of course, the silicates of metals which are to be discarded, and not the silicates of the valuable metals. These are calcium-aluminum silicates in iron smelting, and calcium-iron-(aluminum) silicates in non-ferrous smelting.

**Aluminates.**—In many cases the $Al_2O_3$ in a slag behaves as an acid giving rise to such compounds as $CaAl_2O_4$. Some of the most troublesome compounds formed in slags are the *spinels*, which tend to crystallize out of the slag at high temperatures. The spinels have the general formula $R''O \cdot R'''_2O_3$, where $R''$ and $R'''$ represent divalent and trivalent metals, respectively. When considerable zinc and alumina are present in a lead blast-furnace charge the spinel zinc aluminate, $ZnO \cdot Al_2O_3$ or $ZnAl_2O_4$, often crystallizes out of the slag.

**Arsenides and Antimonides.**—These compounds somewhat resemble the sulfides in physical appearance and are usually found associated with the sulfides in nature. Their chemical properties are similar to those of the sulfides.

Artificial arsenides or antimonides formed in smelting operations are known as *speiss*.

**Sulfates.**—Chalcanthite, $CuSO_4 \cdot 5H_2O$, is a minor ore mineral of copper. Anglesite, $PbSO_4$, is a minor ore mineral of lead, but none of the other natural sulfates are of importance as sources of metal.

Sulfates are formed:

1. By natural or artificial weathering of sulfide ores (notably copper ores).

2. By heating sulfides in air at relatively low temperatures (sulfatizing roast).

$$ZnS + O_2 \rightarrow ZnSO_4$$

$$CuS + O_2 \rightarrow CuSO_4$$

$$PbS + O_2 \rightarrow PbSO_4$$

Sulfates may be decomposed:

1. By dissolution in an aqueous solvent (hydrometallurgy) followed by electrolytic precipitation of the metal (electrometallurgy). The most important application of this method is to the sulfates of copper and zinc, both of which are soluble in water.

2. In the roasting of lead ores, any sulfate formed may be decomposed by the action of silica.

$$2PbSO_4 + SiO_2 \rightarrow Pb_2SiO_4 + 2SO_3$$

3. By simple heating to yield sulfides, basic sulfates or oxides, or by heating with carbon.

$$PbSO_4 + 2C \rightarrow PbS + 2CO_2$$

$$2ZnSO_4 + C \rightarrow 2ZnO + 2SO_2 + CO_2$$

**Carbonates** are usually dissociated into metallic oxides and $CO_2$ by the heating associated with pyrometallurgical operations, so that their essential chemistry is the same as that of the oxides. Siderite, $FeCO_3$, is fairly important as an iron ore; it is also a gangue mineral in many non-ferrous ores. Cerussite, $PbCO_3$; smithsonite, $ZnCO_3$; rhodochrosite, $MnCO_3$; and the basic copper carbonates, malachite and azurite, are minor ore minerals.

This brief introduction to the important metallic compounds will be of some assistance to us when we consider some typical processes of pyrometallurgy. The reader must bear in mind that all extraction and refining processes depend upon the differences in the chemical properties of different metals—if all metals had the same affinity for sulfur, for example, the matte smelting of copper ores would be impossible. All the processes of extractive metallurgy are designed to take the best advantage of the differences in chemical properties of the metals, and all improvements on existing processes and development of new processes must come from a study of the fundamental chemistry of metals and their compounds.

## EXERCISES

1. At a temperature of 25° C and a pressure of 750 mm. what is the weight in pounds of 1000 cubic feet of carbon monoxide?

2. What is the volume in cubic feet of acetylene produced from 2 pounds of calcium carbide?

$$CaC_2 + H_2O \rightarrow CaO + C_2H_2$$

3. How many cubic feet of air are necessary to burn completely 1000 cubic feet of gas of the following composition?

| | |
|---|---|
| Methane $CH_4$ | 40% (by volume) |
| Ethylene $C_2H_4$ | 10% |
| Carbon monoxide CO | 20% |
| Hydrogen $H_2$ | 30% |

4. Find the volume in liters at standard conditions of 500 grams of chlorine gas.

5. Two liters of acetylene are exploded with 50 liters of air. Consider the water as condensed and its volume negligible. What volumes of what gases remain?

6. An ore consists of $SiO_2$, $Fe_2O_3$, and $FeS_2$. After dead roasting (all iron to $Fe_2O_3$; S to $SO_2$) it assays 65.089 per cent Fe and loses 3.8 per cent of its weight. Determine the rational analysis of the original ore.

7. One ton of pure FeS is burned to $SO_2$ and $Fe_2O_3$. Calculate the total heat evolved in pound calories, and the heat evolved per pound of iron, per pound of sulfur, and per pound of FeS.

8. A zinc retort requires 900 pounds of 7500-calorie (pound calories per pound) coal to distil 1000 pounds of zinc (from solid at 0° C.). What is the theoretical efficiency of the operation, assuming that the vapors pass off at 930° C. (normal boiling point)?

| | |
|---|---|
| Mean specific heat of solid zinc .. | $(0.096 + 0.000044t)$ |
| Heat of fusion . .. ........ . | 28.13 cal. per gm. |
| Specific heat of liquid zinc . .. | 0.179 |
| Heat of vaporization . . . | 446 cal. per gram |

9. A roasting furnace roasts 30 tons of concentrate per 24 hours.

| Analysis of raw concentrate | | |
|---|---|---|
| | PbS | 60% |
| | FeS | 20% |
| | ZnS | 5% |
| | $SiO_2$ | 15% |

80% of the FeS goes to $Fe_2O_3$
10% of the FeS goes to $FeSO_4$
10% of the FeS is unaltered
40% of PbS goes to PbO
30% of PbS goes to $PbSO_4$
90% of ZnS goes to ZnO
10% of ZnS goes to $ZnSO_4$

The process is autogenous.
Calculate:

1. Total heat evolved per 24 hours in pound calories.
2. The theoretical amount of air required in cubic feet at standard conditions.
3. Using 100 per cent excess air, what is the volume of gases resulting at 250° C. and 760 mm.?
4. At a velocity of 15 feet per second how many 10-inch pipes are required to handle this volume?

10. Calculate the heats of reaction of the following.

(*a*) $CaC_2 + H_2O \rightarrow CaO + C_2H_2$
(*b*) $BaO + CO_2 \rightarrow BaCO_3$
(*c*) $Al_2O_3 + SiO_2 \rightarrow Al_2SiO_5$
(*d*) $3Al_2O_3 + 2SiO_2 \rightarrow Al_6Si_2O_{13}$
(*e*) $Fe_2O_3 + FeO \rightarrow Fe_3O_4$

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# CHAPTER XII

# PYROMETALLURGY—2. HEAT

## FUELS

A fuel is any substance which may be burned rapidly enough in air so that the heat resulting from the oxidation is capable of being applied to industrial operations. *Combustion* is the term applied to the burning of fuel. *Incomplete combustion* is a term applied to combustion in which not all the fuel is burned (leaving unburned carbon in ashes, for example); *imperfect combustion* means that not all the fuel is oxidized to its highest degree (if CO is formed, for example, instead of $CO_2$). The ignition temperature of fuel is the temperature at which combustion begins. The ignition temperature is not definite for any substance but depends upon its physical condition and the atmospheric pressure. Combustion is always accompanied by the evolution of heat and light.

*Ash* is the non-combustible inorganic matter in solid fuel; *ashes* (or cinder) are the residue left after the fuel has been burned. If the ashes weigh more than the ash, the difference is due to unburned carbon left by incomplete combustion.

**The Heat-Producing Elements.**—The heat producing elements found in metallurgical fuels in approximate order of their importance are C, H, S, Si, Mn, Al, and P. The metals themselves may be used as fuels; for example, the oxidation of manganese contributes considerable heat in the Bessemer process.

Carbon and hydrogen are by far the most important of the heat-producing elements, and taken together constitute the bulk of the combustible material of all fuel gases, both natural and manufactured; all coals and cokes; and all the fuel oils. Carbon may be in the elemental form as in charcoal and coke, entirely in the combined form as in hydrocarbons and cellulose, or partly free and partly combined as in bituminous and lignite coals. Hydrogen occurs free in some gaseous fuels, and combined as hydrocarbons in gaseous, liquid, and solid fuels. Sulfur is important as a primary fuel in matte converting and roasting. In fuels such as coke and coal, it is of more importance as an impurity which may contaminate a furnace charge.

Ash in fuels generally consists of silica, lime, and ferric oxide. It has no heating value, and its form and amount often lower the value of a fuel considerably. Fuel oils and fuel gases are free from ash.

**Classification of Fuels.**—At this point we shall give an outline of the classification of fuels followed by brief discussions of the more important types.

I. Solid fuels.
    A. Natural fuels.
        1. Wood.
        2. Peat.
        3. Lignite coal.
        4. Bituminous coal.
        5. Anthracite coal.
    B. Prepared (artificial) fuel.
        1. Pulverized coal.
        2. Compressed fuels (briquettes).
        3. Carbonized fuels.
            a. Charcoal.
            b. Coke.

II. Liquid fuels.
    A. Natural fuel.
        1. Petroleum or crude oil.
    B. Prepared fuel.
        1. Distilled oils.
        2. Coal tar.

III. Gaseous fuels.
    A. Natural fuels.
        1. Natural gas.
    B. Prepared fuel.
        1. Coal gas.
        2. Oil gas.
        3. Iron blast-furnace gas.
        4. Producer gas.
            a. Water gas.
            b. Air gas.
            c. Mixture of air and water gases.

**Wood.**—The use of wood as a metallurgical fuel is of little importance except in remote districts where timber is plentiful and transportation difficult. Freshly felled wood contains from 40 to 50 per cent moisture, and therefore must be seasoned or dried before it can be used as fuel. Air-dried wood contains from 15 to 25 per cent moisture and has a calorific power (heat generated by burning a unit of fuel) of 5000 to 6800 B.t.u. per pound. Bone-dry wood has a calorific power of 7000 to 9000 B.t.u. per pound.

**Charcoal.**—Charcoal is the residue left after the destructive distillation or charring of wood. It is a good fuel and is used in a few special cases where high-purity fuel is desired, since it contains little ash and no sulfur. The calorific power of charcoal is about 11,000 B.t.u. per pound. Charcoal, however, is not to be classed as an important metallurgical fuel.

**Analysis of Coal.**—Before proceeding to a discussion of the various types of coal, it will be necessary to consider the meaning of certain terms used in reporting the chemical analysis of solid fuels. A *proximate analysis* is most frequently used for coals and coke. It is carried out under certain standard procedures and reports the following constituents:

1. Fixed carbon.
2. Volatile (combustible) matter (V. C. M.).
3. Moisture.
4. Ash.
5. Sulfur.

The moisture is determined as the loss in weight of a small sample in heating for 1 to 1½ hours at 104°–110° C.; volatile matter is determined by heating a 1-gram sample at 950° C. in a closed crucible for 7 minutes, the loss being equal to the percentage of volatile matter plus the percentage of moisture. Ash is the material left after the coal sample has been strongly ignited to burn off all combustible material. The percentage of fixed carbon is equal to (100—[per cent ash + per cent V. C. M. + per cent moisture]). The analysis for sulfur follows the ordinary chemical procedure. The sulfur may be in either the ash or V. C. M., or both.

An *ultimate analysis* of fuel (or any other substance) reports the percentage of each element present. Thus, the ultimate analysis of a coal would show the percentage of oxygen, carbon, hydrogen, sulfur, iron, etc.

**Formation of Coal.**—Apparently coal has been formed from woody vegetal material deposited in swamps and bogs; and peat, lignite, bituminous and anthracite coals appear to represent successive stages in the alteration of woody material to hard, brittle anthracite. Partial decay of the original woody material, followed by the pressure caused by later sediments and the thrust-pressure of other rock layers, brought about the chemical and physical changes which resulted in the formation of coal beds. Wood fiber consists largely of cellulose which has the formula $(C_6H_{10}O_5)_x$ and contains 44.5 per cent carbon, 6.2 per cent hydrogen, and 49.4 per cent oxygen. Compare these figures with the data in Table 1.

TABLE 1 *

COMPOSITION OF WOOD, PEAT AND COALS (ASH AND MOISTURE-FREE BASIS)

| | Proximate Analysis, Per Cent | | Ultimate Analysis, Per Cent | | | | | Calorific Power (B.t.u.per Pound), Moisture- and Ash-free Basis |
|---|---|---|---|---|---|---|---|---|
| | Volatile Matter | Fixed C | Sulfur | Hydrogen | Total Carbon | Nitrogen | Oxygen | |
| Wood | ...... | ..... | ..... | 6.25 | 49.5 | 1.10 | 41.35 | 5,800 |
| Peat | 70.06 | 29.94 | 1.71 | 5.44 | 56.37 | 2.95 | 33.53 | 9,610 |
| Lignite | 60.67 | 39.33 | 1.89 | 4.74 | 72.79 | 0.98 | 19.60 | 12,172 |
| Subbituminous | 38.12 | 61.88 | 0.50 | 4.74 | 76.28 | 1.47 | 17.01 | 12,938 |
| Bituminous | 30.26 | 69.74 | 1.06 | 5.39 | 87.00 | 1.37 | 5.18 | 15,527 |
| Semi-bituminous | 16.12 | 83.88 | 2.52 | 4.37 | 89.07 | 1.40 | 2.64 | 15,683 |
| Semi-anthracite | 9.95 | 90.05 | 0.74 | 3.76 | 92.15 | 1.18 | 2.17 | 15,457 |
| Anthracite | 1.29 | 98.71 | 1.00 | 1.77 | 94.39 | 0.71 | 2.13 | 14,882 |

* Haslam, Robert T., and Russell, Robert P.: Fuels and Their Combustion; McGraw-Hill Book Co., New York, 1926. Reprinted by permission.

The data in Table 1 represent analyses of typical wood, peat, and different classes of coal. The amount of total carbon increases as we pass from wood to anthracite. The amounts of hydrogen and oxygen decrease. The volatile matter consists principally of carbon compounds of hydrogen and oxygen, and the decrease in volatile matter shows that almost all the carbon in the end-product (anthracite) is in the form of fixed or uncombined carbon.

The carbon and hydrogen in coal contribute its heating value, and heat is liberated when these elements combine with oxygen from the air. If, however, the coal contains considerable oxygen, its heating value is lowered, because a certain part of the combustible material is already oxidized, hence, it is not available as a fuel. The assumption is usually made that all the oxygen in coal is tied up with hydrogen so that the *net hydrogen*, or the amount actually available for heating purposes, is

$$\text{\% of net hydrogen} = \text{\% of total hydrogen} - \frac{\text{\% of oxygen}}{8}$$

since water consists of 8 parts of oxygen to 1 part of hydrogen, and the amount of hydrogen tied up by the oxygen is equal to 1/8 of the amount of oxygen.

Probably the most important effect of the coal-making process is the elimination of oxygen from the fuel, thus making all the carbon and most of the hydrogen available for use. Table 1 shows that, in general, the calorific power rises as the oxygen content decreases. The heating value of carbon is only 14,544 B.t.u. per pound, as against 62,000 B.t.u. per pound for hydrogen, so that many bituminous coals have higher heating values than the anthracites because of their larger hydrogen content. However, it is not the total hydrogen content but the net hydrogen that gives this extra heating value.

During the period of coal formation, many substances find their way into the mass of coal besides the organic material of the original vegetal matter. Sand and other mineral grains are deposited with the vegetation; and after the coal bed has been buried and compacted, mineral-bearing solutions often penetrate the coal seam and deposit their load. Consequently, all coal contains more or less non-combustible inorganic matter or *ash*, together with some sulfur, and often a little phosphorus. The ash left after coal has been completely burned is a mixture of oxides, silicates, and sulfates, the relative proportions of which vary widely in different coals. The chief components are $SiO_2$, $Al_2O_3$, FeO, $Fe_2O_3$ and CaO, with smaller amounts of MgO, $TiO_2$, and alkali compounds.

Sulfur occurs in coal as pyrite, $FeS_2$; gypsum, $CaSO_4$; and as organic sulfur combined with carbon and hydrogen. Phosphorus is found mainly as apatite, $Ca_{10}F_2(PO_4)_6$. The constituents found in coal ash do not always have the same form as they have in the unburned coal; e.g., most of the iron oxides come from the combustion of $FeS_2$, and CaO and MgO are formed by the calcination of carbonates. The chemical analysis of coal ash is important, because very often the ash becomes part of the furnace charge after the coal (or coke) has burned, and allowance must be made for its effect on the slag. The sulfur and phosphorus content is also important, and many coals are unsuited for metallurgical processes because of large amounts of these two elements.

In addition to the ash, sulfur, and phosphorus in coal, a certain amount of moisture is always present. The moisture content is greatest in the peats and least in the anthracites. Table 2 gives the actual "as delivered" analyses of the materials listed in Table 1. Note particularly the steady decrease in moisture content and the erratic variation in ash and sulfur content.

When the ash in coal is "free" or in such form as relatively large

TABLE 2 *

| Kind of Fuel | Moisture | Volatile Matter | Fixed Carbon | Ash | Sulfur | Hydrogen | Total Carbon | Nitrogen | Oxygen | Heating Value, B.t.u. per Pound |
|---|---|---|---|---|---|---|---|---|---|---|
| Wood.......... | ...... | ...... | ...... | ...... | .... | 6.25 | 49.50 | 1.10 | 43 15 | 5,800 |
| Peat........... | 56.70 | 26.14 | 11.17 | 5.99 | 0 64 | 8.33 | 21.03 | 1.10 | 62.91 | 3,586 |
| Lignite......... | 34.55 | 35.34 | 22.91 | 7.20 | 1.10 | 6.60 | 42.40 | 0.57 | 42.13 | 7,090 |
| Subbituminous.. | 24.28 | 27.63 | 44.84 | 3 25 | 0 36 | 6.14 | 55.28 | 1 07 | 33.90 | 9,376 |
| Bituminous..... | 3.24 | 27.13 | 62.52 | 7.11 | 0.95 | 5.24 | 78 00 | 1 28 | 7 47 | 13,919 |
| Semi-bituminous | 2.03 | 14.47 | 75.31 | 8.19 | 2.26 | 4.14 | 79.97 | 1 26 | 4.18 | 14,081 |
| Semi-anthracite | 3.38 | 8.47 | 76.65 | 11.50 | 0.63 | 3.58 | 78.43 | 1.00 | 4.86 | 13,156 |
| Anthracite...... | 2.80 | 1.16 | 88.21 | 7.83 | 0.89 | 1.89 | 84 36 | 0.63 | 4.40 | 13,298 |

* Haslam, Robert T., and Russell, Robert P.: Fuels and Their Combustion; McGraw-Hill Book Co., New York, 1926.

pieces of slate, the coal can often be washed or beneficiated to reduce the ash content.

**Behavior of Coal on Heating.**—When a coal containing an appreciable amount of volatile matter is subjected to *destructive distillation* (heating in a closed container so that no air reaches the hot coal), a certain amount of the volatile combined carbon is driven off in the form of chemical compounds of carbon, hydrogen, and oxygen. The lighter compounds such as methane, $CH_4$, and other hydrocarbons escape as coal gas, and the heavier volatile compounds form coal tar. The solid residue left contains the fixed carbon and the ash. In the case of coking coals, the solid residue becomes coke.

**Peat** is an accumulation of compacted and partially devolatilized vegetable matter containing high percentages of moisture and oxygen. None of the peats have any importance as metallurgical fuels—at least, not in the United States.

**Lignite or brown coal** is an amorphous, woody coal. It is superior to peat as a fuel but decidedly inferior to bituminous coal. Some lignites may eventually become of importance in low-temperature carbonization processes, but at present they have little importance as metallurgical fuels. Subbituminous coal ("black lignite") is intermediate between the lignites and bituminous coals. About one-half of the world's supply of solid fuel is lignite, so that its production will inevitably become of great importance in the future.

**Bituminous coal** is the only solid natural fuel which is important in metallurgical processes, and it is not widely used as such, but rather as a raw material for the manufacture of coke, coal gas, pulverized coal, and producer gases.

Bituminous coals contain rather high percentages of volatile material, and hence burn with a long yellowish flame. These coals have a lustrous black color, a laminated structure, and are fairly hard and brittle. In 1921 [1] about 416 million short tons of bituminous coal were mined in the United States, together with 90 million tons of anthracite. The bulk of this solid fuel consumed by the metallurgical industry was in the form of metallurgical coke which consumed about 15 per cent of the bituminous coal.

The importance of coke in the metallurgical industries has led to the classification of bituminous coals into coking and non-coking coals. Many efforts have been made to predict the coking properties of coal from its analysis—volatile matter, ash content, oxygen content, etc.—but none of these has been particularly successful. The only definite way to determine the coking properties of a coal is to submit a small sample to destructive distillation in a closed crucible. If the coal softens and partially fuses during the heating, and eventually forms a porous mass of coke in the crucible, the coal is a coking coal. If the residue left after heating is sandy and granular, then the coal is not suited for making coke.

**Anthracite or hard coal** and the *semi-anthracite* coals are hard, heavy coals. Anthracite burns with a short blue flame and in burning requires a deep bed and a strong draft. Anthracite is widely used for domestic heating, but it is not used to any extent as metallurgical fuel. Anthracite coals are not suited for making coke.

**Metallurgical coke** is practically the universal fuel for blast furnaces, both in ferrous and non-ferrous smelting. A little "charcoal iron" is still made by blast furnaces using charcoal as fuel, but this is unimportant in the United States.

Coke is made by the destructive distillation of bituminous coal. It is a porous silvery-gray material, having a crushing strength varying from 300 pounds per square inch for the *beehive* variety to 900 pounds per square inch for *by-product* coke. Coke is low in volatile material and hydrogen and always contains more ash than the coal from which it is made. The sulfur and phosphorus content of coke depends upon the amount of these elements in the raw coal; coke for use in the iron blast furnace should not contain more than 1 per cent sulfur. Coke has a kindling temperature of about 700° C., and requires a deep bed and a strong draft in burning.

**Beehive coke** is made by burning coal with an insufficient supply of air in a beehive-shaped kiln. Coal is loaded into the kiln and

[1] Haslam, Robert T., and Russell, Robert P.: Fuels and Their Combustion; McGraw-Hill Book Co., New York, 1926.

allowed to burn slowly until it is all converted into coke. The combustion of part of the coal—principally the volatile matter—provides the heat necessary for distilling, or coking, the coal.

By-product coke is made by distilling coal in an externally heated vertical oven. The by-product process has the advantage that the coal gas, coal tar, and other valuable by-products of the distillation can be recovered. Also there is less waste of coke than in the beehive process, and the coke has greater mechanical strength.

In 1934 [2] there were produced in the United States about 31 million tons of by-product coke, and a little over 1 million tons of beehive coke. Of the 1934 total, about 15,700,000 tons were consumed by the iron furnaces.

In blast-furnace smelting the fuel is mixed with the solid charge as it enters the furnace; and the fuel must be (1) porous to permit the flow of furnace gases through the charge, and (2) mechanically strong, to support the weight of the column of ore, flux, and fuel. Coke is the only fuel which satisfactorily meets these requirements. Coke is the only fuel used in blast furnaces. Other metallurgical fuels burn with a long flame, and these include powdered coal, fuel oil, and various fuel gases.

The average analysis of metallurgical coke will be as follows:

| | |
|---|---|
| C | 83 to 90% |
| Ash | 4 to 15% |
| V.C.M. | 0.5 to 4% |
| S | 0.5 to 3% |

**Pulverized Coal.**—As the name implies, this is coal that has been pulverized. The terms "pulverized," "powdered," "granulated," and "crushed" are not to be used indiscriminately. In the order given above, they refer to successively coarser products. Pulverized coal is in the finest practicable state of division. It should be about 80 per cent −200 mesh and 95 per cent −100 mesh. When pulverized coal is burned, it is blown into the firebox on a current of air and burned like a gas.

Pulverized coal is used principally for two reasons. In the first place, pulverized coal burns more perfectly and completely than lump coal, and consumes more nearly the theoretical amount of air, that is, requires less excess air. These facts mean that the available calorific power and the calorific intensity of the coal are increased. In the second place, pulverized coal makes possible the profitable use of mine fines and lower grades of coal.

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[2] The Mineral Industry for 1934; McGraw-Hill Book Co., New York.

The requirements of coal for pulverizing are not stringent. Pulverized fuel has been made satisfactorily from almost every kind of coal known. The following specifications are desirable rather than necessary:

| | |
|---|---|
| V.C.M. | 30% |
| Moisture | 2% |
| Low ash content | |

The finished product must be uniformly and finely pulverized, and when burned must be intimately mixed with air. The mixture of coal dust and air must be fed continuously into the heated combustion chamber.

The preparation of pulverized coal is of interest to users of the product, for the pulverized coal cannot be stored longer than 48 hours because of the danger of ignition from spontaneous combustion. Therefore, it must be prepared as it is used. Lump coal is crushed to moderate size, dried if necessary, and then pulverized in a ball mill or some other type of coal pulverizer. One requirement of the crushing and grinding machinery for treatment of coal is that it must be made of metal which will not give off sparks, for a mixture of coal dust and air is highly explosive. The finished coal is drawn off from the pulverizer by fan suction and is conveyed by pneumatic or screw conveyors to the point where it is to be used.

Pulverized coal can be burned only in a hot ignition chamber. The air used may be preheated, but the coal cannot be preheated.

Some advantages and disadvantages of pulverized coal as a fuel may be summed up as follows:

Advantages:

1. It burns with a long flame.
2. It has high efficiency of combustion.
3. It permits the use of low-grade fuel or mine fines.
4. It costs less than producer gas.

Disadvantages:

1. A mixture of air and coal dust is explosive.
2. It cannot be stored.
3. The ash content is often quite high, and the ash may form an insulating blanket on the furnace charge.

**Compressed Fuels (Briquettes).**—The term briquette is applied to any finely divided fuel (coal, wood) that has been mixed with a binder and compressed. Briquetted fuels are widely used in Europe but are rather uncommon in the United States. The binder is for the purpose of holding the briquette in shape. The binder should be an organic material that will add to the calorific power of the briquette. Pitch is the most common binder, although naphthalene, resin, asphalt, and molasses are sometimes used. The metallurgical use of briquetted fuels in this country is of little importance.

**Liquid Fuels.**—Petroleum is a very valuable fuel for metallurgical purposes, since it has a higher calorific power than any solid fuel, has little or no ash, and is easily handled and transported. Petroleum, however, forms explosive mixtures with air and suffers high evaporation losses. Crude oil is widely used as a metallurgical fuel, but most of the prepared liquid fuels (gasoline, refined oil, and coal tar) are too valuable for other purposes to be used as fuel in metallurgical operations.

Liquid fuel must be burned by spraying atomized fuel mixed with air into a heated combustion chamber, and many different types of burners have been devised to insure proper atomization and mixing of fuel and air. Liquid fuel burns with a long flame.

**Gaseous Fuels.**—Gaseous fuels are in many respects the ideal fuels from the standpoint of ease of handling and efficiency of combustion. They contain no ash. A brief list of the most important gaseous fuels follows:

A. *Natural gas* is the best and the most important of the gaseous fuels, and has the highest calorific power of all. It is usually composed principally of methane, $CH_4$, and ethane, $C_2H_6$, with smaller amounts of $H_2$, $CO$, $CO_2$, $N_2$, and $H_2O$. Some natural gases contain other hydrocarbon gases (Table 3).

B. *Coal, or coke-oven gas.* This is a very good fuel gas, probably the next in order to natural gas as far as calorific power is concerned. This gas is a by-product from the destructive distillation of coal. Its principal constituents are methane (about 40 per cent) and hydrogen (about 50 per cent).

C. *Oil gas* has about the same composition as coal gas, and it is formed by the destructive distillation ("cracking") of petroleum products.

D. *Producer gases.* A gas producer is a device in which coal is either partially burned with air or decomposed by steam. In the first instance, the carbon burns to CO,

$$2C + O_2 \rightarrow 2CO \tag{1}$$

and the resulting *air gas* consists essentially of about 30 per cent CO and 60 per cent $N_2$. This gas has a low calorific power.

Hot carbon will decompose steam, thus:

(2) $$C + H_2O \rightarrow H_2 + CO$$

and the resulting *water gas* or *"blue"* gas is about 50 per cent hydrogen and 50 per cent carbon monoxide. Water gas has a much higher calorific power than coal gas. Reaction (1) is exothermic and tends to heat up the charge; reaction (2) is endothermic and requires heat to be supplied. For this reason most gas producers make both air and water gas so that the process may be self-supporting. If the air and steam are fed together in the proper proportions, mixed air and water gases are formed; if air and steam are used in cycles, the producer makes air and water gas alternately.

E. *Blast-furnace gas* is practically the same as air gas.

TABLE 3 *

COMPOSITION OF REPRESENTATIVE FUEL GASES

| | Per Cent by Volume | | | | | | | | | Calorific Power (Net) in B.t.u. per Cubic Foot |
|---|---|---|---|---|---|---|---|---|---|---|
| | $CH_4$ | $C_2H_6$ | $C_3H_8$ | $C_2H_4$ | CO | $CO_2$ | $H_2$ | $O_2$ | $N_2$ | |
| Coal gas | 34.0 | ..... | ..... | 6.6 | 9.0 | 1.1 | 47.0 | .... | 2.3 | 560 |
| Coke-oven gas | 28.5 | ..... | ... | 2.9 | 5.1 | 1.4 | 57.4 | 0.5 | 4.2 | 476 |
| Coke-oven gas | 33.9 | ..... | .... | 5.2 | 6.1 | 2.6 | 47.9 | 0.6 | 3.7 | 538 |
| Blue water gas | ..... | ..... | ..... | ..... | 43.4 | 3.5 | 51.8 | .... | 1.3 | 285 |
| Carburetted water gas† | 14.8 | ..... | ..... | 12.8 | 33.9 | 1.5 | 35.2 | .... | 1.8 | 529 |
| Oil gas | 27.0 | ..... | ..... | 2.7 | 10.6 | 2.8 | 53.5 | .... | 3.4 | 461 |
| Producer gas (air gas) | 2.6 | ..... | ..... | 0.4 | 22.0 | 5.7 | 10.5 | .... | 58.8 | 128 |
| Blast-furnace gas | ..... | ..... | ..... | ..... | 26.2 | 13.0 | 3.2 | .... | 57.6 | 91.6 |
| Natural gas Follansbee, W. Va. | ..... | 31.8 | 67.7 | ..... | ..... | ..... | ..... | .... | 0.5 | 2,268 |
| Natural gas, Follansbee residual | ..... | 79.4 | 20.0 | ..... | ..... | ..... | .... | .... | 0.6 | 1,711 |
| Natural gas, McKean County, Pa. | 32.3 | 67.0 | ..... | ..... | ..... | ..... | ..... | .... | 0.7 | 1,350 |
| Natural gas Sandusky, Ohio | 83.5 | 12.5 | ..... | ..... | ..... | 0.2 | ..... | .... | 3.8 | 946 |

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* Haslam, Robert T., and Russell, Robert P.: Fuels and Their Combustion; McGraw-Hill Book Co., New York, 1926. Reprinted by permission.

† Water gas enriched by the addition of high-grade oil gas.

**Analysis of Fuel Oil and Gas.**—The analysis of fuel oil is practically always given as an ultimate analysis. Analysis of gases is invariably made by successively absorbing or burning the various gaseous constituents in a suitable apparatus and measuring the decrease in volume for each gas removed. The analysis is then given as a proximate or rational analysis showing the percentage by volume of each gas present. Thus, instead of reporting the percentage of hydrogen in a gas, the analysis would show the percentages of $H_2$, $H_2O$, $CH_4$, $C_6H_6$, etc.

**Flame.**—Whenever a gaseous or liquid fuel is burned, or a solid fuel containing much volatile material, a flame is formed. The flame is simply a zone of combustion in which the volatile substances are burning. Coke and anthracite coal burn without flame, since they contain little or no volatile matter. Hydrogen and CO gases burn with a blue, almost colorless flame; but any fuel containing hydrocarbons burns with a luminous, bright yellow flame. This color may be due to small particles of incandescent burning carbon formed by the "cracking" or decomposition of the hydrocarbon compounds.

If the flame contains an excess of oxygen over the amount theoretically required, it has an oxidizing effect on material in contact with it, and is known as an oxidizing or "cutting" flame. Flame containing an excess of reducing gases is a reducing flame. A neutral flame is practically impossible to obtain, and in any furnace which is heated by a flame the condition ("atmosphere") must be either oxidizing or reducing.

## COMBUSTION

In the selection of a fuel for metallurgical purposes, the following items are of paramount importance:

1. The cost and availability of the fuel.

2. The suitability of the fuel for the process in question. For example, the blast furnace requires coke as a fuel. Reverberatory furnaces require long-flame fuels such as pulverized coal, fuel oil, or gas.

3. The purity of the fuel, or its freedom from excess amounts of ash and harmful elements such as sulfur and phosphorus.

4. The calorific power of the fuel or the heat generated by the complete and perfect combustion of a unit weight or volume of the fuel.

5. The calorific intensity or the temperature that can be attained by burning the fuel.

In combustion problems we are primarily interested in the following topics:

1. The amount of air theoretically required to burn a unit of the fuel.
2. The amount of excess air used.
3. Volume of the products of combustion.
4. The calorific power of the fuel.
    - (*a*) As experimentally determined.
    - (*b*) As calculated.
5. The calorific intensity of the fuel.
    - (*a*) As experimentally determined.
    - (*b*) As calculated.

The calculation of items 1, 2, and 3 is based on the laws of stoichiometry and the simple gas laws. Example 1 illustrates the method involved. Note that excess air is reported as percentage of the theoretical air, and "products of combustion" means all the gases escaping from the combustion. It includes the nitrogen from the air and oxygen and nitrogen from the excess air.

### Example 1

A metallurgical furnace used bituminous coal of the following composition:

| | | | |
|---|---|---|---|
| C | 72.2% | O | 7.8% |
| H | 5.0% | S | 0.8% |
| N | 1.7% | Ash | 12.5% |

The ashes from the furnace are one-fourth unburned carbon. The outside air is at 22° C. and 751 mm. Fifty per cent more air is used than the theoretical requirement.

**Required:**

1. The cubic feet of air (at standard conditions) theoretically required to burn 1 pound of coal.
2. The cubic feet of air actually used at the given conditions.
3. The volume of the products of combustion (flue gases) in cubic feet, and their percentage composition.
4. The cubic meters of air (at standard conditions) actually used per kilogram of coal.
5. The volume of the products of combustion in cubic meters and their percentage composition.

**Solution:** The reactions involved are:

$$C + O_2 \rightarrow CO_2$$

$$2H_2 + O_2 \rightarrow 2H_2O$$

$$S + O_2 \rightarrow SO_2$$

$$\frac{0.125}{3} = 0.042 \text{ lb. unburnt C}$$

$0.722 - 0.042 = 0.680$ lb. C burnt

$$\frac{0.680 \times 16}{12} \times 22.4 = 20.35 \text{ cu. ft. } O_2 \text{ for C}$$

$$\frac{0.05 \times 16}{4} \times 22.4 = 4.48 \text{ cu. ft. } O_2 \text{ for H}$$

$$\frac{0.008 \times 16}{32} \times 22.4 = 0.09 \text{ cu. ft. of } O_2 \text{ for S}$$

Total $O_2$ required $= 24.92$ cu. ft.

$$\frac{0.078 \times 16}{32} \times 22.4 = 0.87 \text{ cu. ft. } O_2 \text{ in the coal}$$

$24.92 - 0.87 = 24.05$ cu. ft. $O_2$ required from air

$$\frac{24.05}{0.21} = 114.5 \text{ cu. ft. air theoretically required (S. C.)} \qquad (1)$$

$114.5 - 24.05 = 90.45$ cu. ft. $N_2$ from theoretical air
$114.5 \times 1.5 = 172$ cu. ft. of air at S. C.

$$172 \times \frac{295}{273} \times \frac{760}{751} = 188 \text{ cu. ft. of air actually required at given conditions} \qquad (2)$$

$$\frac{.017 \times 16 \times 22.4}{28} = 0.22 \text{ cu. m. of } N_2 \text{ from coal}$$

$172 - 114.5 = 57.5$ cu. ft. excess air
$57.5 \times 0.21 = 12.05$ cu. ft. of $O_2$ in excess air
Products of combustion (S. C.)

| | $CO_2$ | $H_2O$ | $SO_2$ | $N_2$ | $O_2$ |
|---|---|---|---|---|---|
| Combustion . | 20.35 | 8.96 | 0.09 | 0.22 | |
| Theoretical air | | | | 90.45 | |
| Excess air . | | | | 45.45 | 12.05 |
| Total . . . . . . . | 20.35 | 8.96 | 0.09 | 136.12 | 12.05 |

Volume of products of combustion

$CO_2 = 20.35$ cu. ft. $= 11.5\%$
$N_2 = 136.12$ cu. ft. $= 76.6\%$
$SO_2 = 0.09$ cu. ft. $= 0.05\%$
$H_2O = 8.96$ cu. ft. $= 5.1\%$
$O_2 = 12.05$ cu. ft. $= 6.8\%$

Total $= 177.57$ cu. ft. $= 100.05\%$ (3)

$$\frac{172}{16} = 10.75 \text{ cu. m. air for 1 kg. coal (S. C.)} \qquad (4)$$

$$\frac{177.6}{16} = 11.08 \text{ cu. m. flue gas at S. C. per kg. of coal} \qquad (5)$$

**Calorimetry.**—The calorific power of a fuel is determined experimentally by burning a known quantity of it in a calorimeter. Solid and liquid fuels are burned in a bomb calorimeter (Fig. 1), and gaseous fuels are burned in a gas calorimeter.

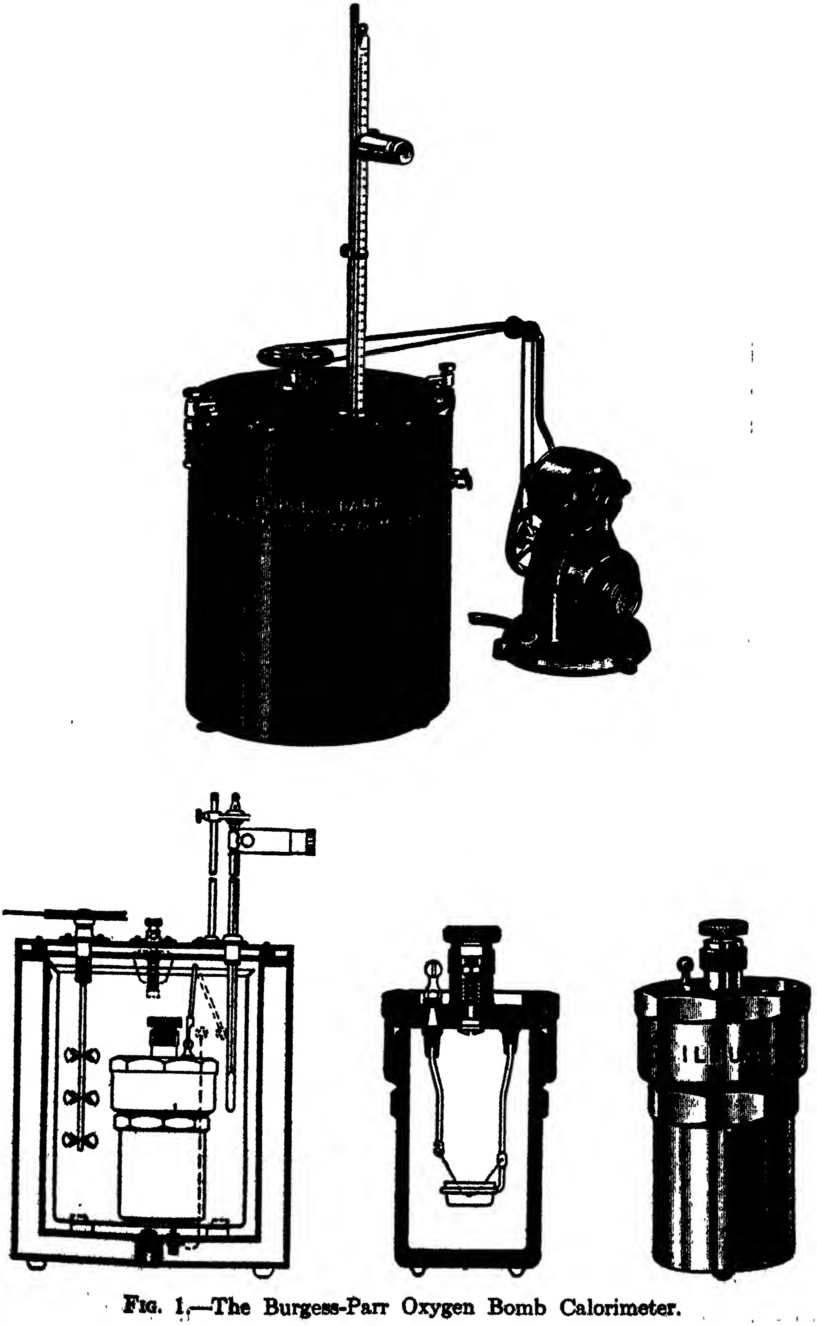

FIG. 1.—The Burgess-Parr Oxygen Bomb Calorimeter.

In the operation of a bomb calorimeter, the fuel is placed in the combustion pan and a small piece of iron wire is connected to the two terminals so that it is in contact with the fuel. The bomb is then sealed and oxygen is introduced under a pressure of several atmospheres. After the bomb has been loaded, it is placed in a bucket holding a known amount of water, which is surrounded by another water-filled jacket (see Fig. 1). A Beckmann thermometer (or other thermometer which will read to 0.01 or 0.02° C.) is now placed in the inner bath, an ordinary thermometer is inserted in the outer water jacket, the stirrer is started, and the assembly is ready for the test.

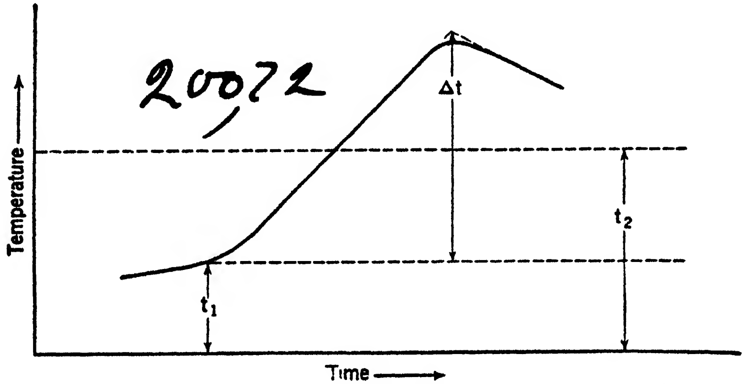

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FIG. 2—Time-Temperature Record of a Calorimeter Test.

Readings of the inner temperature are taken every 30 seconds. When the rate of change of temperature (due to heat transfer between the outer jacket and the water in the calorimeter bucket) becomes constant, a current is sent through the iron wire, the fuel is burned almost instantaneously, and the heat generated passes through the bomb and into the water about it. From the rise in temperature of this water, the heat generated by burning the fuel is calculated. When plotted, the complete time-temperature record of a calorimeter determination looks like the curve shown in Fig. 2.

The heat from the burning fuel raises the temperature of the known weight of water surrounding the bomb, and also the bomb itself, the stirrer, and the calorimeter bucket, by the amount $\Delta t$. This cannot be read directly from the temperature rise shown by the highest temperature because some heat begins to leave the water as soon as its temperature rises above its surroundings. If the original temperature of the water surrounding the bomb is approximately as far below the temperature of the water-jacket as the total rise is above it (as shown in Fig. 2), then the true temperature rise $\Delta t$ may be approximated by extrapolation to locate the point as shown. For more accurate and elaborate methods of computing the correction due to heat losses, the reader should consult one of the treatises on calorimetry. In the modern *adiabatic* calorimeter there is no need of this correction. In this type of calorimeter, two sensitive thermometers are used—one in the calorimeter bucket and the other in the outer water-jacket. The outer jacket water is constantly flowing in and out of the jacket, and it is formed by mixing a stream of cold water with a stream of hot water. By manipulating the water taps, the operator can keep the readings of the two thermometers exactly the same at all times during the firing of the bomb. No heat is lost to or gained from the water jacket, and the indicated temperature rise is the true value for $\Delta t$.

By burning a fuel of known calorific power (cane sugar or naphthalene) in the calorimeter, the *water-equivalent* of the bomb, stirrer, and bucket can be determined; this is the number of grams of water that would have the same thermal capacity. For illustration, if there were 2000 grams of water in the bucket, the water-equivalent of the bomb, etc., was 500 grams, and the corrected rise in temperature $\Delta t = 1.04°$ C., the number of calories evolved would be $(2000 + 500)1.04 = 2600$ calories. If 0.635 gram of fuel had been used, the calorific power, or the number of calories liberated by the burning of 1 gram of fuel, would be $\frac{2600}{0.635} = 4090$ calories. If the calorific power of the fuel (2600) were known, the value for the water-equivalent (500) could be calculated.

There are other minor corrections to make. For example, the heat generated by the burning of the iron wire must be deducted from the total heat measured, as well as the heat generated by the formation of $HNO_3$ and $H_2SO_4$.

Calorimeter bombs and the internal terminals and pan are commonly made of illium or some other metal which is highly resistant to corrosion. Some bombs are designed to use sodium peroxide rather than oxygen as the oxidizing agent, e.g., the Parr peroxide bomb calorimeter.

Gas calorimeters are of the continuous type. Gas is burned at a steady rate in a burner, and all the heat is absorbed in water flowing through an external jacket placed over the flame. If the entering and terminal temperatures of the jacket water are $t_2$ and $t_1$ respectively, the calorific power per liter is

$$\text{Calorific power} = \frac{(t_1 - t_2)g}{V} \tag{1}$$

where $g$ is the number of grams of water, and $V$ is the number of liters of gas flowing per second.

**Calculation of the Calorific Power.**—The calorific power of a fuel can be calculated if the complete rational analysis of the fuel is known, as shown by the following example of the calculation for a gas. If the calorific powers of the individual gases are not known, these can be calculated from the heats of reaction of the oxidation reactions.

### EXAMPLE 2

Calculate the calorific power in Calories per cubic meter of the gas whose analysis is:

$CH_4 = 94.2\%$ $\quad O_2 = 0.6\%$
$C_2H_4 = 0.8\%$ $\quad CO = 0.8\%$
$CO_2 = 0.4\%$ $\quad N_2 = 3.2\%$

The calorific powers of the various gases in Calories per cubic meter are:

$CO = 3{,}034$
$C_2H_4 = 14{,}250$
$CH_4 = 8{,}590$

and

$$\begin{aligned} 8{,}590 \times 0.942 &= 8090 \text{ Cal.} \\ 14{,}250 \times 0.008 &= 114 \text{ Cal.} \\ 3{,}034 \times 0.008 &= \underline{24 \text{ Cal.}} \\ \text{Total} \quad & \phantom{=} 8228 \text{ Cal. per cu. m. of the gas.} \end{aligned}$$

In all calorimeter determinations, the products of combustion are cooled to room temperature, and the water present condenses, thus giving up its heat of vaporization (586 Cal. per kg. of water). In actual practice, the water in the gases escapes as a gas and does not condense. Consequently, the values given by calorimeter determinations of heat of combustion (*high*, *gross*, or *calorimetric* values) must be corrected by subtracting the heat of vaporization of the water formed to give the *low*, *net*, or *practical* calorific power. In the previous example of the calculation of calorific power of a gas, the value given is the practical calorific power because the values given for the constituent gases are low calorific powers.

A formula which can be used for the calculation of the low calorific power of a coal is *Dulong's formula* given below. The assumption is made that only the net hydrogen is available for combustion. The numerical values are the heats of combustion of the respective elements.

$$\text{Low calorific power} = 8100\,C + 34{,}200\left(H - \frac{O}{8}\right) + 2200\,S - 586(9H + W) \qquad (2)$$

where the symbols $C$, $H$, $O$, $S$, and $W$ represent respectively the fraction of a kilogram of carbon, hydrogen, oxygen, sulfur, and water per kilogram of coal. This formula gives Calories per kilogram. To obtain B.t.u. per pound the formula is:

$$\text{Low calorific power} =$$

$$14{,}600\,C + 61{,}500\left(H - \frac{O}{8}\right) + 4000\,S - 1050(9H + W) \qquad (3)$$

Dulong's formula is sometimes applied to fuel oils when the ultimate analysis is known. The calorific power of fuel oil [3] is directly proportional to its specific gravity expressed in degrees Baumé (°Bé). The lower the gravity of the oil (larger the number of °Bé), the greater the calorific power per pound. A crude oil of 15° Bé will have a heating value of 18,680 B.t.u. per pound, and a 45° Bé oil will have a value of 20,400 B.t.u. per pound. As the relation is linear, calorific powers for other oils may be obtained by interpolation. When the heating value per gallon is considered, however, the positions are reversed. A 15° Bé oil will contain 150,500 B.t.u. per gallon as compared with 136,400 B.t.u. per gallon for higher-priced 45° Bé oil. As a rule the oil that is the cheapest per gallon will also have the highest B.t.u. per gallon. The light oils such as gasoline (about 60° Bé) have the highest calorific value per pound, but the lowest calorific value per gallon.

**Determination of Calorific Intensity.**—The temperature attained by the combustion of a given fuel is determined experimentally by means of pyrometers. The theoretical maximum temperature of any fuel can be calculated as outlined below.

The calorific power of a fuel gives the total amount of heat produced by burning a unit quantity of the fuel. In order to calculate the temperature attained, we must know the mass and specific heat of the materials which absorb the heat. In other words, we must know the capacity factor of the energy in order to calculate the intensity factor. The heat generated by the burning of a fuel may pass into furnace walls or be lost by radiation and conduction, but all the products of combustion must be heated; and evidently the highest possible temperature is that obtained when all the heat generated passes into the products of combustion, and none escapes to other materials. By making this assumption, we can calculate the theoretical maximum temperature. Let us consider an illustrative example.

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[3] Haslam, Robert T., and Russell, Robert P.: Fuels and Their Combustion; McGraw-Hill Book Co., New York, 1926.

### EXAMPLE 3

Calculate the theoretical temperature of the oxyhydrogen flame.

$$2H_2 + O_2 \rightarrow 2H_2O + 115{,}680 \text{ Cal.}$$

For every 44.8 cubic meters of $H_2$ used, 115,680 Calories are liberated. This heat passes into 44.8 cubic meters of water vapor. The mean specific heats of gases (at constant pressure) are commonly given in Calories per cubic meter at standard conditions. The mean specific heat of water vapor $= (0.373 + 0.000050t)$. Let $t$ degrees Centigrade equal the theoretical maximum temperature; then the total heat content of the gases is:

$$44.8(0.373 + 0.000050t)t \text{ Cal.} = 16.7t + 0.00224t^2 \text{ Cal.}$$

Since all the available heat passes into the gases, we may write

$$16.7t + 0.00224t^2 = 115{,}680$$

Solving for $t$: $t = 4350°$ C.

(Note: This value is high because the expression given for the specific heat of water does not hold accurately at very high temperature, owing principally to the fact that some of the $H_2O$ dissociates and hence absorbs heat.)

What is the temperature of the air-hydrogen flame?

The calculation is the same as before except that now we have $22.4 \times \frac{0.79}{0.21} = 84.2$ cu. m. of nitrogen passing into the products. This will absorb

$84.2(0.302 + 0.000022t)t$ Cal.
or $25.4t + 0.00185\ t^2$ Cal.

and the total heat absorbed by the gases =

$$\begin{array}{l} 25.4t + 0.00185t^2 \\ \underline{16.7t + 0.00224t^2} \\ 42.1t + 0.00409t^2 \end{array}$$

and the solution of $42.1t + 0.00409t^2 = 115{,}680$ gives $t = 2240°$ C.

Note the pronounced effect of the inert diluent nitrogen on the flame temperature. It follows from this that the maximum temperature is attained when a fuel is burned with exactly the theoretical amount of air, since excess air dilutes the products of combustion and lowers the flame temperature.

In both the above instances we have assumed that both hydrogen and oxygen (or air) were cold (at 0° C.). If one or both are preheated, the sensible heat content must be added to the calorific power of the fuel. If we burn hydrogen in air preheated at 500° C., the sensible heat in the air is ($N_2$ and $O_2$ have the same specific heats):

$106.6(0.302 + 0.000022 \times 500)500$ Cal.
$= 10{,}660 \times 5 \times 0.313 = 16{,}700$ Cal.
$115{,}680 + 16{,}700 = 132{,}380$

and our equation is

$$42.1t + 0.00409t^2 = 132{,}380$$

whence $t = 2450°$ C.

The maximum theoretical temperature can never be attained in practice, but it gives two important facts about fuels: (1) it indicates the upper limit of temperature of the fuel in question, and (2) it provides a means of comparing the relative actual calorific intensities of different fuels. Study of this problem indicates the reason for trying to use as nearly as possible the amount of air theoretically required — no more and no less.

## PYROMETRY

We have already mentioned some of the effects of temperature, and the fact has been implied that proper control of temperature is of considerable importance in metallurgical operations. Of course, if we are to control temperature, we must have accurate means of measuring it. We shall now consider some of the most common types of *pyrometers*, which is the generic term to describe instruments for measuring high temperatures. Instruments for measuring ordinary temperatures are commonly called thermometers; but the two terms are to a certain extent interchangeable, and the distinction between them is of little importance.

**Heat and Temperature.**—Temperature cannot be measured directly. All devices for recording temperature measure some change in properties of the heated object. From this measurement the temperature may be calculated. One should not lose sight of this fact, even when using a thermometer with a scale plainly marked "degrees Centigrade," for the thermometer does not measure degrees Centigrade, but the expansion of a certain volume of mercury. In order to make clear what we mean by "heat" and "temperature" let us set up a few definitions.

In the first place, "heat" and "temperature" are not interchangeable terms, in spite of a widespread popular belief to the contrary. The expression "degrees of heat" has no meaning whatever. Heat is the energy associated with the random motions of atoms and atomic groups of material substance. To define a unit in which to measure heat, we say that the amount of energy which must be added to 1 gram of water to change its temperature from 19.5° C. to 20.5° C. shall be our unit, and that all other quantities of heat shall be measured in terms of this calorie. This definition implies that we have already defined temperature, and we will assume for the present that this is so.

Heat is a form of energy, and energy of all kinds is peculiar in that it requires two variables to define a quantity of energy—a *capacity factor* and an *intensity factor*. To illustrate, if we measure the kinetic energy of a moving body, we find that it depends upon the mass of the body and its velocity or

$$\text{K.E.} = \frac{mV^2}{2} = \frac{1}{2}(mV)V \tag{4}$$

Here the capacity factor is the momentum $(mV)$ and the intensity factor is the velocity. We can increase the total kinetic energy in either of two ways. If we double the mass, we double the kinetic energy, because we have increased the capacity factor. If we double the velocity, we quadruple the kinetic energy, because we have doubled both the capacity and the intensity factor.

Electrical energy is another form of energy, and electrical energy in joules is defined as

$$J = VQ \tag{5}$$

where $V$ is electrical pressure in volts and $Q$ is the quantity of electricity moving in coulombs. The voltage is the intensity factor in this case, and the quantity of electricity is the capacity factor. If either factor is increased, the energy will increase in the same ratio. Likewise, if either factor vanishes, the energy becomes zero, regardless of the magnitude of the other factor.

In measuring heat energy, we must likewise specify two factors—the heat capacity of the body, and the temperature which is the intensity factor of heat energy. We have mentioned this fact before, but we emphasize it again because of its importance. The heat capacity is the product of the mass by the specific heat. If 1 kilogram of copper is heated 10° C., the number of calories of heat required is

$$(1000 \times 0.08) \times 10 = 800 \text{ cal.}$$

If we heat the same block of copper 20°, the intensity factor has been doubled, and the heat content is

$$(1000 \times 0.08) \times 20 = 1600 \text{ cal.}$$

If we double the capacity factor by using 2 kg. of copper, the heat content for a 10° rise is

$$(2000 \times 0.08) \times 10 = 1600 \text{ cal.}$$

**Effect of Temperature on Physical Properties.**—We have already noted that the increased thermal energy of atoms and electrons caused by an increase in temperature causes certain changes in the physical properties of a given substance. Among the properties whose changes are susceptible of accurate measurement, and which can be used for temperature measurement, are the following:

1. Volume (at constant pressure).
2. Pressure (if confined).
3. Electrical resistance.
4. Phase.
5. Sensible heat content.
6. Vapor pressure of the free electron gas.
7. Nature of emitted radiant energy.

**The Normal Hydrogen Thermometer.**—In order that we may define temperature quantitatively, it is necessary to pick out some specific property of a certain substance and use this for the basis of our definition. An ideal gas obeys the law

$$PV = RT \tag{6}$$

where $P$ is the pressure and $V$ the volume of the gas, $T$ is the absolute temperature, and $R$ is a proportionality constant whose value depends upon the units employed to measure $P$, $V$, and $T$. Hydrogen is the nearest approach to an ideal gas that can be obtained, and the standard temperature scale is defined in terms of the pressure of a constant volume of hydrogen. Assuming that hydrogen obeys the ideal gas law, if we fix the volume, we may write

$$P = KT \tag{7}$$

and the Centigrade temperature is defined as follows:

The pressure shall be adjusted so that the hydrogen is under 100 mm. of mercury at the temperature of melting ice, and this temperature shall be called 0°. The temperature of water boiling under a barometric pressure of 760 mm. of mercury shall be called 100° at $P_{100}$, then the change in pressure per degree Centigrade is

$$\frac{(P_{100} - P_0)}{100} = a \tag{8}$$

The numerical value of any temperature $T$ is then

$$T = \frac{P_T - P_0}{a} \tag{9}$$

The above definition gives us a definite scale of temperature and also a standard thermometer by which temperature may be measured exactly. To put our definition another way, we may say that those changes in temperature which produce equal changes in the pressure of a constant volume of hydrogen are to be regarded as equal intervals of temperature.

Since hydrogen is not a true ideal gas, the question may arise as to how far the hydrogen scale deviates from the "true temperature" scale. The theoretically correct temperature scale is the thermodynamic or Kelvin scale, which is based on certain thermodynamic principles and which is independent of any physical substance. It differs from the hydrogen scale by a very small amount at all ordinary temperatures (0.032° at 250° C.).

The normal hydrogen thermometer is a very complicated and unwieldy device, and its use involves a great many corrections for volume changes of the container and changes in barometric pressure, so that it cannot be used for ordinary temperature measurements. The principal use of the normal hydrogen thermometer is to determine accurately the melting and boiling points of pure substances, and these points can then be used in the calibration of thermometers and pyrometers of other types.

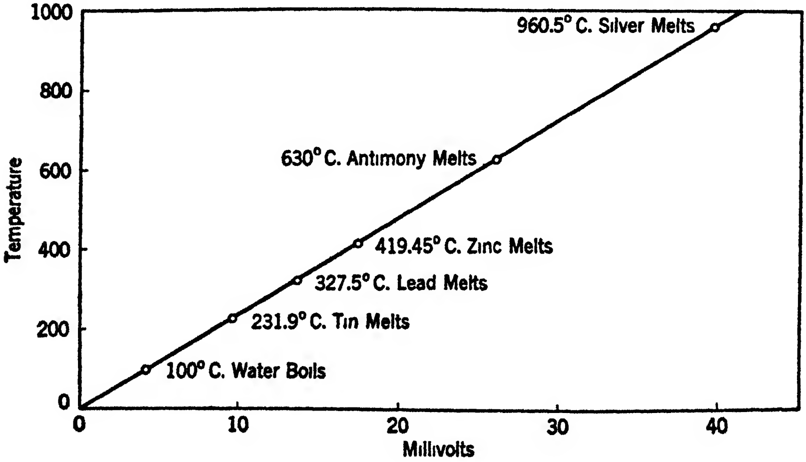


FIG. 3.—Calibration Curve for a Thermocouple.

**Calibration.**—All pyrometers and thermometers must be calibrated before they can be used. A pyrometer may utilize a millivoltmeter, a potentiometer, a Wheatstone bridge, or some other device as an indicator, the problem of calibration being to establish the relation between the units measured (millivolts, ohms, length of an expanding column) and the corresponding temperatures. After the instrument has been calibrated, the indicator may be provided with a scale which reads temperatures directly, or a calibration curve may be drawn (Fig. 3) and temperatures read from this.

There are two methods of calibration—*primary calibration* in which fixed temperatures such as boiling or freezing points of pure substances are used to determine points on the calibration curve, and *secondary calibration* in which the readings of the pyrometer are compared with those of a calibrated instrument. When an instrument equipped with a temperature scale is recalibrated, the scale is usually not changed, but a curve or table of corrections is made. These corrections are then applied to the readings of the original scale. The following list gives some points which are useful for primary calibrations.

Water freezes at 0° C.
Water boils at 100° C.
Tin freezes at 232° C.
Lead freezes at 327° C.
Sulfur boils at 445° C.
Antimony freezes at 630° C.
Copper freezes at 1083° C.
Nickel freezes at 1452° C.

**Temperature Scales.**—The essential differences between temperature scales are the size of the degree used and the location of the zero point. The most common scales are the Centigrade and Fahrenheit scales. Readings from one scale may be converted to the other by the following formulas:

$$F = \tfrac{9}{5}C + 32 \tag{10}$$

$$C = \tfrac{5}{9}(F - 32) \tag{11}$$

The absolute scale is a temperature scale in which the zero is absolute zero or − 273° C. Although the Centigrade absolute scale (*Kelvin scale*) is most common, the Fahrenheit absolute scale (*Rankine scale*) can be used in the same way.

## CONTACT PYROMETERS

The various types of temperature measuring devices may be divided into two classes: (1) those instruments which utilize the change of some physical property with temperature, and (2) pyrometers which determine temperature by analyzing the radiant energy emitted from the heated body. The instruments of the first class require that some part of the pyrometer shall be in contact with the heated body, so that it may assume the same temperature. These we have designated as contact pyrometers. Pyrometers of the second class operate at a distance and do not require any physical contact between the pyrometer and the heated object.

**Mercury Thermometers.**—The familiar mercury-in-glass thermometer is the most common of all thermometers which utilize the expansion of a liquid to indicate temperature. The range of the ordinary type of mercury thermometer is from − 40° C. to about 350° C.; but by sealing the mercury under pressure to prevent its vaporization, the upper limit of the thermometer may reach the softening point of glass (about 650° C.). Because of its portability and simplicity, the mercury thermometer is often used around boiler plants and lead refineries where the temperatures to be read are well within the range of the instrument. This thermometer, however, is not as accurate as some other devices which are useful in the same range of temperature.

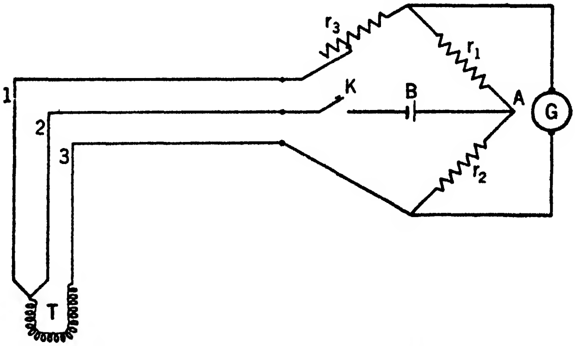


FIG. 4.—Diagram to Illustrate a Bridge for Measuring Resistance.

**Resistance Thermometers.**—The resistance thermometer (or pyrometer) depends upon the fact that the electrical conductivity of metals varies with temperature. The most common resistance thermometer measures the change in resistance of a coil of platinum wire when heated to the temperature to be measured. The only detail of the operation of resistance thermometers that requires discussion is the method of measuring the resistance of the platinum coil. This involves the use of a balancing bridge of the Wheatstone or Kelvin type with compensating leads. Figure 4 is a diagram of a simple type of bridge, and this figure also illustrates the three-wire compensating lead.

The coil *T* which is uniformly heated to the desired temperature is connected by the three lead wires as shown in the diagram to the battery *B*, and the three resistances $r_1$, $r_2$, and $r_3$; $r_1$ and $r_2$ are fixed resistances, and $r_1 = r_2$; $r_3$ is a variable resistance. Now, when the key *K* is closed, the current from the battery splits at the point *A*, and travels in the two opposing circuits 2-1-$r_3$-$r_1$ and 2-$T$-3-$r_2$. When the resistances in these two circuits are equal, the galvanometer $G$ indicates a null point. To operate such a bridge, the variable resistance $r_3$ is adjusted until the galvanometer shows no deflection. The resistance of $T$, then, is equal to $r_3$. In order that this be true, it is evident that resistances of the lead wires 1, 2, and 3 must all be equal, and to insure this these compensating leads are made of wires of exactly the same length, diameter, and composition. Since they run side by side, they are all subjected to the same thermal effects. If the temperature changes the resistance of one, it changes the resistance of both the others by exactly the same amount.

The resistance pyrometer is probably the most accurate of all pyrometers. It is said to have an error less than 0.05 per cent in a range up to 1000° C. Platinum resistance thermometers can be used in the range from − 273° to 1000° C. Nickel alloy and copper wires are sometimes used at lower temperatures. The principle of the resistance pyrometer can also be applied to determine the average temperature of a region by making the coil large enough to extend throughout the region in question.

In spite of its high accuracy, the resistance pyrometer is seldom used outside of the laboratory. Some of the reasons for its limited application in industry are as follows:

1. Platinum is very expensive. Since the coil can be easily damaged by overheating or exposure to certain gases, cheaper and more rugged pyrometers are generally used.
2. Small resistance changes due to faulty contacts will have proportionately large effects on the accuracy of the instrument, so that very careful manipulation is required.
3. The device for measuring the resistance must be so constructed that practically no current flows through the measuring coil, for the heating effect of even a small current would raise the temperature of the coil considerably. A properly designed bridge for making resistance readings is usually quite complicated and expensive.

**Platinum Temperatures.**—Often the assumption is made that the resistance of platinum is directly proportional to the temperature, or that the law connecting resistance and temperature is

$$R_t = R_0(1 + \alpha_0 t) \tag{12}$$

where $R_t$ is the measured resistance at $t$ degrees Centigrade, $R_0$ is the resistance at 0°, and $\alpha_0$ is the zero thermal coefficient of resistance.

The determination of $\alpha_0$ is made by defining $R_{100}$ as the resistance at 100° C. so that

$$R_{100} = R_0(1 + \alpha_0\,100)$$

or

$$R_{100} = R_0 + \alpha_0\,100R_0$$

$$\alpha_0 = \frac{R_{100} - R_0}{100R_0} \qquad (13)$$

The temperatures computed from equation (12) are called *platinum temperatures* and are obtained from the assumption that the resistance of platinum is directly proportional to temperature, just as we assumed that the pressure of hydrogen was directly proportional to temperature in defining the standard or hydrogen temperature scale. Actually, however, the temperature-resistance curve for platinum is not a straight line but a curve, and the accurate expression which holds in the range − 40° C. to 1000° C. is

$$R_t = R_0(1 + \alpha t + \beta t^2) \qquad (14)$$

$$\alpha = 0.00392$$

$$\beta = -\,0.000000588$$

Because of the assumptions we have made in defining the constants $R_0$ and $\alpha_0$, the platinum temperatures coincide with the true temperature at 0° and 100° C. only. If we let $t_{Pt}$ be any platinum temperature and $t$ be the corresponding true temperature, the conversion can be made as follows:

$$R_t = R_0(1 + \alpha_0 t_{Pt}) = R_0(1 + \alpha t + \beta t^2)$$

but at 100° C., $t = t_{Pt}$, and therefore

$$100\alpha_0 = 100\alpha + 100^2\beta$$

$$\alpha_0 = \alpha + 100\beta$$

$$1 + \alpha t_{Pt} + 100\beta t_{Pt} = 1 + \alpha t + \beta t^2$$

$$t_{Pt}(\alpha + 100\beta) = \alpha t + \beta t^2$$

$$t_{Pt} = \frac{\alpha t + \beta t^2}{\alpha + 100\beta} = t + \frac{\beta(t^2 - 100t)}{\alpha + 100\beta} \qquad (15)$$

Since the values for $\alpha$ and $\beta$ are known, a given platinum temperature can be converted to true temperature, or vice versa.

**Thermocouples.**—The thermoelectric effect is based on the Thomson and Peltier effects; but since we are interested more in the application of the effect than in a discussion of the physical laws which account for it, we will merely give a qualitative description. Assume that we have two wires of copper and nickel respectively joined as shown in Fig. 5—the joints may be welded or soldered, for the interposition of foreign metal or metals between the two parts of a junction does not affect the properties of the junction as long as both terminals and the intermediate substance are at the same temperature.

The two dissimilar wires form a complete circuit (thermocouple). If we now maintain one junction (the cold junction) at $t_1$ degrees Centigrade and heat the other junction (the hot junction) to $t_2$ degrees, a current will flow in the circuit as may be indicated by the galvanometer $G$, and a potential difference will exist between the two junctions which may be measured by the voltmeter $V$. This is an illustration of the thermoelectric effect which is the governing principle of all thermocouples. It is due fundamentally to the fact that the change in the vapor pressure of the free electron gas with temperature is different for each different metal or alloy. Theoretically, any two dissimilar metals or alloys could be used to form a thermocouple, but practical considerations such as cost, magnitude of the e.m.f. generated, resistance of metals to corrosion, and the melting points of metals, limit the choice of metals and alloys which can be used for thermocouples. Among the most common are the following:

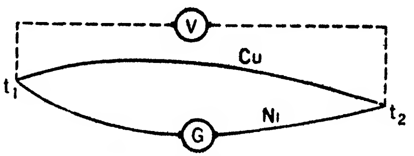


FIG. 5.—Diagram of a Simple Thermoelectric Circuit.

1. Noble-metal thermocouples:
   Pt + Pt alloyed with 10 per cent rhodium (the Le Chatelier couple).
2. Base-metal thermocouples:
   Pairs of the following metals or alloys.
   - (1) Constantan—60 per cent Cu, 40 per cent Ni.
   - (2) Iron.
   - (3) Copel—55 per cent Cu, 45 per cent Ni.
   - (4) Alumel—94 per cent Ni, 2 per cent Al, 3 per cent Mn, 1 per cent Si.
   - (5) Chromel—90 per cent Ni, 10 per cent Cr.
   - (6) Copper.

The e.m.f. in millivolts generated by any thermocouple is a function of the difference in temperature between the hot and cold junctions.

$$E = f(t_2 - t_1) \tag{16}$$

in our example. The calibration of a thermocouple requires the determination of the form of this function and expression of it either as an empirical formula or as a curve connecting millivolts with temperature. If $t$ denotes, now, the difference in temperature between the cold and hot junctions, the relation between $E$ and $t$ for most thermocouples can be expressed by the equation

$$E = a + bt + ct^2 \tag{17}$$

and the values of $a$, $b$, and $c$ may be determined by calibrating at three different temperatures.

**Construction of Thermocouples.**—Figure 6 is a diagram of a thermocouple of an ordinary type. Note that the hot junction, cold junction, leads, protecting tube, and millivoltmeter are the principal parts of the assembly. The leads and millivoltmeter are technically a part of the cold junction.

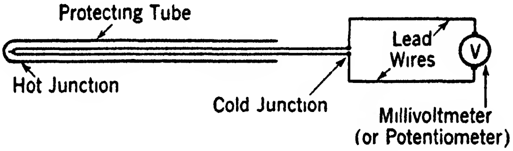


FIG. 6.—The Essential Parts of a Thermocouple.

The millivoltmeter now measures the difference in potential across its terminal posts. This is proportional to the potential between the hot and cold junctions and is, therefore, a measure of the temperature difference between the hot and cold junctions. If the cold junction is at 0° C., then the temperature difference is equal to the temperature of the hot junction in Centigrade degrees. If the instrument has been calibrated with the cold junction at 0° and later used with the cold junction at a higher temperature, a correction must be added to the observed temperature.

If the resistance of the thermocouple wires in a thermoelectric pyrometer is $r_1$, the resistance of the lead wires $r_2$, and the resistance of the galvanometer is $R$, then the total resistance of the circuit is $R + r_1 + r_2$, and the fraction of the total e.m.f. which is read on the millivoltmeter is the potential drop across its terminals or $\frac{R}{R + r_1 + r_2}$. If the resistance of the millivoltmeter is high, small changes in $r_1$ and $r_2$ will not greatly affect its readings, with the result that, when a high-resistance meter (about 150 ohms internal resistance) is used, the lengths of the thermocouple wires and lead wires can be changed without seriously affecting the calibration of the instrument. With low-resistance meters (2 ohms to a fraction of 1 ohm internal resistance), however, the set-up must be recalibrated for each new set of thermocouple or lead wires used.

In order to escape the difficulties caused by variable lead wires and the effect of the current on the thermoelectric properties of a couple, a potentiometer is often used to determine the e.m.f. of the couple. This instrument measures e.m.f. by opposing a known e.m.f. against it No current flows during the process, and consequently its readings are not affected by such factors as the resistance of lead wires. The following brief description of the slide-wire potentiometer will demonstrate the potentiometer principle (Fig. 7).

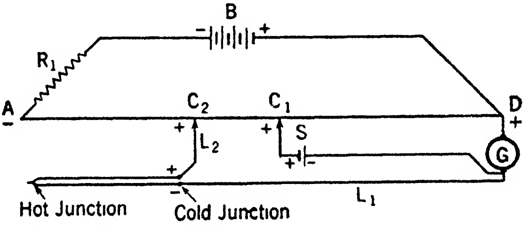


FIG. 7.—Diagram to Illustrate the Potentiometer Principle.

By means of the resistance $R_1$, the potential drop across the uniform wire *AD* may be adjusted to any desired figure (the e.m.f. is due to the battery *B*). Since the wire *AD* is uniform in composition and cross-section, the potential drop along any segment is proportional to the length of the segment. Now, the potential drop per unit length of wire is accurately measured by adjusting the sliding contact $C_1$ until no current passes through the galvanometer *G*. Then the potential drop in the thermocouple can be determined by adjusting $C_2$ until no current passes through *G*. It will be seen that the essential step in the process is the comparison of the unknown e.m.f. with the accurately known potential of the standard cell *S*. Let us take a numerical example for illustration.

Suppose that the wire *AD* is 200 cm. long and that $C_1D$ is 110 cm. The voltage of *S* is 1.018 volts. Then the potential drop across *AD* is

$$\frac{1.018 \times 200}{110} = 2.25 \text{ volts}$$

Now, if $C_2D = 163$ cm., the potential drop in the thermocouple circuit is

$$\frac{2.25 \times 163}{200} = 1.836 \text{ volts}$$

It must be remembered that a simple potentiometer of this type actually could not be used with a thermocouple because of the low voltages generated (practically always less than 65 millivolts or 0.065 volt).

Thermocouples are often sold as complete units. The millivoltmeter or potentiometer is calibrated at the factory and provided with scales which read temperatures directly. Such installations can usually be provided with new couples without altering the calibration. In the commercial use of thermocouples, many methods are used to correct for variations in cold junction temperature, to protect the hot junction from molten metals and hot gases, etc., but we cannot enter into a discussion of all these technical details. Standard industrial thermoelectric pyrometers are usually made with the thermocouple wires and insulators sealed into a protecting tube with a terminal head for attaching lead wires to the couple. The head is often provided with water pipes to keep the cold junction at approximately constant temperature. The two wires are generally insulated by fire clay, and the protecting tube is a metal which will not melt or corrode under conditions of use (iron, Nichrome, nickel, Chromel). Metal protecting tubes are often better than non-metallic refractories, because they resist sudden changes of temperature and their relatively high thermal conductivity reduces the "thermal lag" of the instrument.

Of all the various forms of pyrometers, the thermocouple is the most common in metallurgical work. The Le Chatelier noble-metal couple has the highest range of any. It can be used at all temperatures as high as 1500° C. Copper-Constantan couples are used up to about 500°, iron-Constantan up to 900°; and Chromel-Alumel up to about 1100°. The noble-metal thermocouples are the most accurate, but well-made base-metal couples are satisfactory for many purposes.

**Thermopiles.**—In certain applications, when it is necessary to increase the electromotive power of a thermoelectric pyrometer, particularly for the measurement of small temperature differences, a thermopile is used. This consists of a number of thermocouples joined in series so that the total e.m.f. is equal to the sum of the e.m.f.'s of the separate thermocouples.

**Calometric Pyrometers.**—The temperature of a furnace may be measured by determining the sensible heat in a block of metal (copper, nickel, platinum) which has been heated to furnace temperature. To determine the sensible heat, the heated block is dropped into a known volume of water, and the heat content is calculated from the rise in temperature of the water, as is illustrated by the following simple example.

### Example 4

A cylinder of metal weighing 100 grams and having an average specific heat of 0.1 is taken from a hot furnace and dropped into 2000 grams of water. The heat from the cylinder raises the temperature of the water 5° C.

Required: The temperature of the furnace.

Solution: The heat abstracted by the water is

$$2000 \times 5 \times 1 = 10{,}000 \text{ calories.}$$

If $t$ = temperature of the furnace above the water temperature

$$100t \times 0.1 = 10{,}000$$

$$t = \frac{10{,}000}{10} = 1000 \text{ C.}$$

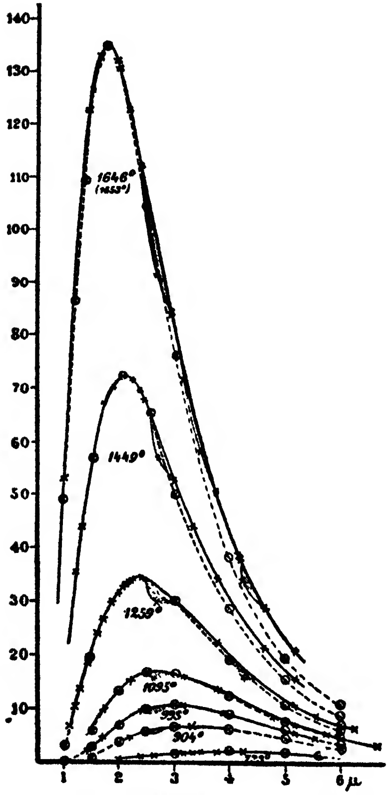
**Fusion Pyrometers.**—The principle of the fusion pyrometer is that if copper and silver, for example, are placed in a furnace, and the silver melts but the copper does not, the temperature of the furnace must be between 960° and 1083° C. In other words, fusion pyrometers do not give exact temperature, but locate the temperature within certain limits.

*Seger cones* are the most common fusion pyrometers. These are small triangular pyramids made by mixing together varying amounts of silica, lime, sodium oxide, potassium oxide, alumina, etc., so that each particular cone softens at some definite temperature. The softening temperature depends not only on the composition of the cone, but also on the particle size of the constituent oxides (*vide:* discussion of formation temperatures of slags). The temperature at which the cone bends or "weeps" until its point touches the plane of the base is taken as the softening temperature. Seger cones are widely used in the ceramic industry. They are made with softening points at 20° intervals in a range from 600° to 2000° C.

## RADIANT-ENERGY PYROMETERS

**The Nature of Radiant Energy.**—All bodies are continually emitting part of their heat energy in the form of radiation or electromagnetic ether waves. This radiation ordinarily consists of a mixture of various wave lengths and is called a *spectrum.* The energy in each particular wave length and the total energy of the spectrum depend upon (1) the *absolute temperature* of the radiating body above its surroundings, and (2) the *emissivity* of the surface of the radiating body. The energy content or intensity of a particular wave length, or of the entire spectrum, is determined by the pyrometer, and from this the temperature of the radiating body.

**Black-Body Radiation.**—If incident radiation falls upon a body, it may be: (1) reflected, (2) transmitted, or (3) absorbed (and converted to heat energy). We define a *black body* as a body which does not reflect or transmit any energy, but absorbs all incident radiation. It can be shown that such a perfect absorbing material also has the highest possible radiating power. We introduce the conception of a black body here because all the laws of radiation are derived for radiation from a black body. We shall not attempt to give a complete discussion of the properties of a black body, but we do wish to call attention to the fact that our basic formulas apply only to black-body radiation. Later we shall consider radiation from bodies other than black bodies.



*(Lummer and Pringsheim, in "Heat" by James M. Cork, John Wiley and Sons, New York, 1933)*

Fig. 8.—The Distribution of Intensity with Wave-length in the Radiation from a Black Body at Various Temperatures.

**Energy Distribution in the Spectrum.**—Figure 8 shows the distribution of energy in typical black-body spectra. Note that there is a definite curve corresponding to each temperature and that the ordinates (energy associated with single wave lengths) and the areas under the curves (total spectral energy) both increase as the temperature rises, and that the maximum point moves toward the shorter wave lengths. The radiation from a body is said to include "heat" and "light" waves. Actually, these waves differ only in wave length, and the various types of electromagnetic waves are as follows:

| Wave | Wave-Length (λ) Range |
|---|---|
| Gamma rays | 0.005 → 0.150 × $10^{-8}$ cm. |
| X-rays | 0.10 → 150 × $10^{-8}$ cm. |
| Ultra-violet | 100 → 3700 × $10^{-8}$ cm. |
| Visible (light) | 3700 → 7000 × $10^{-8}$ cm. |
| Infra-red (heat) | 0.00007 → 0.04 cm. |
| Radio | 0.04 cm. → 10 × $10^{8}$ cm. |

The various wave lengths of the visible spectrum produce different color sensations varying from red for the longest (7000 Å) to violet for the shortest (3700 Å). The Ångström unit, Å, is $10^{-8}$ cm. Wave lengths may also be measured in microns, $\mu$ ($10^{-4}$ cm.), or in millimicrons, m$\mu$ ($10^{-7}$) cm. One Ångström unit = $10^{-4}\mu$.

**Determination of Temperature by Color.**—A black body is not necessarily black in color unless its temperature is below the point at which visible radiant energy is emitted. After a body begins to give off visible radiation, the color of the emitted light may be used to judge the approximate temperature of the object. *Howe's scale* which correlates the color of a body with its temperature is given below.

| | |
|---|---|
| Lowest visible red | 475° C. |
| Dull red | 550–625 |
| Full cherry red | 700 |
| Light red | 850 |
| Orange | 900 |
| Full yellow | 950–1000 |
| Light yellow | 1050 |
| White | 1150 up |

Experienced men can judge temperatures quite accurately by means of color, but the above scale is not to be considered as something that can be used by anyone, because different observers have different opinions as to what is meant by a certain color; and the lightness or darkness of the surroundings also influence the apparent color of a heated body.

**The Radiation Pyrometer.**—The total amount of energy radiated per second from a black body is given by the Stefan-Boltzmann law as:

$$W = \sigma A(T^4 - T_0^4) \tag{18}$$

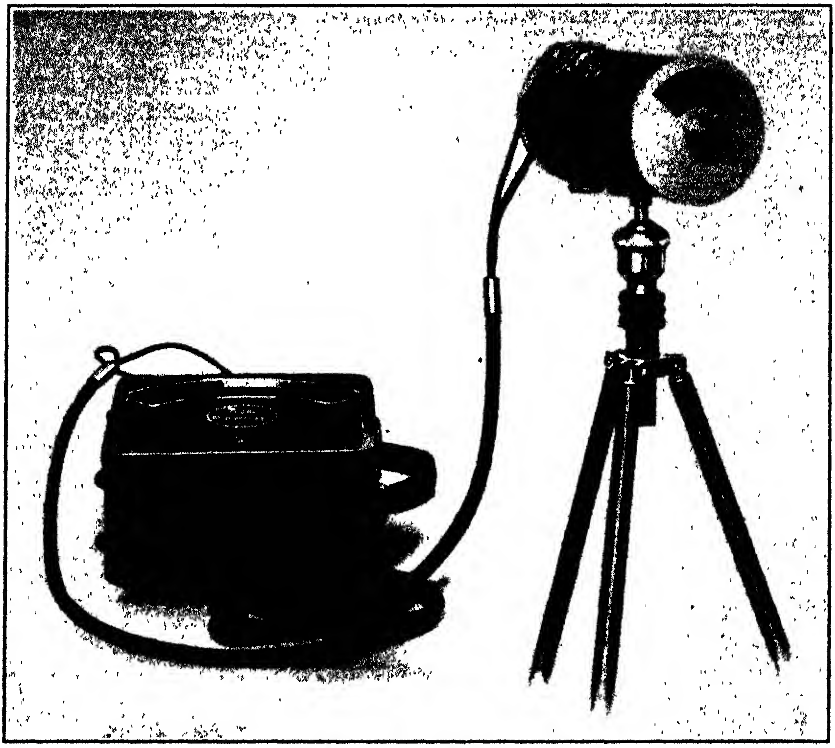
where $\sigma$ is a universal constant having the value of $5.735 \times 10^{-12}$ when $W$ is in watts, $A$ is the area of the radiating surface in square centimeters, and $T$ and $T_0$ are the absolute (Kelvin) temperatures of the heated body and the surroundings respectively. This law is the basis upon which the total radiation pyrometer operates.

Figure 9*b* is a cross-section of the Fery radiation pyrometer. The radiation from the heated body enters the opening of the cylindrical tube and is reflected from the concave (parabolic) mirror upon a thermocouple junction. The incident radiation heats the junction, and its temperature rise sets up an e.m.f. which is recorded on the millivoltmeter. Let us find the relationship that exists between the galvanometer deflection $D$, and the temperature of the emitting body, by making the following assumptions:

(*a*) The deflection $D$ is proportional to the e.m.f. applied to the galvanometer.

(*b*) The e.m.f.-temperature relationship of the thermocouple is linear, and therefore $D \sim (T_2' - T_1')$.

(*c*) The equilibrium temperature of the thermocouple junction is governed by Newton's law of cooling, which states that the temperature of the couple above its surroundings $(T_2' - T_1')$ is proportional to the rate at which heat is being supplied. The thermocouple junction is assumed to be a black body; i.e., it absorbs all the incident energy, so that we may write



*(Courtesy Taylor Instrument Companies, Rochester, New York)*

FIG. 9*a*.—The Fery Radiation Pyrometer.

$$D \sim \text{e.m.f.} \sim (T'_2 - T'_1) \sim (T^4 - T_0^4) \qquad (19)$$

or

$$D = aT^4 + b \qquad (20)$$

where $a$ and $b$ are constants. If $T_0$ is small compared to $T$, $b$ may be neglected, and we have

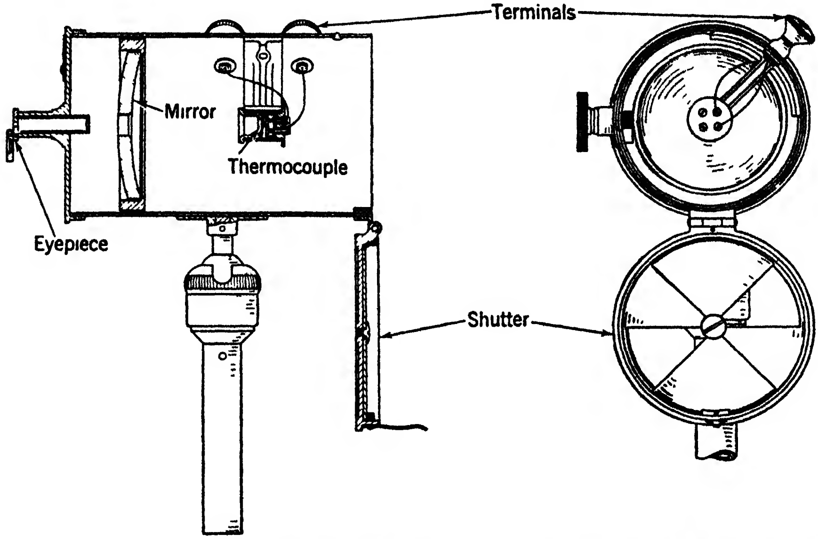
$$D = aT^4 \tag{21}$$

or

$$\log D = A + 4 \log T \tag{22}$$

Hence, if we plot log $D$ against log $T$, we should obtain a straight line having a slope = 4. In practice it has been found that this is very nearly true, and a calibration at two points gives a complete calibration of the instrument.

**Effect of Distance from the Source of Radiation.**—As long as the radiation pyrometer is close enough to the source so that the image of the heated object entirely covers the thermojunction, then the distance has no effect on the reading. Although if the distance from the source to the pyrometer is doubled, the amount of energy received by the mirror is one-fourth of the original amount (by the inverse square law), at the same time the image on the thermojunction is also decreased to one-fourth of its original size. This means that the energy per square millimeter on the junction is constant.



*(Courtesy Taylor Instrument Companies, Rochester, New York)*

FIG. 9*b*.—The Fery Radiation Pyrometer—Section.

**Non-Black Bodies.**—In measuring the temperature of bodies which are not full radiators (black bodies) by means of a radiation pyrometer, it is necessary to take into account the *total emissivity*, *E*, of the surface, where *E* is defined as

$$E = \frac{\text{Energy actually radiated}}{\text{Energy emitted from a black body at the same temperature}}$$

Hence, $E$ is always a fraction less than 1. If $E = 1$, the radiator is a black body. For a non-black body of emissivity, $E$, the energy radiated per second is

$$W = E\sigma A(T^4 - T_0^4) \tag{23}$$

If a radiation pyrometer is used to read the temperature of a non-black body, it will indicate the temperature which the body would have if it were a black body. Let us call this the black body temperature, $T_P$. Then, from the definition given above

$$E = \frac{T_P^4 - T_0^4}{T_A^4 - T_0^4} \tag{24}$$

where $T_A$ is the true temperature of the body. The relation between true and observed temperature is then

$$T_P = \sqrt[4]{ET_A^4 + (1 - E)T_0^4} \tag{25}$$

Enclosed furnaces, together with objects within them, are very close to theoretical black bodies, and their emissivity $E$ may be taken as 1. Objects in the open, particularly those with good reflecting surfaces, have lower emissivities. Table 4 gives values for $E$ for a few common substances.

TABLE 4

TOTAL EMISSIVITIES OF VARIOUS SURFACES

| Material | $E$ | Temperature at Which $E$ is Measured, Degrees Centigrade |
|---|---|---|
| Brass, polished....... | 0 04 | 50 |
| | 0 59 | 600 |
| Graphite............. | 0 90 | 50 |
| | 0 92 | 400 |
| Sheet iron............ | 0 56 | 50 |
| | 0.89 | 1200 |

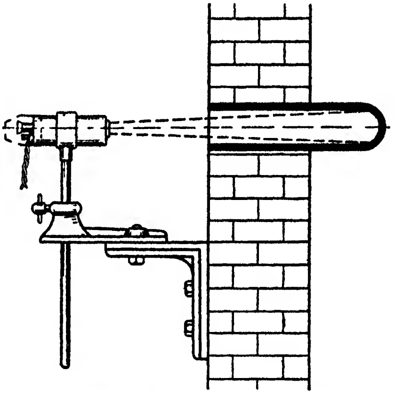
Note that the total emissivity of material increases as the temperature rises. At high temperatures all bodies approach the condition of black bodies because of the roughening of their surface by the thermal agitation of the atoms.

**Effect of Absorbing Media on a Radiation Pyrometer.**—A radiation pyrometer cannot be used to sight through glass windows, smoke banks, or even clouds of colorless $CO_2$ gas, for these materials absorb large amounts of the infra-red or heat radiation even though they may be transparent to visible light. In order to use the radiation pyrometer at very high temperatures, the instrument is often provided with a shutter or diaphragm which cuts off a definite fraction of the incident radiation. A simple example will show the effect of such a shutter on temperature readings. If we let $T_P$ be the temperature observed with the shutter cutting off $(1 - N)$ of the original area ($N =$ a proper fraction which represents the fraction of the original area which is open) and $T_A =$ the true temperature, such as would be observed if the shutter were open, then the actual temperature may be calculated from the observed temperature by the following:

$$\frac{T_P^4 - T_0^4}{T_A^4 - T_0^4} = N \tag{26}$$

In some cases a closed tube is inserted in a furnace wall, and readings are taken by sighting the radiation pyrometer into the tube (Fig. 10). A long, narrow tube of this kind is for all practical purposes a black body, and the pyrometer is not affected by furnace gases and smoke.

Another type of radiation pyrometer (Pyro Radiation Pyrometer) is a self-contained instrument with the millivoltmeter mounted in the pyrometer tube, and the radiant energy is concentrated by means of an objective lens (quartz or fluorite) rather than by a reflecting mirror.

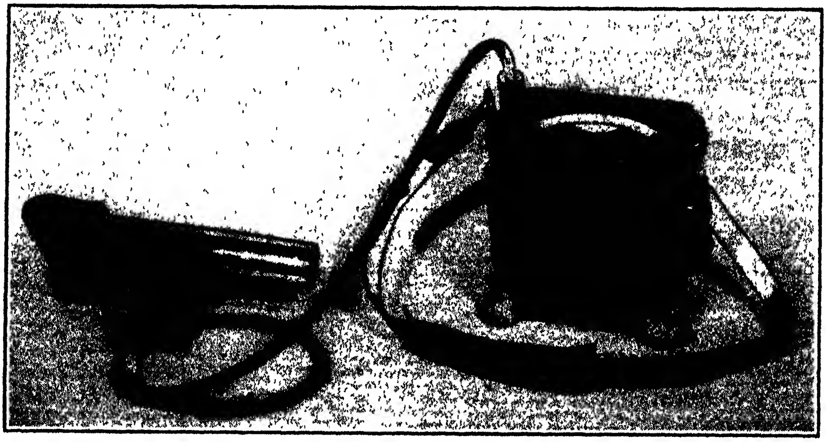


*(Courtesy The Pyrometer Instrument Company, New York)*

FIG. 10.—Tube Set in Furnace Wall to Serve as a Target for a Radiation Pyrometer.

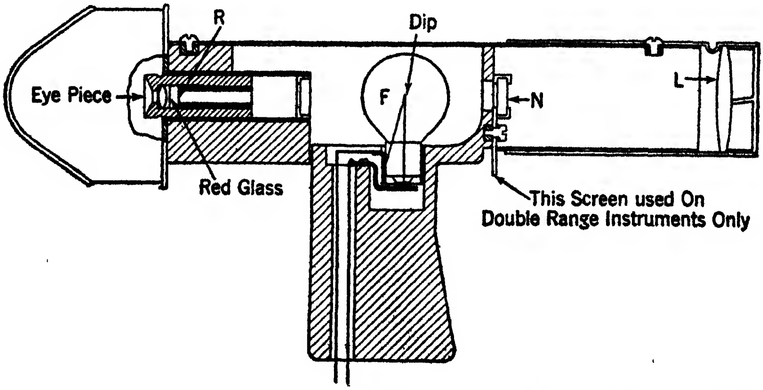
**The Optical Pyrometer.**—The optical pyrometer differs from the radiation pyrometer in that it uses only a narrow band of light rather than the entire spectrum of the radiating object. The most common type of optical pyrometer is the *disappearing filament pyrometer* as shown in Fig. 11.

The optical pyrometer consists essentially of an optical telescope with a U-shaped lamp filament ($F$) at the common focal plane of the objective ($L$) and the eyepiece (Fig. 11). In front of the eyepiece is a red glass filter which absorbs all the incident radiation except a narrow band, generally in the neighborhood of $\lambda = 6300\,\text{Å}$ $(0.63\mu)$. In operation, the telescope is focused on the source of high temperature, and the observer sees the image of the filament superimposed on the image of the source. If now the current through the filament is adjusted (by means of a rheostat in series with the battery) until the image of the filament merges into the background (disappears—see Fig. 12), the source and filament are at the same temperature, since the intensity of the radiation at $\lambda = 0.63\mu$ is the same from each. This last statement is based on Wein's law



(*Courtesy Leeds and Northrup Company, Philadelphia*)

FIG. 11*a*.—The Leeds and Northrup Optical Pyrometer.



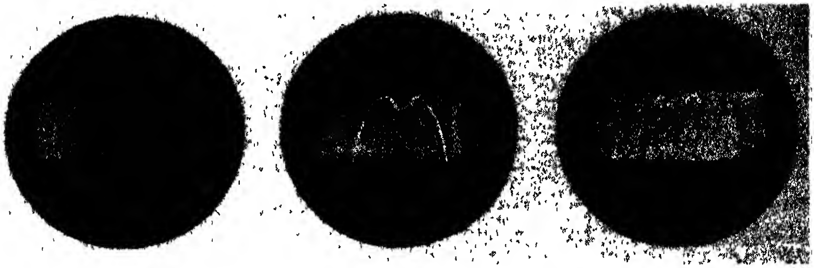
(*Courtesy Leeds and Northrup Company, Philadelphia*)

FIG. 11*b*.—The Leeds and Northrup Optical Pyrometer—Section.

$$J_\lambda = C_1\lambda^{-5}e^{\frac{-C_2}{T}} \tag{27}$$

in which $J_\lambda$ is the intensity of the radiation of wave length $\lambda$; $T$ is the absolute temperature of the source; and $C_1$, $C_2$, and $e$ are constants.

The current flowing through the milliammeter is a measure of the temperature of the filament, and hence the temperature of the source. We could make certain assumptions and calculate the relation between the deflection of the milliammeter and the temperature of the source, but experiment shows that such a law does not hold in practice so that the optical pyrometer must be calibrated over its entire range.



*(Courtesy Leeds and Northrup Company, Philadelphia)*

Filament too cold. Filament too hot. Filament at correct temperature

FIG. 12.—Appearance of Object and Filament in Leeds and Northrup Optical Pyrometer.

**Non-Black-Body Radiation.**—In using an optical pyrometer to measure the temperature of a non-black body, we proceed in the same manner as we did with the radiation pyrometer; but the calculation is different because the radiation laws involved are different. As before, we require the emissivity of the source, but this time it is the monochromatic emissivity, $E_\lambda$, which is defined as follows:

$$E_\lambda = \frac{J_\lambda\ (\text{Actual})}{J_\lambda\ (\text{Black body})} = \frac{C_1\lambda^{-5}e^{\frac{-C_2}{T_P}}}{C_1\lambda^{-5}e^{\frac{-C_2}{T_A}}} \tag{28}$$

where $T_P$ is the observed or apparent temperature and $T_A$ is the true temperature.

$$E_\lambda = e^{(C_2/\lambda)\left(\frac{1}{T_A} - \frac{1}{T_P}\right)}$$

$$\frac{C_2}{\lambda}\left(\frac{1}{T_A} - \frac{1}{T_P}\right) = \ln E_\lambda$$

$$\frac{1}{T_A} - \frac{1}{T_P} = \frac{\lambda}{C_2}\ln E_\lambda \tag{29}$$

But for most optical pyrometers $\lambda = 0.63\mu$, and the constant $C_2 = 14{,}320$ and ($\log = \log_{10}$)

$$\frac{1}{T_A} - \frac{1}{T_P} = \frac{0.63\ (2.302)}{14{,}320} \log E_\lambda = \frac{\log E_\lambda}{9874} \tag{30}$$

Hence, if $E_\lambda$ is known for a given source, the true temperature can be calculated from the observed temperature. The emissivity $E_\lambda$ must not be confused with the total emissivity $E$ used with the radiation pyrometer. The effect of $E_\lambda$ is not as great as might be expected. For a body of $E_\lambda = 0.50$ at an apparent temperature of 1500° C., the error is only about 100° C.

**Absorbing Materials and the Extension of the Range of Optical Pyrometers.**—If the absorption coefficient of any material for red light ($0.63\mu$) is known, the effect of a window of this material (glass of some sort) on the temperature indicated by an optical pyrometer can be calculated. We could not do this with the radiation pyrometer because here all wave lengths are used and the coefficient of absorption varies with the wave length of the light (or heat) absorbed.

When radiation of intensity $I$ passes through a layer of material $dx$ in thickness, the intensity is reduced by the amount $dI$. The quantity $dI$ is proportional to $dx$, to the absorption coefficient $\mu$ of the material, and to the intensity $I$. Hence

$$dI = -\ \mu I dx \tag{31}$$

(since $dI$ decreases as $x$ increases)

$$\frac{dI}{I} = -\ \mu dx$$

$$\ln I = -\ \mu x + C$$

but when $x = 0$, $I = I_0$, the original intensity, and

$$\ln I = -\ \mu x + \ln I_0$$

$$\ln I - \ln I_0 = -\ \mu x$$

$$\ln \frac{I}{I_0} = -\ \mu x$$

$$\frac{I}{I_0} = e^{-\mu x} \tag{32}$$

but $\frac{I}{I_0}$ is the fractional part of the intensity which passes through the screen, and plays the same role as $E_\lambda$ in equation (29) and therefore

$$\frac{1}{T_A} - \frac{1}{T_P} = \frac{-\mu x \lambda}{C_2} \tag{33}$$

where $x$ is the thickness of the screen in centimeters and $\mu$ is the absorption coefficient for red light.

The incident radiation may also be cut down by interposing a slotted disk or diaphragm as in the radiation pyrometer. If the ratio of open space to total space $= R$, then $R$ has the same effect as $E_\lambda$, and

$$\frac{1}{T_A} - \frac{1}{T_P} = \frac{\log R}{9874} \tag{34}$$

By using screens or diaphragms on optical pyrometers, or diaphragms with radiation pyrometers, the instruments can be used to measure indefinitely high temperatures.

## RECORDING PYROMETRY

Where a permanent installation of a pyrometer is made in a furnace, kiln, stack, or other heated chamber, it is often desirable to make the instrument self-recording. All the important pyrometers (see summary below) can be equipped with automatic recording devices except the optical pyrometer (and, of course, Seger cones). In some cases the pyrometer actuates a relay which controls the fuel feed to the furnace and thus maintains the temperature constant between limits.

TABLE 5

Modern Temperature-Measuring Devices

| Device | Practical Temperature Range, Degrees Centigrade | Effect Utilized |
|---|---|---|
| Mercury thermometer—glass | −59 to 525 | Expansion of a fluid |
| Mercury thermometer—fused silica | −39 to 800 | Expansion of a fluid |
| Gas expansion thermometer ($N_2$) | −130 to 540 | Expansion of a gas |
| Metal expansion thermometer | 0 to 500 | Expansion of a solid |
| Resistance pyrometer | −180 to 1000 | Change of electrical resistance |
| Thermoelectric pyrometer (Le Chatelier) | 0 to 1500 | Thermoelectric effect |
| Thermoelectric pyrometer (base metal) | 0 to 1000 | Thermoelectric effect |
| Seger cones | 600 to 2000 | Fusion (softening) |
| Radiation pyrometer | 400 up | Radiation (total) |
| Optical pyrometer | 650 up | Radiation (monochromatic) |

## HEAT TRANSFER

The same laws which we have considered under the thermal conductivity of metals apply also to other materials. Most *refractories* have much smaller values for $k_1$ (thermal conductivity) than metals and alloys.

The question of the thermal conductivity of non-metallic refractories has two aspects. When the refractory acts as a containing vessel for fuel and charge (as in a blast furnace), it should have a low heat conductivity in order to conserve as much heat as possible. On the other hand, refractories through which the heat must pass before it can reach the charge (muffles, for example) should have good thermal conductivity.

Heat energy may pass from one body to another in three different ways, as outlined below. Heat flows only from a hot body to a cooler one. Heat cannot flow against a thermal gradient (second law of thermodynamics).

1. *Conduction.* The collision of moving atoms, molecules, and electrons causes the transfer of heat energy through any material body or from one body to another in contact with it. The rate at which heat is conducted is measured by the thermal conductivity, which we have already described in Chapter IV.

2. *Convection.* When heat passes from a solid to a fluid (liquid or gas), convection currents are set up in the fluid. The resulting motion assists in removing heat from the solid surface. When the fluid is set in motion by external forces, the convection is greatly accelerated. Such "forced convection" is utilized in cooling metallic refractories by means of a current of water and in blowing a current of air against such heating devices as radiators (more properly convectors). At the junction of solid and fluid there is a thin adsorbed layer of liquid or gas which does not move with the convection currents. This skin has a relatively high thermal resistance. In calculating convection losses, the assumption is often made that this skin is a layer of uniform thickness, and values are given for its thermal conductivity. These are used as if the thickness of the layer were unity (1 cm.).

3. *Radiation.*—The vibrating particles of all bodies are continually emitting energy in the form of electromagnetic waves or disembodied radiation. We have already mentioned the laws of radiation in the section on Pyrometry. Radiation losses are negligible near room temperatures; but since the energy lost by radiation increases as the fourth power of the absolute temperature of the radiating surface, considerable heat is lost by radiation at high temperatures.

TABLE 6

THERMAL RESISTIVITY OF VARIOUS MATERIALS

| Material | Resistivity, Thermal Ohms, per Cubic Centimeter | Conductivity, English Units, ($k_2$) | Temperature, °C., at Which Determined |
|---|---|---|---|
| Iron | 1.65 | 420 | |
| Graphite | 9.7 | 71.9 | |
| Magnesite brick | 41.0 | 17.0 | 1135 |
| Fire brick | 56–69 | 10.1–12.4 | 1135 |
| Bauxite brick | 74.0 | 9.41 | 1000 |
| Asbestos paper | 555 | 1.250 | 65 |
| Wood, pine | 876 | 0.792 | 150 |
| Cork board | 2,480 | 0.279 | 25 |
| Air | 3,965 | 0.175 | 25 |
| Vacuum | 17,000 | 0.041 | 150 |

## EXERCISES

1. Why should 26 grams of acetylene generate more heat when burned than 24 grams of carbon + 2 grams of hydrogen?

2. Calculate the low calorific power of the following coal by Dulong's formula:

| | |
|---|---|
| C | 64.0% |
| O | 10.9% |
| H | 5.0% |
| $H_2O$ | 8.3% |
| Ash | 11.8% |

3. Calculate the calorific power of air gas ($CO$, $N_2$) and water gas ($H_2$, $CO$) in Calories per cubic meter and B.t.u. per cubic foot.

4. Calculate the theoretical maximum temperature of water gas when burned with 50 per cent excess air, all the air being preheated to 800° C.

5. List the common fuels which can be preheated; those which cannot. Give reasons.

6. The coal given in problem 2 is burned completely and the products of combustion contain 4 per cent free oxygen. What percentage of excess air was used?

7. If a fuel consists principally of carbon, the volume of the flue gases may be taken as approximately equal to the volume of air consumed. Explain.

8. In tables, two values for the heat of formation of water are given; viz:

($H_2O$) (gas) 57,840

and

($H_2O$) (liquid) 68,380

Calculate the heat of vaporization of water in calories per gram.

9. A gas containing 20 per cent $H_2$ by volume and the remainder CO and $N_2$ is burned in a gas calorimeter. The temperatures of inflowing and outflowing water are respectively 12.16° and 21.60° C. While 4 kg. of water are flowing through the calorimeter, 19.15 liters of gas (measured at 10° C. and 730 mm.) are burned. Calculate: (1) the *low* calorific power of the gas, and (2) the percentage composition of the gas.

10. The heat of the following reaction is as shown:

$$H + H \rightarrow H_2 + 50{,}400 \text{ cal.}$$

Calculate the theoretical maximum temperature of the atomic hydrogen flame.

11. If three conductors in series (arranged so that the heat must pass through all three in succession) have specific heat conductances of $k_1$, $k_2$, and $k_3$, respectively, and thicknesses of $l_1$, $l_2$, and $l_3$, find the conductivity of a plate 1 cm. square consisting of these three substances.

12. A silver plate 1 square foot in area and ¼ inch thick conducts 577,257 gram calories of heat in 1 hour when the difference in temperature between the two sides is 0.1° C. Calculate the coefficient of thermal conductance ($k_1$).

13. A rotary drier is made of an iron shell 40 feet long, 0.5 inch thick, and 36 inches inside diameter. This shell is lined with fire brick to a thickness of 4 inches.

Gases pass through the drier at an average temperature of 320° C., and with an average velocity of 10 feet per second. The outside air at a temperature of 20° C. is blown against the iron shell with a velocity of 4 miles per hour. The thermal conductances are as follows ($k_1$, metric system):

| | |
|---|---|
| Fire brick.......................... | 0.0014 |
| Iron shell.......................... | 0.15 |
| Gases to fire brick.................. | $0.000028\,(2 + \sqrt{v})$ |
| Air to iron shell.................... | $0.000028\,(2 + \sqrt{v})$ |

where $v$ is the velocity of the gas concerned in centimeters per second.

Required:

(1) For the above series find the unit thermal conductance per square centimeter of surface.

(2) For purposes of plotting, assume that the "skins" of gas and air are each 0.01 inch thick, and plot temperature against distance from the hot gas to the air to obtain a graphic representation of the *thermal gradient* through the shell.

(3) How many gallons of 11,000-calorie fuel oil (7.5 pounds per gallon) does the heat lost in 24 hours represent?

(4) What percentage saving in heat will be made by covering the shell with a 1-inch layer of infusorial earth ($k_1 = 0.0018$)?

14.[4] A certain resistance thermometer is observed to have the following resistances: 11.00 ohms in melting ice, 15.247 ohms above boiling water at 760 mm. pressure, and 28.887 ohms above boiling sulfur at 760 mm. pressure (444.55° C.). Find the values of $\alpha$ and $\beta$ in the empirical equation

$$R = R_0(1 + \alpha t + \beta t^2)$$

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[4] Cork, James M.: Heat, John Wiley & Sons, New York, 1933.

15.[4] From the result of problem 14, what would be the observed platinum temperature with this thermometer when immersed in melting tin (232° C.)?

16.[4] An optical pyrometer when sighted upon the inside of a hollow metallic wedge (black-body radiation) indicates a temperature of 1200° C., whereas, when focused upon the outside, the apparent temperature is 1160°. What is the emissivity ($E_\lambda$) of the material of the wedge? (Note: the temperatures, $T$, in the radiation formulas are absolute temperatures.)

17.[4] It is desired to observe the temperature of the sun (5800° C.) on a pyrometer so that its apparent temperature is 2000° C. By using an interposed rotating disk, what should be the total angular opening of the slots to permit this: (*a*) if an optical pyrometer is used, and (*b*) if a radiation pyrometer is used?

18.[4] The true temperature of a certain source is 950° C., and when viewed through a certain absorbing glass of 4-mm. thickness, the apparent temperature is 890° C. What is the absorption coefficient of the absorbing material for the radiation of the wave length employed by the pyrometer ($\lambda = 0.63\mu$)?

19.[4] A radiation pyrometer when sighted upon a molten metal surface indicates a temperature of 900° C., while a thermocouple indicates a temperature of 960° C. If there is no error in the instruments, what is the total emissivity of the surface?

20. Why can glass lenses be used to form an image in an optical pyrometer but not in a radiation pyrometer?

21. The total emissivity of a certain surface is 0.86. If a radiation pyrometer indicates 1750° C., what is the true temperature of the surface?

22. Calculate the radiation loss in watts from a surface of 20 sq. cm. at 1000° C. having an emissivity of 0.04. Use the formula

$$W = 5.735\, EA\left[\left(\frac{T_2}{1000}\right)^4 - \left(\frac{T_1}{1000}\right)^4\right]$$

and show that this is the same as the formula given in the text. Temperature of the surroundings is 20° C.

23. Standard conditions are 273° K. and 760 mm. Express these in English units—Fahrenheit absolute temperature and inches of mercury.

24. A 10-gram cube of metal, $S_m = 0.2925 + 0.000019t$, is placed in a furnace and allowed to reach the temperature of the furnace. It is then dropped into 500 grams of water, and the heat from the metal raises the temperature of the water 2.0° C. What is the temperature of the furnace?

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# CHAPTER XIII

# PYROMETALLURGY—3. PROCESSES

In the discussion of the various pyrometallurgical processes, it will be necessary to digress from time to time to consider such topics as refractories, slags, fluxes, smoke, and furnace gases. At this point we shall give brief definitions of the important types of processes, and then we shall take these up in proper sequence with the auxiliary topics.

## THE DIVISIONS OF PYROMETALLURGY

**Drying** is the term applied to the removal of water from material. We shall be interested in (1) the drying of solid ore, concentrate, or flux by means of heat; and (2) the drying of air for the iron blast furnace.

**Calcining** refers to the decomposition of carbonates by means of heat.

**Roasting** is a process whereby a solid ore or concentrate is oxidized by the oxygen of the atmosphere. The primary purpose of most roasting operations is the oxidation of sulfide minerals to oxides or sulfates. In roasting, the charge is solid material, and no part of it ever becomes liquid. In *roast-sintering* there is an incipient fusion which causes a finely divided solid charge to form a porous cake; but there never is any substantial liquefaction of the solid material. Three important types of roasting are:

1. Roasting in a multiple-hearth furnace.
2. Flash, or suspension, roasting.
3. Blast roasting (sinter-roasting) in the Dwight-Lloyd machine.

**Sintering** is a process whereby finely divided solid material is agglomerated into a porous cellular cake, by means of heat. The Dwight-Lloyd machine is most commonly used for this operation. Sintering may or may not be also a roasting operation (roast-sintering).

**Smelting** will be used in our discussion to refer to two operations, namely:

(1) Reduction smelting.
(2) Matte smelting.

In both types of smelting the charge consists of solid material—ore or concentrate, flux, and (in the blast furnace) fuel—and the products of the smelting operation are in the liquid state. Reduction smelting produces an impure liquid metal and a liquid slag; matte smelting produces liquid matte and liquid slag.

In many cases the term smelting is used in a broader sense to refer to all pyrometallurgical operations. Pyrometallurgical plants are usually called smelters. The distilling process for recovering zinc from its ores is called zinc smelting, etc.

**Converting** is a process by means of which a liquid material is oxidized by blowing air through it. The operation is carried out in a special furnace known as a converter. Converting has two important applications: (1) the converting of pig iron to oxidize and remove C, Si, and Mn (also P in the basic process); and (2) the converting of mattes to oxidize and remove S and Fe. Converting practice is characterized by the facts that the charge must be in the molten state, and that the oxidation reactions provide the necessary heat so that no extraneous fuel is required.

**Distillation** involves the vaporization of the metal to be recovered and its subsequent condensation to the liquid state. Zinc, mercury, and cadmium are the principal metals recovered by distillation.

**Fire refining** includes a number of processes for the purification of the impure metal produced in smelting and non-ferrous converting. Refining is carried out upon liquid metal, and in general the process is one of oxidation—the impurities are oxidized and converted into compounds which can be readily separated from the purified liquid metal.

## REFRACTORIES

In pyrometallurgical processes it is necessary to provide apparatus (furnaces, converters, roasters) in which high-temperature reactions can take place; the materials of construction which are exposed to high temperatures and molten, corrosive liquids are known as *refractory materials* or *refractories.* Most of the common refractories are produced in the form of bricks of standard and special shapes, and these bricks are used for furnace construction, converter linings, etc. Monolithic (one-piece) refractories such as the bottoms of reverberatory furnaces are made by sintering a granular refractory after it has been set in place.

**Requirements of a Good Refractory.**—Depending upon the use for which it is intended, a refractory must possess some or all of the following qualifications:

1. It must have a high melting point.
2. It must withstand sudden changes of temperature. The fracture of refractories caused by sudden temperature changes is known as *spalling*. Magnesia brick, for example, spalls readily.
3. It must withstand abrasion.
4. It must be mechanically strong.

The strength and resistance to abrasion at operating temperatures are most important.

5. It must withstand chemical corrosion.
6. The cost must be reasonably low.
7. It must possess sufficient plasticity (clays).
8. If used in electrical furnaces, it must have low electrical conductivity.
9. It must have proper thermal conductivity.
10. It must have a small coefficient of thermal expansion (and contraction).

Refractories in general should consist of relatively pure oxides rather than of mixtures or compounds of two or more oxides. Aluminum silicates found in fire brick, and chromite, $FeO \cdot Cr_2O_3$, are the most important salts used as refractories. Both of these have high fusing points.

**Refractory Materials.**—Most commercial refractories are composed of one of the following substances:

1. $xAl_2O_3 \cdot ySiO_2$.
2. $Al_2O_3$.
3. $SiO_2$.
4. $CaO$.
5. $MgO$.
6. $Fe_2O_3$ or $Fe_3O_4$.
7. $FeO \cdot Cr_2O_3$.
8. Carbon (graphite).
9. Metals (water-jacketed).

**Fusing Points of Refractories.**—The fusing points of some common refractories are:

| | |
|---|---|
| Silica | 1750° C. |
| Kaolin | 1740 |
| Bauxite brick | 1600–1820 |
| Alumina | 2050 |
| Magnesia brick | 2165 |
| Chromite | 2050–2200 |
| Carborundum | (Does not soften at 2240° C.) |
| Carbon | (Solid at 3600° C.) |

It must be remembered that refractories often soften considerably at temperatures well below their melting points.

In connection with the above list the following temperatures attained in metallurgical processes are of interest:

| | |
|---|---|
| Copper smelting | 1000–1100° C. |
| Zinc retorts | 1400–1600 |
| Bessemer converter | 1600 |
| Tuyères in iron blast furnaces | 1900 |
| Electric arc | 3600 |

**Classification of Refractories.**—In this section we shall outline the classification of various kinds of refractories, and later we shall discuss the important ones in more detail.

I. *Acid Refractories.*

A. Alumina-siliceous materials. The use of these depends upon the infusibility of aluminum silicate. There must be as little free silica as possible, because it lowers the fusing point of this type of refractory. These materials occur in three forms:

1. Natural rock.
2. Prepared mass (fire clay).
3. Burned brick (fire brick).

B. Siliceous materials. These consist mainly of $SiO_2$ and must be low in metallic oxides and alkalies. They are commonly used in the following forms:

1. Natural rock.
2. Prepared mass.
3. Burnt brick.
4. Electrically fused quartz.
5. Silica brick (Dinas brick).
6. Quartz furnace sand (ganister).
7. Quartzite.

II. *Basic Refractories.*

A. Aluminum oxides. There are two important classes of these:

1. Bauxite or bauxite brick.
2. Alundum (electrically fused bauxite).

B. Oxides of Ca and Mg. The common forms are produced by calcining:

1. Magnesite to give magnesia.
2. Limestone to give lime.
3. Dolomite to give a mixture of lime and magnesia.

C. Iron oxides. These are used principally in the manufacture of wrought iron.

1. Hematite.
2. Magnetite.
3. "Blue Billy," a by-product consisting of $Fe_2O_3$ and $Fe_3O_4$.

III. *Neutral Refractories.* These are materials which are attacked by neither acids nor bases, and are used to replace basic refractories where the corrosive action is strong. The aluminum silicate refractories are sometimes classified as neutral refractories, but they show an acid reaction when exposed to basic slags.

A. Forms of carbon.
  1. Graphite.
  2. Charcoal.
  3. Coke.
B. Chromite.
C. Artificial refractories. Most of these are manufactured in electric furnaces and are used for special purposes. Three typical refractories of this class are:
  1. Zirconium carbide.
  2. Titanium carbide.
  3. Silicon carbide.
D. Metals. Metals commonly used as refractories are: Fe, Cu, Mo, Ni, Pt, Os, Ta, Th, Ti, W, Va, and Zr.
E. Sundry. A few other materials which are occasionally used as refractories are:
  1. Concrete.
  2. Talc.
  3. Serpentine.

IV. *Rarer Refractories.* These are used chiefly in crucibles for experimental work. The following is a list of a few of these with their approximate melting points:

| | |
|---|---|
| 1. $Be_2O_3$ | 2200° C. |
| 2. $CeO_2$ | 1950 |
| 3. $La_2O_3$ | 1840 |
| 4. $Ta_2O_5$ | 1875 |
| 5. $ThO_2$ | 2470 |
| 6. $TiO_2$ | 1350 |
| 7. $Y_2O_3$ | 2400 |
| 8. $ZrO_2$ | 2570 |

**Fire-Clay Refractories.**—Good fire clay consists of hydrous aluminum silicate minerals, together with small amounts of other minerals such as quartz, feldspar, and mica. An important property of clays is their *plasticity* or ability to absorb water to form a plastic putty-like mass which can easily be molded into the proper shape. When moist clay is dried, it loses some of its absorbed water and forms a firm solid which is fairly strong. When the dried clay is then *burned* by heating to about 1300° C., the absorbed water and chemically combined water (from the silicates) are driven off, and the solid remaining sinters to a hard, strong refractory consisting essentially of anhydrous aluminum silicate.

Highly plastic clays are known as *fat clays.* They will absorb about 35 per cent of their weight of water. *Lean clays* are non-plastic and absorb only about 14 per cent water. The plasticity of clays is lost on burning.

The manufacture of fire brick illustrates many points which are common to all refractory-brick manufacturing After grinding and mixing with water and *grog* (if necessary), the clay is molded into the proper shapes and then dried. Drying is usually carried out by slowly passing cars loaded with raw brick through a tunnel kiln where hot gases aid in the drying. This commonly takes from 24 to 36 hours. The dried brick is *fired* or *burned* by heating in a beehive kiln. Heating and cooling must be done slowly, and the common procedure is to heat gradually for 3 to 5 days until a temperature of 1280° to 1350° C. is reached, hold the brick at this temperature for 2 or 3 days, and then allow 3 days for cooling.

When clays are fired or burned, they suffer a shrinkage which is usually measured in percentage contraction of linear dimensions. Bricks must be molded oversize so that they will have the proper dimensions when finished. Fat clays form harder and stronger brick than lean clays, but the shrinkage is often so great that cracks form in the brick and it is difficult to form well-shaped brick by using fat clays alone. This is the reason for using grog in the clay mixture. Grog is any non-plastic material (usually made by grinding up old burned refractory material) which is used to diminish shrinkage. In some refractories, especially when molded in large sections, as much as 50 to 64 per cent of the raw material may be grog. Lean clays have a shrinkage of about 2 per cent, fat clays 12 per cent, and average clays about 5 or 6 per cent. The best fire brick should approximate the composition of sillimanite ($Al_2O_3 \cdot SiO_2$) or mullite ($3Al_2O_3 \cdot 2SiO_2$).

In all forms of refractory material where two solids are present which might react to form a low-melting slag, the particle size should be as large as possible.

Fire brick is very widely used in all types of furnace construction. It is the most common refractory of all. Fire clay is sometimes used to form furnace bottoms. The clay is rammed into place and gradually dried and burned by the heat of the furnace. This procedure gives a monolithic refractory as distinguished from a jointed refractory formed by laying brick.

Refractory brick is not laid in heavy mortar as is common (red) brick. The mortar used should be of approximately the same composition as the brick itself and must be used sparingly. Fire brick is usually laid in a mortar made of fire clay, sand, and water.

**Silica Brick.**—Silica brick is made by burning crushed silica rock with about 2 per cent lime to serve as a binder. The molded brick is dried quite rapidly and is then burnt for about 20 days at a temperature of 1450° to 1470° C. Good silica brick should contain about 96 to 98 per cent free $SiO_2$, with 2 per cent lime and the rest alumina.

Silica brick is highly refractory, porous, hard, and very difficult to cut. In color it is yellow with specks of brown throughout. Silica brick should be laid in a mortar containing sand and clay in the ratio 60 : 40.

In laying brick in furnaces, allowance must be made for the thermal expansion of the brick. This is usually done by inserting wooden strips at intervals in the courses. As the furnace comes to temperature, the strips burn out and allow the brick to expand. When silica refractories are used, the fact must also be borne in mind that $SiO_2$ has three crystalline modifications. At 870° C., quartz alters to tridymite, and tridymite changes to cristobalite at 1470°. There is an expansion of 13.6 per cent when quartz transforms to tridymite, and a total expansion of 16.8 per cent in the quartz-cristobalite transformation. Well-burned silica brick, however, should consist almost entirely of tridymite and cristobalite. Silica fuses at 1700° C. and softens at 1500°. Natural quartz decrepitates at 570°, owing to the vaporization of minute drops of water contained in the mineral.

Silica sand and quartzite are often used to form monolithic furnace bottoms.

**Magnesia.**—Magnesia brick made of calcined magnesite is the most common basic refractory. The burned brick has a chocolate-brown color caused by impurities (notably iron oxide which aids in the sintering). Magnesia brick should be laid with very thin joints using a slurry of linseed oil or tar and magnesia as a mortar.

Magnesia brick is very sensitive to sudden temperature changes, and spalls easily.

**Bauxite Refractories.**—Bauxite is a hydrous aluminum oxide which yields $Al_2O_3$ when dehydrated. Bauxite is usually made into brick when used as a refractory, and the manufacturing procedure is much the same as that outlined for the making of fire brick.

**Lime.**—Burned lime is almost worthless as a refractory because of its strong tendency to absorb water and $CO_2$ and form a crumbly mixture of hydroxide and carbonate (slaking). Dolomite calcines to yield a mixture of CaO and MgO, and often this is suitable as a refractory.

**Chromite.**—Chromite, $FeCr_2O_4$, is one of the best neutral refractories, but it has two major defects: (1) it is relatively expensive, and (2) it absorbs matte or metal to form a refractory mass from which the metal cannot be recovered by smelting. Chromite refractories are usually in the form of chrome brick.

**Carbon.**—Graphite is the most refractory substance known. It does not liquefy, and the solid does not begin to sublime below 3600° C. Graphite may be obtained from natural deposits or manufactured in electric furnaces. Some of the good features of graphite refractories are:

1. Graphite is a neutral refractory and resists the action of both acids and bases. It is readily attacked by oxidizing agents, however, particularly at high temperatures.
2. It has a relatively high thermal conductivity, and is the only common refractory that is a good electrical conductor. This latter property makes it invaluable in many electrothermic processes.

**Metals.**—In certain cases metals may be used as refractories in conjunction with a cooling water bath or spray. The comparatively low melting point of the metal is counterbalanced by its high thermal conductivity which permits rapid transfer of heat to the cooling water.

**Slags and Refractories.**—The type of refractory to be used in a given furnace is often governed by the nature of the slag produced. Most refractories are not attacked by molten metal or matte, but the acid or basic oxides in slags may react with the furnace walls to form a fusible slag. When the slag is acid, an acid refractory is used. For basic slags a basic refractory is required. A highly basic slag will rapidly corrode an acid refractory but will have very little chemical action on a basic refractory. Similarly, an acid slag will quickly attack a basic refractory.

**Thermal Conductivity of Refractories.**—Most refractory materials are relatively poor heat conductors. When a refractory is used to contain a charge which is heated from the inside, its thermal conductivity should be as low as possible in order to conserve heat. If, however, the heat which reaches the charge must be conducted through refractory walls (as in zinc retorts, for example), the thermal conductivity of the refractory should be as high as possible. When, however, the primary considerations for choosing a refractory (cost, fusing point, chemical composition, etc.) are taken into account, there is usually very little choice left between refractories of varying thermal conductivity. Asbestos, kieselguhr, and other insulating materials are sometimes used as an outside layer to conserve heat, but these substances cannot be exposed to very high temperatures and are not classed as refractories.

## DRYING AND CALCINING

Often the ore, concentrate, or flux supplied to a smelter will contain moisture which must be removed before the material can be used. The roasting or smelting furnace itself may serve as a drier, and drying as a separate operation is necessary only if:

1. The charging of wet material into a furnace would materially reduce the efficiency of the process because of the extra heat required to evaporate the water, or

2. The process in question requires dry material. For example, converter flux used in copper converting must be dried, because the moisture in wet flux reacts explosively with the liquid matte in the converter.

Drying is commonly done in a drying furnace or kiln which is designed so that the wet material is brought in contact with hot gas or air. The drier must be constructed so that all the solid material comes in contact with the hot gases. It is necessary to supply heat to a drying furnace for two reasons: (1) to raise the temperature of the liquid water and hence increase its vapor pressure and rate of evaporation, and (2) to supply the latent heat of vaporization absorbed when the vapor forms. It is also necessary to exhaust the gas rapidly enough to prevent the concentration of water vapor reaching the point where liquid water begins to condense. Example 1 illustrates some of the factors involved in drying operations. Note the application of the countercurrent principle.

### EXAMPLE 1

Ore is dried by passing hot flue gases upward through a drying furnace which is so designed that the ore enters the top and is discharged at the bottom. The entering gases which pass upward through the furnace amount to 10,000 cu. m. per hour (referred to standard conditions) and contain 15 per cent water vapor and the remainder $CO_2$, $N_2$, and $O_2$. The wet ore carries 13 per cent moisture, all of which is removed. The gases enter at 500° C., and are discharged at 100°, and on leaving are 28 per cent saturated with water vapor. Barometer = 740 mm.

**Required:** The weight (short tons) of ore dried per day (24 hours).

**Solution:** The gases entering in 24 hours contain:

$$10{,}000 \times 24 \times 0.15 = 36{,}000 \text{ cu. m. } H_2O \text{ (vapor at S. C.)}$$

At 100 degrees, the vapor pressure of water = 760 mm. and $760 \times 0.28 =$

213 mm. partial pressure of $H_2O$ in the gases leaving the drier. The volume of non-condensible gas entering the drier in 24 hours is

$$10{,}000 \times 24 \times 0.85 = 204{,}000 \text{ cu. m. (S. C.)}$$

and according to Dalton's principle the concentration of any gas in a mixture is proportional to its partial pressure. The pressure due to the non-condensible gases leaving the drier is

$$740 - 213 = 527 \text{ mm.}$$

and the volume of $H_2O$ vapor in the gases is

$$204{,}000 \times \frac{213}{527} = 82{,}500 \text{ cu. m.}$$

The water removed from the ore is

$$82{,}500 - 36{,}000 = 46{,}500 \text{ cu. m. } H_2O$$

$$46{,}500 \times \frac{18}{22.4} = 37{,}400 \text{ kg. } H_2O$$

$$\frac{37{,}400}{0.13} = 288{,}000 \text{ kg. of wet ore dried in 24 hours}$$

$$\frac{288{,}000 \times 2.204}{2000} = 318 \text{ short tons of wet ore dried per 24 hours}$$

The temperature maintained in a drier should be high enough to cause rapid evaporation, but not so high as to start other reactions such as the roasting of sulfide particles. Of course as long as the ore is wet, its temperature cannot rise above 100° C.

**Drying of Gases.**—The most important application of gas drying in metallurgy is the drying of the air (blast) used in the iron blast furnaces. At the temperature of the smelting zone of the furnace (about 1600° C.), water is decomposed by hot carbon

$$H_2O + C \rightarrow CO + H_2 - 28{,}680 \text{ Cal.}$$

and since this reaction is strongly endothermic, it absorbs heat and lowers the temperature of the smelting zone. This effect of moisture in the blast is so pronounced that many modern furnaces use only dried air for the blast.

There are two important methods of removing water vapor from air, and both are in use. The most common method is to pass the moist air over a drying agent such as sulfuric acid, calcium chloride, or silica gel. Another way is to refrigerate the air to a temperature so low that practically all the water vapor condenses.

**Calcining.**—Calcining is the decomposing of carbonates into metallic oxides and $CO_2$, as shown by the following reactions:

$$FeCO_3 \rightarrow FeO + CO_2$$

$$CaCO_3 \rightarrow CaO + CO_2$$

These reactions are endothermic, and the carbonates must be heated above a certain temperature before calcination begins. Calcining operations are similar to drying, except that higher temperatures must be maintained and more heat applied. Provision must also be made to remove the $CO_2$ to prevent the reversal of the reaction. The calcining of limestone to form quicklime is sometimes called *burning*. The term "calcining" is often used to denote the driving off of any volatile material by heating ($CO_2$, $H_2O$, organic matter, etc.). It differs from roasting, however, in that roasting generally implies some oxidation of the material.

## ROASTING AND SINTERING

Roasting is essentially an oxidizing process, and in most cases its primary purpose is to oxidize sulfide minerals, as in the reaction

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$$

Treatment of this sort, called an oxidizing roast, is by far the most important type. Air is universally used as the oxidizing agent in roasting processes.

Reducing roasting consists of the heating of an ore or concentrate in contact with a reducing agent so as to effect the reduction of certain compounds. A chloridizing roast is used to convert certain metals into chlorides by roasting in contact with $Cl_2$, HCl, NaCl, or $CaOCl_2$. Both these types of roasting have certain applications, but they are not of major importance. A sulfatizing roast is a modification of the oxidizing roast.

**Chemistry and Physics of Roasting.**—Practically all the sulfide ore minerals are combustible—there are stopes in the Butte mines, for example, where a fire has started in heavy sulfide ore and burned for years. For this reason, some high-sulfide products (rich ores and concentrates) may often be roasted *autogenously*; i.e., the heat generated by oxidation of the sulfides is sufficient to propagate the reaction. In other cases this heat is not sufficient, and some fuel must be used with the roasting furnace to maintain the required temperature. Whether or not material will roast autogenously depends upon three factors: (1) the type of sulfide present, (2) the percentage of sulfide minerals in the ore or concentrate, and (3) the type of roasting furnace used.

The principal object of most roasting operations is to oxidize the sulfide particles to oxides or sulfates which are required for subsequent operations. The oxidation must be carried out without fusing the charge. Other reasons for roasting are to volatilize certain impurities and/or to convert the roaster charge into a porous sinter. Whatever the type of roaster used, the sulfide particles must be exposed to a current of air and ignited. As the air strikes the heated particles, they begin to burn with some such reaction as

$$4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2$$

$$4CuFeS_2 + 13O_2 \rightarrow 2Fe_2O_3 + 4CuO + 8SO_2$$

and the current of air carries the $SO_2$ away.

The roasting reaction begins at the surface of the particles, and as the reaction continues, the oxide formed remains as a porous coating. In order for the $O_2$ to continue to react with the sulfide and for the $SO_2$ to escape, the gases must pass through the layer of oxide to get to or from the interior of the particle. This means that, as the layer of oxide becomes thicker, the roasting reaction tends to reverse since the concentration of $O_2$ decreases and the concentration of $SO_2$ increases. As a result, the removal of the last of the sulfur is often quite difficult. However, this tendency has a useful application, for in some cases, such as the roasting of copper sulfides for matte smelting, it is necessary to roast to a certain sulfur content without removing all of the sulfur; and, by regulating the speed at which the ore passes through the roaster, it is possible to produce a roasted product having any desired sulfur content. A roast in which all the sulfur is removed is called a *dead* or *sweet* roast.

Another important chemical reaction which takes place in many roasting operations is *sulfatizing* or the formation of metallic sulfates rather than oxides. Hot $SiO_2$ and $Fe_2O_3$ which are always present in roasting operations act as catalysts to promote the reaction

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

and some of the $SO_2$ formed by the burning of sulfur combines with $O_2$ to form $SO_3$. The $SO_3$ in turn reacts with metallic oxides to form sulfates:

$$Fe_2O_3 + 3SO_3 \rightarrow Fe_2(SO_4)_3$$

$$CuO + SO_3 \rightarrow CuSO_4$$

$$ZnO + SO_3 \rightarrow ZnSO_4$$

Whether or not sulfates will be formed depends upon (1) the partial pressure of $SO_3$ in the roaster gases, and (2) the temperature, which determines the dissociation tension of the sulfates. Any particular sulfate will form only when the partial pressure of $SO_3$ is greater than the dissociation tension of the sulfate. Tables 1 and 2 give the values of the dissociation tensions of some sulfates at various temperatures.

### TABLE 1*

### Equilibrium Conditions for Sulfates

| $Fe_2(SO_4)_3 \rightleftharpoons Fe_2O_3 + 3SO_3$ | | $Al_2(SO_4)_3 \rightleftharpoons Al_2O_3 + 3SO_3$ | | $CuSO_4 \rightleftharpoons CuO + SO_3$ | | $(CuO)_2 \cdot SO_3 \rightleftharpoons 2CuO + SO_3$ | | $ZnSO_4 \rightleftharpoons ZnO + SO_3$ | |
|---|---|---|---|---|---|---|---|---|---|
| Temp. ° C. | Tension in mm. | Temp. ° C. | Tension in mm. | Temp. ° C. | Tension in mm. | Temp. ° C. | Tension in mm. | Temp. ° C. | Tension in mm. |
| 553 | 23 | 572 | 28 | 546 | 43 | 600 | 62 | 675 | 5 |
| 570 | 33 | 621 | 51 | 588 | 55 | 653 | 98 | 690 | 6 |
| 592 | 45 | 681 | 120 | 615 | 70 | 686 | 123 | 720 | 24 |
| 614 | 70 | 702 | 180 | 642 | 98 | 705 | 139 | 750 | 61 |
| 634 | 113 | 720 | 261 | 665 | 130 | 728 | 173 | 775 | 112 |
| 650 | 149 | 731 | 356 | 700 | 233 | 745 | 209 | 800 | 189 |
| 660 | 182 | 742 | 480 | 714 | 324 | 775 | 298 | | |
| 680 | 286 | 748 | 692 | 725 | 460 | 805 | 542 | | |
| 690 | 401 | | | 731 | 647 | | | | |
| 699 | 560 | | | | | | | | |
| 707 | 715 | | | | | | | | |

* Fulton, C. H.: Principles of Metallurgy; McGraw-Hill Book Co., New York, 1910. Reprinted by permission.

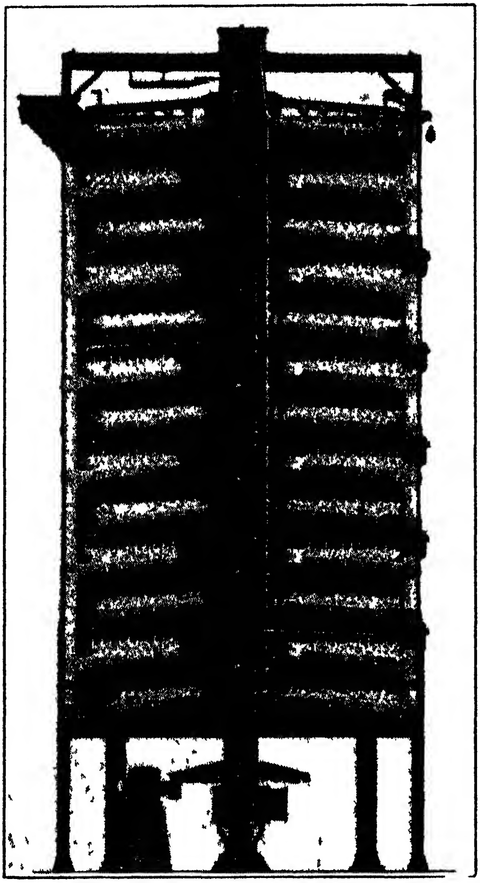
### TABLE 2*

### Partial Pressure of $SO_3$ Necessary for the Formation of Certain Basic Sulfates

| Temp. ° C. | Partial Pressure of $SO_3$ in mm. | | | |
|---|---|---|---|---|
| | $Fe(SO_4) \cdot Fe_2O_3$ | $CuSO_4 \cdot (CuO)_2 \cdot SO_3$ | $(CuO)_3 \cdot SO_3$ | $ZnSO_4 \cdot ZnO$ |
| 550 | 12.0 | 27 | | |
| 600 | 22.5 | 29 | 29 | |
| 650 | 61.5 | 40 | 33 | |
| 700 | 244.0 | 99 | 35 | 1.0 |
| 750 | | | 52 | 8.7 |
| 800 | | | 104 | 28.5 |

* Fulton, C. H.: Principles of Metallurgy; McGraw-Hill Book Co., New York, 1910. Reprinted by permission.

The formation of sulfates is promoted by low roasting temperatures and high $SO_3$ concentration. In general, high roasting temperatures will decompose sulfates into oxides and $SO_3$. In some operations the formation of sulfates is desirable; in others, not.



*(Courtesy Pacific Foundry Company, Ltd., San Francisco)*

FIG. 1.—The Nichols Herreshoff Furnace.

**Hearth Roasting.**—The multiple-hearth roaster is in the shape of a vertical cylinder containing a number of superimposed horizontal hearths (Fig. 1). The air enters from the bottom and is heated by contact with the roasting material. If the roasting is not autogenous, there will be a gas flame or other auxiliary heater for one or more of the lower hearths. The ore or concentrate enters at the top and drops from hearth to hearth in succession, until it is discharged at the bottom. In the downward progress of the ore, the sulfide particles are roasted as they come in contact with the heated air. Often the first hearth serves merely as a drier.

In hearth roasting, only the particles at the surface come in contact with air. It is necessary to stir or *rabble* the ore on the hearth in order to promote oxidation. This is done by slowly revolving rabble arms which not only stir the charge but also plow it toward the opening through which it drops to the next lower hearth.

The multiple-hearth roasting furnace contains a number of circular horizontal hearths, a steel shell to support the hearths, and a rotating central shaft which carries the rabble arms. The temperature in this type of furnace must not become high enough to cause any fusion or sintering of the charge. A typical multiple-hearth furnace is 25 feet in diameter and has from 6 to 12 hearths; such a furnace can roast from 100 to 200 tons of material per day, depending upon the amount of sulfur to be removed. The metal rabble arms of these furnaces are hollow to permit air- or water-cooling.

**Flash Roasting.**—It has long been known that most of the roasting done in a hearth roaster takes place in the brief interval while the ore is falling from one hearth to the next; for as the sulfide particles fall through the air, they have their entire surface exposed to the oxygen. Thus they burn very rapidly. When the roasting operation is so designed that all the roasting is done while the particles are falling through heated air, the process is known as *flash roasting* or *suspension roasting.* Flash roasting bears about the same relation to hearth roasting as the burning of powdered coal does to the burning of lump coal on a grate, except that in hearth roasting the air passes over the ore charge and not through it.

Flash roasting requires that the ore or concentrate be ground to a fine size, and the dust loss in the roaster is likely to be high. This method roasts very rapidly, and a flash roaster has a much greater capacity than a hearth roaster of the same size.

**Blast Roasting.**—In the multiple-hearth roaster the air circulates by natural draft and is not forced through the charge. In blast roasting the charge to be roasted is held stationary (i.e., is not rabbled), and a current of air is drawn through it. The early attempts at blast roasting were failures because the reaction was so rapid that the intense heat either fused the sulfides (to "matte") or caused a liquid slag to form. In both cases the fused material stopped the free passage of the blast and spoiled the roasting operation. In the first successful blast roasting process, Huntington and Heberlein solved the problem by mixing a certain amount of limestone with the roaster charge, and the heat absorbed in heating and decomposing the $CaCO_3$ lowered the temperature to a point where fusion of the charge was avoided. The Huntington-Heberlein process employed updraft roasting pots with grated bottoms. This method was intermittent, and today it has been largely replaced by the continuous, down-draft Dwight-Lloyd process.

In the straight-line Dwight-Lloyd machine the charge is mixed, moistened with water, and spread in a uniform, continuous layer on moving pallets which have grated bottoms. As the charge moves along, it passes over a suction windbox and at the same time the upper layer is ignited by a flame from a small ignition furnace. After the upper layer of sulfides begins to burn, the reaction progresses downward until the combustion zone has passed through the entire charge.

In blast roasting the temperature of the zone of combustion is quite high (about 1000° C.), while the raw ore or concentrate below this layer, and the roasted product above it, are relatively cool. The narrow combustion zone gradually passes through the entire thickness of the layer from top to bottom, and the speed of the pallets is adjusted so that the roasting is complete before the roasted material is discharged from the machine.

The high temperature in the combustion zone causes a partial fusion of the charge, but the thinness of the charge layer and the cooling effect of the air blast prevent extensive liquefaction. Blast roasting causes a *sintering* of the charge. The fusion followed by rapid cooling in the air blast leaves the charge in the form of a porous, cellular biscuit. In the hearth roaster the entire charge is roasting as long as it is in the furnace, but in the Dwight-Lloyd machine only a small zone of the ore is being roasted at any one time. The design of the Dwight-Lloyd roaster permits the formation and handling of a sintered product; but if any sintering were to take place in the hearth furnace, the material would stick to the hearths and rabble arms and seriously impair the efficiency of the roasting operation.

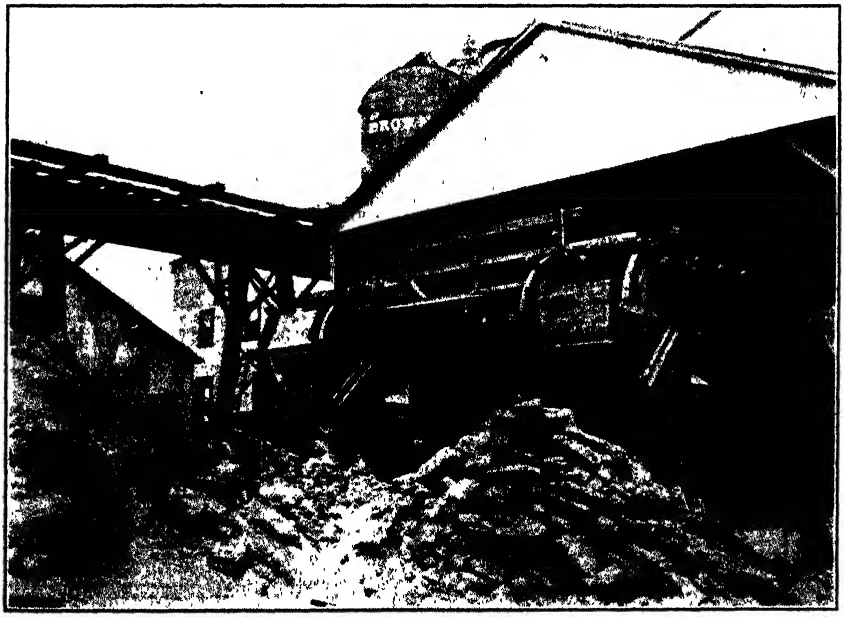
**Sintering.**—The Dwight-Lloyd process gives a sintering roast, and the term sintering is applied to any similar process which results in the agglomeration of fine particles. Sintering is not necessarily roasting. Fine oxide ores of iron, for example, may be mixed with coal and sintered in a Dwight-Lloyd machine. A standard Dwight-Lloyd machine is 42 inches wide and 264 inches long and has a capacity from 100 to 160 tons per day.

**Other Purposes of Roasting.**—In addition to the primary purpose of roasting, which is to convert metallic sulfides into other forms (oxides, sulfates) which are amenable to subsequent chemical treatment, one or more of the following purposes may be fulfilled by roasting.

1. The removal of impurities by the volatilization of certain oxides such as $SO_2$, $SO_3$, $As_2O_3$, $Sb_2O_3$, $TeO_2$, and $SeO_2$.
2. The formation of chlorides by roasting in contact with a chloridizing agent.
3. The formation of sulfates by controlling the air supplied and temperature in an oxidizing roast.
4. The reduction of certain metallic oxides by heating in contact with coal or other reducing agent (reducing roast). Roasting is often employed to convert non-magnetic compounds into magnetic com-

(*Courtesy Dwight and Lloyd Sintering Company, Inc., New York*)

FIG. 2*a*.—Dwight-Lloyd Sintering Machines.



(*Courtesy Dwight and Lloyd Sintering Company, Inc., New York*)

**FIG. 2*b*.—Discharge End of Dwight-Lloyd Sintering Machines.**

pounds as a preliminary to magnetic concentration. By a reducing roast, for example, non-magnetic $Fe_2O_3$ may be converted into magnetic $Fe_3O_4$.

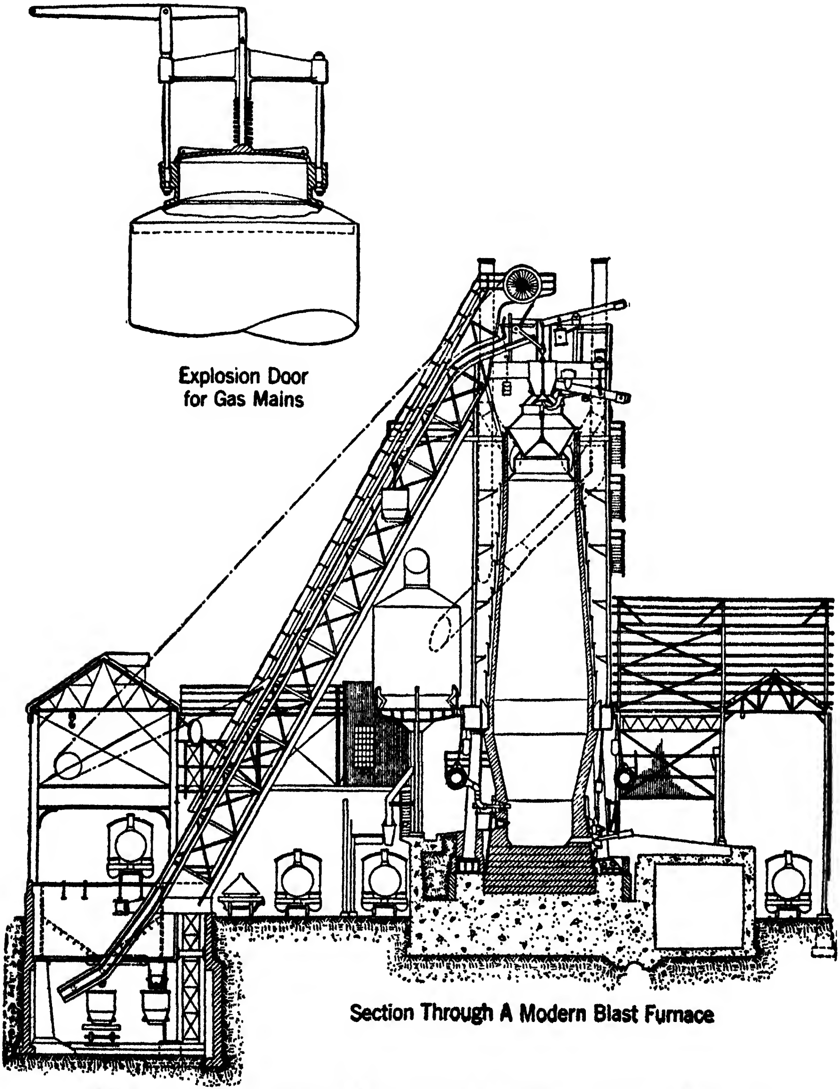
5. Alteration of the physical condition of the material (sintering).

**Roasted Products.**—The cellular, porous cake produced in blast roasting is called *sinter*, and the fine pulverulent product from a hearth or flash roasting process is called *calcine* or *calcines*. Because of the large amount of finely divided flotation concentrate being roasted in modern plants, the present trend of roasting practice is roughly as follows: (1) blast roasting or sintering is used to prepare charges for blast furnace smelting; and (2) hearth or flash roasting is used preparatory to leaching and reverberatory smelting.

The roasting of high-sulfide ores and concentrates is often done in two stages. The primary roast is quite rapid and removes the bulk of the sulfur. The secondary roast produces a finished calcine or sinter. If two passes are made in Dwight-Lloyd machines, the primary sinter must be crushed to make up the secondary charge.

## SMELTING

**Reduction Smelting of Iron Ores.**—The iron blast furnace has three essential parts: the hearth, or crucible; the bosh; and the shaft. Iron blast furnaces have a circular cross-section. The shaft increases slightly in diameter from top to bottom to permit easy descent of the solid charge and prevent it from hanging up at any point. The bosh is the smelting zone and the hottest portion of an operating furnace. Here the fusion of the reduced iron and the formation of the liquid slag take place. The liquid products then settle out in the crucible. The bosh is flared upward for three reasons: (1) It permits partial expansion of the hot gases from the combustion at the tuyères with resultant cooling. This tends to keep more heat in the smelting zone where it is needed. (2) The contraction from the upper part of the bosh to the top of the hearth allows for the shrinkage in volume which takes place when the porous solid charge melts down to the liquid state. (3) The sloping walls of the bosh support part of the weight of the charge so that the total weight does not come upon the crucible. This last item is probably the most important of all, and all types of blast furnaces are boshed in a similar manner. In the modern iron blast furnace the slope of the bosh walls is much steeper than in older furnaces, and eventually furnaces may be built in which the bosh has perpendicular walls. Better distribution of blast and the use of higher blast pressures (since the pressure of the blast supports part of the weight of the charge) have made this change possible.



*(From Iron and Steel by H. M. Boylston, John Wiley and Sons, Inc., New York)*

FIG. 3*a*.—Sectional View Through Iron Blast Furnace Showing Charging Skip.

The following details of construction are important:

1. The shaft and superstructure are suspended on columns independent of the bosh and hearth. This prevents the entire weight of

the furnace from resting on the hearth, and allows the hearth and bosh to be removed for replacement or repairs.

2. The tuyères are located so that the blast enters at the bottom of the boshed section. This detail is common to all blast furnaces.

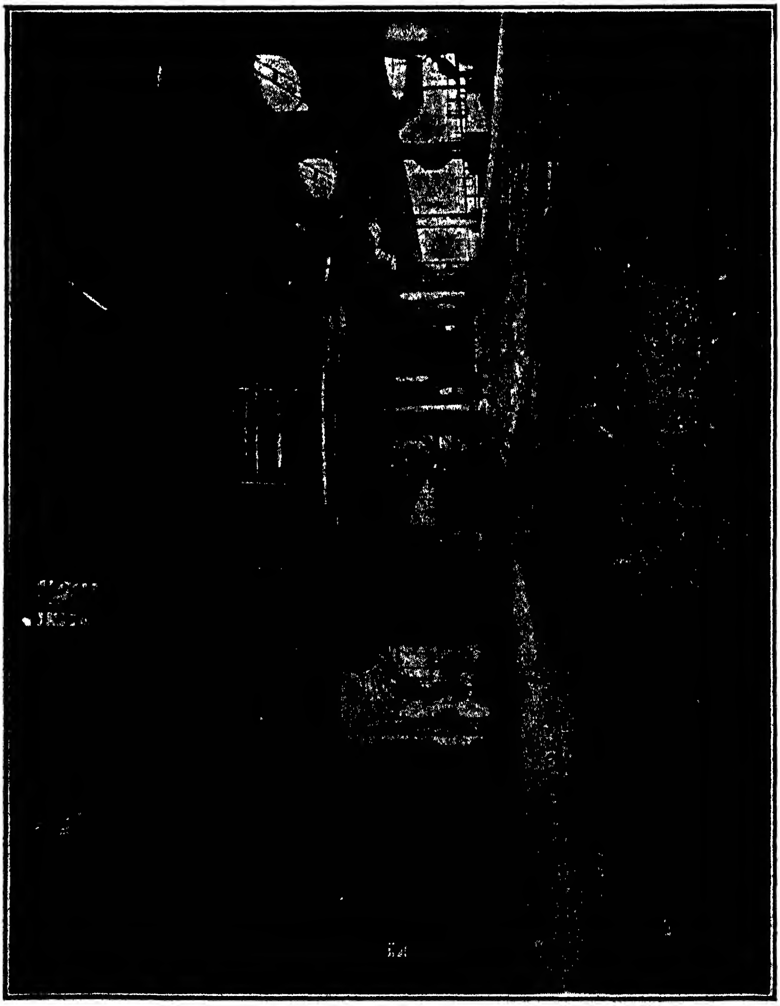


FIG. 3b.—Lower Part of Iron Blast Furnace, Showing Runners for Carrying Iron to Hot-metal Car

*(From Iron and Steel by H. M. Boylston, John Wiley and Sons, Inc., New York)*

3. The tuyères, or openings through which the blast enters, are connected by blow pipes to the bustle pipe which passes entirely around the furnace and distributes the blast from the blowers to the tuyères.

4. The tuyères are provided with hollow metal cooler plates, and

water is kept circulating through these to cool the furnace walls and keep the refractory brick and tuyères from fusing.

5. The furnace is charged from the top (as are all shaft furnaces), and by means of the double bell arrangement the charge can be introduced without permitting gases to escape.

6. The interior of the furnace is built of high-grade fire brick.

The average iron blast furnace is 90 feet high and 22 feet in diameter at the largest portion. It will produce about 1000 tons of pig iron in 24 hours. Blast-furnace operation must be continuous, and after a furnace is blown in, it is kept going day and night until the lining is worn out and must be replaced. The period between relinings is known as a *run* or *campaign*, and an ordinary iron blast furnace has an average campaign of three years of continuous operation, in which time it can produce 1 million tons of pig iron and consume about 3½ million tons of smelting materials.

The charge to an iron blast furnace consists of ore, fluxes, and coke. These are mixed together in the proper proportions and charged at the top of the furnace. Air or blast is blown in through tuyères at the bottom of the shaft. As the charge moves downward, the coke burns to CO at the tuyères, and the ascending gases which are rich in CO account for most of the reducing action. It appears that most of the coke remains unaltered until it reaches the tuyères. Just above the tuyères is the *smelting zone*, which is the hottest portion of the furnace; and it is here that the liquefaction of the charge takes place. Below the tuyères is a well or hearth in which the liquid furnace products collect and from which they are tapped at intervals. The charge without the fuel is called the *burden* of the furnace; it consists almost entirely of oxides (silicates and other salts may be considered as combinations of acid and basic oxides as we have noted before). The action of carbon and CO reduces the oxides of the metal desired. Thus, in the iron blast furnace there will be reactions such as:

$$2Fe_2O_3 + 8CO \rightarrow 7CO_2 + 4Fe + C$$

$$Fe_2O_3 + 3C \rightarrow 2Fe + 3CO$$

$$FeO + C \rightarrow Fe + CO$$

and the reduction is entirely finished before the charge reaches the smelting zone, leaving the iron in the form of solid, spongy, metallic iron; and in the smelting zone both the reduced metal and the unreduced oxides are liquefied. The purpose of the flux added in the charge is to form a fusible slag with the unreduced oxides (impurities or gangue minerals) in the ore or concentrate. Since the gangue is largely $SiO_2$, a basic flux, $CaCO_3$, is used, and this calcines to CaO before it reaches the smelting zone. Later we shall consider the subject of slags in more detail, but for our present purposes we need keep in mind only that these salts or slags are fused much more easily than pure acid or basic oxides. The governing principle of all pyrometallurgical operations involving fusion is that *the reduced elements pass into the metal; the oxidized elements pass into the slag, or form a slag if one is not already present.* This simply means that the two liquids formed in reduction smelting—molten metal and slag—are immiscible.

In the iron blast furnace the charge contains iron oxides (the ore minerals), $SiO_2$, $P_2O_5$, $Al_2O_3$, MnO, MgO (impurities in ore and coke ash), and CaO (from the limestone flux). Under the conditions in the blast furnace the iron oxides are completely reduced, as is the $P_2O_5$. The MnO and $SiO_2$ are partly reduced, but the $Al_2O_3$, CaO, and MgO remain intact. Accordingly, the pig iron contains iron, phosphorus, manganese, and silicon (not silica) together with carbon dissolved from the coke. The slag contains CaO, MgO, MnO, $Al_2O_3$, and $SiO_2$; and because CaO and $SiO_2$ are present in large amounts, the iron blast furnace slag is essentially a molten calcium silicate in which are dissolved the oxides MnO, MgO, and $Al_2O_3$.

The function of a blast furnace is twofold: (1) to reduce the oxides of the metal to be recovered, and (2) to fuse the entire charge so that the metal and slag will separate. The specific gravity of molten iron is so much greater than that of the slag that these two immiscible liquids separate readily in the hearth of the furnace.

The metal produced by reducing smelting is never pure, and because of the impurities, the crude metal must be refined. Whether or not an oxide will be reduced in a given operation depends upon the chemical strength of the metal concerned, the amount of the oxide present, and the reducing action of the furnace.

**Reduction Smelting of Lead Ores.**—The lead blast furnace is smaller than the iron blast furnace and usually has a rectangular rather than a circular cross-section. It has tuyères along both sides but not on the ends. An average lead furnace is 15 feet high (from tap-hole to charging floor), 10 to 18 feet in length, and 3½ feet wide. It has a capacity of 150 to 250 tons of charge per day. The bosh or smelting zone of the lead blast furnace is usually made of hollow iron water-jackets instead of refractory brick. The shaft is lined with fire brick. The shaft flares slightly upward so that the top of the furnace has the largest cross-section—this differs from the iron blast furnace where the largest cross-section is at the top of the bosh. The tuyères are located at the bottom of the bosh.

The lead blast furnace runs at a lower temperature and has a weaker reducing action than the iron furnace. The blast for the iron furnace is practically always preheated, but lead furnaces and other non-ferrous blast furnaces use cold blast. In an iron blast furnace, the iron and slag ("cinder") are tapped directly from tap-holes in the crucible, but the lead blast furnace commonly employs a siphon-tap by means of which molten lead is drawn from the bottom of the crucible. Lead blast-furnace slag is removed through a tap-hole in the crucible. Lead slag is often allowed to overflow one or two forehearths or settlers to permit the separation of any entrained metal or matte. The three factors which determine the efficiency of separation of molten furnace products are:

1. Specific gravities of the liquids.
2. Time allowed for settling.
3. Viscosity of the slag.

The charge to a lead blast furnace consists of sinter, flux, and coke. The sinter contains the lead in the form of oxides and silicates, together with some sulfides and sulfates. Reduction of the oxides takes place in the upper part of the furnace; the slag forms in the smelting zone, and the two molten products collect in the crucible. Some characteristic reactions are:

$$PbO + CO \rightarrow Pb + CO_2$$

$$\left.\begin{aligned} PbS + 2PbO &\rightarrow 3Pb + SO_2 \\ PbS + PbSO_4 &\rightarrow 2Pb + 2SO_2 \end{aligned}\right\}\text{"roast-reaction"}$$

Other easily reduced metals come down with the lead—copper, antimony, arsenic, bismuth, tin, etc. All the iron, calcium, magnesium, and other strong metals remain oxidized and combine with the silica to form slag which is principally calcium-iron silicate containing some $Al_2O_3$ and other dissolved oxides. If zinc is present on the charge, it remains oxidized and passes out in the slag.

**Reduction Smelting of Copper.**—The direct smelting of oxidized copper ores to metallic copper is no longer of any importance in this country, largely for two reasons: (1) the supply of suitable oxidized ores is practically exhausted, and matte smelting is much more suitable for smelting sulfide ores; and (2) the "black copper" produced by reduction smelting is a very impure product and requires much refining. The blast furnace used for the reduction smelting of copper ores is similar to the lead blast furnace.

**The Blast Furnace.**—Practically all reduction smelting is done in blast furnaces, and matte smelting may be done in either reverberatory furnaces or blast furnaces. We shall summarize a few of the outstanding characteristics of blast furnaces, and later compare them with those of *reverberatory furnaces.*

1. The blast furnace requires a fuel which is porous to permit thorough circulation of the gases rising from the smelting zone, and which is strong enough to support the weight of the charge column. The fuel must also burn without flame. Coke and charcoal are the only two fuels which possess these characteristics, and coke is practically the universal blast-furnace fuel in this country, because of the higher price and inferior mechanical strength of charcoal. Some attempts have been made to use such fuels as powdered coal or fuel oil in the blast furnace by blowing them through the tuyères, but this practice has not been adopted to any extent.

2. The ore and flux charged to the blast furnace must be in the form of fairly large lumps and cannot contain more than a small amount of fines. Fine material in any quantity cannot be used in the blast furnace because such material tends to pack and obstruct the free passage of the gases, and also because the dust loss is excessive. The coarse cellular sinter from the Dwight-Lloyd machine makes excellent blast-furnace feed, but the pulverulent calcine from hearth roasting is not satisfactory.

3. In blast-furnace smelting most of the coke does not oxidize until it reaches the tuyères, and there it is consumed by the reaction

$$C + \tfrac{1}{2}O_2 \rightarrow CO + 29{,}160 \text{ Cal.}$$

The heat of this reaction is absorbed by the CO and $N_2$ and passed on to the solid materials in the charge to bring about their fusion. The CO gas then passes up through the column of charge and reduces the metallic oxides. In blast-furnace problems it is usually assumed that all the oxygen entering the tuyères combines with carbon to form CO; and if the amount of blast per unit of time is known, it is possible to calculate the weight of carbon burned at the tuyères during that period.

Every blast-furnace operation has a "critical temperature" above which the smelting zone must be maintained before the liquid products will melt down and discharge properly. Usually the critical temperature is the lowest temperature at which the slag will flow freely, since the melting point of slag is ordinarily higher than that of the metal or matte. Suppose, for example, that in an iron blast furnace it was necessary to have the iron and slag discharge into the crucible at 1500° C. and that the temperature of the gases formed by the combustion of carbon at the tuyères was 2000° C. Obviously, only the heat content of the gases above 1500° C. would be available to do actual smelting, since if the temperature of these gases were 1500° C. or less they could not give up their heat to raise the solid or liquid material to 1500° C. The number of calories of sensible heat in the furnace gases calculated *from the critical temperature as a base* is a measure of the *smelting power* of a furnace. If the temperature of the combustion gases at the tuyères were only, for example, 1400° C., then no smelting would be done, no matter how long the process continued nor how much fuel was burned. We would simply be circulating a large amount of hot gas through a semi-solid charge.

Since it is only the last few hundred degrees of temperature which are important in blast-furnace smelting, it is easy to see why so many precautions are taken to insure uniformly high temperatures in the smelting zone, particularly in iron smelting. Preheating the blast may raise the temperature of the smelting zone only 500° C.; but since all this increase is above the critical temperature, it may double the smelting power of the furnace. Dry blast is used because the cooling effect of the endothermic reaction of water vapor with hot carbon

$$C + H_2O \rightarrow CO + H_2 - 28{,}680 \text{ cal.}$$

may reduce the temperature at the tuyères enough seriously to impair the smelting power of a furnace. All the heat needed to heat the inert nitrogen in the air up to the critical temperature is wasted as far as the smelting zone is concerned, and this suggests the advantage of "sweetening" the blast with pure oxygen—the high cost of oxygen, however, makes this impractical at the present time.

4. The blast furnace uses the countercurrent system, since the cold charge flows in the opposite direction from that of the hot gases. Consequently, the gases discharging at the top of the furnace are relatively cool, since most of their sensible heat has been absorbed by the descending charge.

**Matte Smelting.**—Smelting for *matte* instead of reduced metal is standard practice in the metallurgy of copper and nickel. The chemical reactions involved in matte smelting are principally due to metathesis, and there is very little reducing action.

The charge to a copper matting furnace ordinarily consists of copper calcines with enough flux to slag the gangue minerals. The calcines contain copper, iron, gangue minerals, and a certain amount of sulfur, since not all the sulfur is removed in roasting. Copper has the greatest affinity for sulfur of any of the common metals; and when the charge melts down, all the copper combines with sulfur to form $Cu_2S$. Some of the remaining sulfur is oxidized to $SO_2$ and escapes as a gas. The rest of the sulfur combines with iron to form FeS. The two artificial sulfides $Cu_2S$ and FeS are soluble in one another in the liquid state, and this solution of sulfides is the matte. At the same time, as the matte is forming, the rest of the iron (oxide) lime, silica, alumina, etc., are combining to form a liquid slag, which is immiscible with the matte. Slag and matte form two liquid layers, and are tapped from the furnace in the same way as the slag and metal in reduction smelting.

Matte smelting is primarily a simple melting operation, since all the materials for the reactions are present in the charge. When the charge is liquefied, its components react with one another to form matte and slag. There is no need for the reducing action of C or CO, and the fuel used in a matting furnace is required to supply only the necessary heat for melting down the charge—it has no reducing action.

The *grade* of the matte (copper content) and the *matte fall* (weight of matte produced per ton of charge expressed as percentage) is determined entirely by the sulfur content of the charge which in turn is governed by the roasting operation. Example 2 is a simplified problem which illustrates this point.

### EXAMPLE 2

An ore contains 8 per cent Cu, 24 per cent S, and all the iron necessary to form matte. Assuming that no sulfur is lost by volatilization, calculate (1) the grade of matte; and (2) the matte fall per ton of ore (*a*) when the raw ore is smelted, and (*b*) when the ore is smelted after being roasted to the point where the calcine contains 8 per cent Cu and 8 per cent S.

Solution (*a*). In 100 pounds of ore there are 8 pounds of Cu and 24 pounds of S. In $Cu_2S$ the ratio of $\frac{S}{Cu}$ by weight $= \frac{32}{128} = \frac{1}{4}$, so that the weight of S combined with Cu as $Cu_2S$ is

$$8 \times \tfrac{1}{4} = 2 \text{ pounds}$$

$24 - 2 = 22$ pounds of S to form FeS; in FeS the ratio of $\frac{Fe}{S} = \frac{56}{32} = \frac{7}{4}$, and the ratio $\frac{FeS}{S} = \frac{88}{32} = \frac{11}{4}$. Hence, the weight of FeS formed is

$$22 \times \frac{11}{4} = 60.5 \text{ pounds}$$

Weight of $Cu_2S = 8 + 2 = 10$ pounds
Weight of matte from 100 pounds of ore = 70.5 pounds

Matte fall per ton of ore $= 70.5 \times \frac{2000}{100} = 1410$ pounds (2*a*)

The grade of matte, or the percent of Cu, is

$\frac{8}{70.5} \times 100 = 11.33\%$ Cu (1*a*)

(*b*) Assume that we now have 8 pounds of Cu and 8 pounds of S in each ton of calcine charged.

As before, 2 pounds of S will form $Cu_2S$, leaving 6 pounds to form FeS

$6 \times \frac{11}{4} = 16.5$ pounds of FeS

$8 + 2 = 10$ pounds of $Cu_2S$

Weight of matte (matte fall) = 26.5 pounds per 100 pounds of calcine

or $26.5 \times \frac{2000}{100} = 530$ pounds per ton of calcine (2*b*)

Grade of matte $= \frac{8}{26.5} \times 100 = 30.2$ per cent Cu. (1*b*)

**The Reverberatory Furnace.**—Most of the large copper matting furnaces are reverberatory furnaces. This type of furnace is the most common in pyrometallurgy—it is made in many styles and sizes, and it is used for smelting and refining non-ferrous metals and for the manufacture of open-hearth steel. Copper matting furnaces (Fig. 4) are the largest of the reverberatory furnaces.

This furnace consists of a long *hearth* or *laboratory* with a monolithic refractory bottom, walls of refractory brick, and an arched roof of refractory brick. At one end of the furnace are burners in which a long-flame fuel may be burned. When the furnace is in operation, the flame fills the entire space above the hearth. The charge on the hearth is heated only by the radiation from the flame, and the flame should be adjusted so that it does not impinge on the charge nor upon any of the refractory brick (ends, side walls, or roof). If the flame is oxidizing, there may be some oxidation of the surface of the charge, but usually there is very little chemical action between the flame gases and the charge. The charge must contain within itself all the necessary components for the reaction. Thus, for example, in the reduction smelting of tin in reverberatory furnaces the heating is done by the reverberatory flame, but the carbon (usually crushed anthracite) for reduction of the $SnO_2$ must be mixed with the furnace charge.

Fuels for reverberatory furnaces should burn with a long flame.

Early reverberatory furnaces had grate fires at one end for burning lump coal or wood. The flame was drawn over a fire bridge and through the laboratory by the natural draft. Such furnaces were necessarily small because of the comparatively short flame, and all modern furnaces use fuels which can be blown directly into the laboratory through burners set into the end wall. Natural and artificial fuel gases, fuel oil, and powdered coal are the principal fuels for reverberatory furnaces.

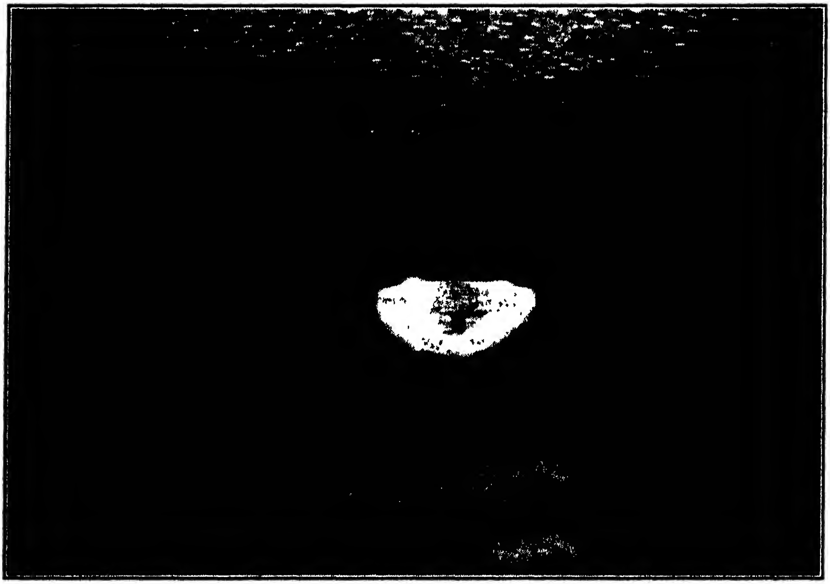


FIG. 4.—Interior of a Reverberatory Copper Matting Furnace Looking Toward the Skim End.

Let us now compare some of the outstanding features of the reverberatory furnace with those of the blast furnace.

1. The reverberatory furnace is charged through doors in the roof or in the side walls, and once the charge reaches the hearth, it is not disturbed by the flame gases passing over it. This means that finely divided material such as roaster calcines can be smelted successfully in a reverberatory furnace. Copper matting was originally done in blast furnaces, but the large amount of fine feed produced by the roasting of flotation concentrates has resulted in the displacement of blast-furnace smelting by reverberatory smelting.

Frequently it is desirable to introduce liquid material (refinery slag, etc.) into a smelting furnace. This can be easily accomplished in a reverberatory furnace, but liquid material cannot be charged to a blast furnace. In many refining operations much of the material entering the furnace is in the liquid state, and the reverberatory furnace is well adapted for handling both liquid and solid charges.

2. The reverberatory fuel must burn with a long flame in contrast to blast-furnace coke which burns with little or no flame.

3. In a reverberatory furnace the smelting zone includes practically the entire furnace, and consequently the gases from the combustion enter the exhaust ports at a very high temperature. Because of the sensible heat content of these gases, the thermal efficiency, or the percentage of the heating value of the fuel actually used in the furnace, is very low in reverberatory practice—usually only about 10 or 15 per cent. The blast furnace has a much higher thermal efficiency (30 to 50 per cent), because the cold charge moving down in the furnace abstracts most of the sensible heat in the uprising current of hot gas from the smelting zone. Most reverberatory furnaces have some equipment, such as regenerators or waste-heat boilers, installed to make use of the sensible heat in the waste gases.

**Matte Smelting in the Blast Furnace.**—Matte smelting can be performed in a blast furnace as well as in a reverberatory, provided that the physical state of the charge is suitable. Originally, all copper matte was produced in blast furnaces, and the blast furnace is still used in smelting for copper-nickel mattes.

The type of furnace used resembles the lead blast furnace, and the operation is the same except that the coke is used only to supply heat for melting down the charge, and there is little or no reducing action. The "atmosphere" in the furnace is neutral or oxidizing; i.e., not reducing as in the lead and iron blast furnaces.

A special case of matte smelting is known as *pyritic smelting.* It has been employed in the smelting of copper ores, although it is no longer of great importance. Pyritic smelting is adapted for smelting massive pyrite ores which contain small amounts of copper minerals. The charge consists of the massive pyrite and silica flux, and no other fuel is used. The smelting is done in a blast furnace; and the heat evolved by the burning of $FeS_2$ to FeO and $SO_2$, and the subsequent combination of the FeO and $SiO_2$ to form slag, provide the necessary heat. The copper sulfides, together with some unoxidized iron sulfides, form the matte. In *partial pyritic smelting* some coke is used in addition to the pyrite. Pyritic smelting is sometimes called *oxidizing smelting,* because the pyrite is oxidized by the action of the air. This nomenclature may be confusing, however, because the metal to be recovered (copper) is not oxidized, and we do not think of oxidizing smelting as the antithesis of reduction smelting where the metal to be recovered is actually reduced from its compounds. In pyritic smelting, however, the gases (atmosphere) in the furnace are highly oxidizing and not reducing in their action as are the CO-laden gases in lead and iron blast furnaces.

## SLAGS

Slags may be roughly divided into two classes—smelting slags and by-product slags. The former class includes the slags formed in blast-furnace and reverberatory-furnace smelting. These slags are invariably silicates, and, as far as the immediate operation is concerned, they are waste products. In some cases improved smelting technique has made it possible to smelt at a profit slags that were at one time regarded as worthless. In lead smelting it is sometimes possible to treat a blast-furnace slag to recover zinc, and some slags can be used for such purposes as road ballast, raw material for portland cement, and slag wool. By and large, however, these smelting slags are usually discarded as waste products.

By-product slags include converter slags and refinery slags, and these are always re-treated to recover the contained metals. In addition to silicates, these slags may contain considerable quantities of other salts such as stannates, plumbates, antimonates, arsenates, phosphates, borates, chlorides, and fluorides. The principal part of this discussion will be concerned with smelting slags, and the term "slag" as used in the remainder of this chapter will refer to smelting slags, unless otherwise specified.

**Properties Required of Slags.**—A good slag for smelting must have the following qualifications:

1. *Proper melting temperature.* The slag must be fusible enough to melt completely at furnace temperature, and yet not so fusible that it will run off before the charge has been sufficiently heated.
2. *Proper specific gravity.* Slags must have a low specific gravity so that they will separate quickly and cleanly from liquid metal or matte. Slags have an average specific gravity of about 3.0. Magnesia slags may be as low as 2.0, and lead blast-furnace slags as high as 3.6.
3. *Low viscosity.* Slags must be fluid, i.e., not viscous, for the same reason that they must have low specific gravity—to permit rapid segregation of the molten furnace products. In addition to the fact that a viscous slag tends to entrain particles of metal or matte, such a slag does not flow readily enough to permit easy tapping. Slags

which are raked rather than poured (puddling furnace slags), or slags formed in an operation where a clean separation is not a prime essential (refinery slags which are to be re-treated), may have a much higher viscosity than smelting slags.

4. *Low solubility for metal or matte.* The molten slag must not dissolve the other liquid products of the furnace. Most silicate fusions have no appreciable solvent power for reduced metals or sulfides, and metal losses in slag are usually due to mechanically entrained particles, or to imperfect reduction of the metallic oxides which are therefore dissolved, i.e., slagged.

## CLASSIFICATION OF SLAGS

I. Silicate slags (smelting slags).
  A. Ferrous slags—produced in non-ferrous smelting and converting.
  B. Non-ferrous slags—produced in the iron blast furnace.
II. Non-siliceous slags (refinery slags).
  A. Borates.
  B. Litharge slags.
  C. Phosphates.
  D. Fluorides.
  E. Aluminates.
  F. Antimonates, arsenates, selenates, etc.

**Nomenclature of Slags—Silicate Degree.**—Silicates are classified by chemists and mineralogists as salts of two hypothetical silicic acids, orthosilicic acid, $H_4SiO_4$, $(2H_2O \cdot SiO_2)$; and metasilicic acid, $H_2SiO_3$, $(H_2O \cdot SiO_2)$. There are also two other hypothetical acids, $H_6SiO_5$ and $H_8Si_3O_{10}$; but the salts of these acids are so rare that no chemical names have been assigned to the acids. Molten silicate slags are igneous fusions of one or more of the salts formed by replacing the hydrogen of these hypothetical acids by metals.

The metallurgical nomenclature of silicate slags is based upon their *silicate degree,* which is defined as the ratio of the weight of oxygen in the acid to the weight of oxygen in the base. For example, the slag $CaFeSiO_4$ $(CaO \cdot FeO \cdot SiO_2)$ contains two parts of oxygen in the acid $(SiO_2)$ and two parts oxygen in the $(CaO \cdot FeO)$. Accordingly,

$$\frac{\text{Oxygen in acid}}{\text{Oxygen in base}} = \frac{2}{2} = 1$$

and the silicate degree of this slag is 1.

A slag with a silicate degree of less than 1 is a subsilicate; singulo- or monosilicates have a silicate degree of 1; sesquisilicates have a silicate degree of 1.5; bisilicates have a silicate degree of 2; and trisilicates have a silicate degree of 3. The principal facts about the nomenclature of slags are summed up in the accompanying table.

The silicate degree of a slag is not always one of the numbers given above, and a slag which had a silicate degree of 1.3 would be intermediate between a sesquisilicate and a monosilicate.

It is possible for the silica content to change without altering the silicate degree, as is shown by the silica content of the following slags, all of which have a silicate degree of 1.

| COMPOSITION OF SLAG | PER CENT OF $SiO_2$ |
|---|---|
| $2CaO\cdot SiO_2$ | 34.9 |
| $2FeO\cdot SiO_2$ | 29.4 |
| $2BaO\cdot SiO_2$ | 16.4 |

TABLE 3

CLASSIFICATION OF SILICATES

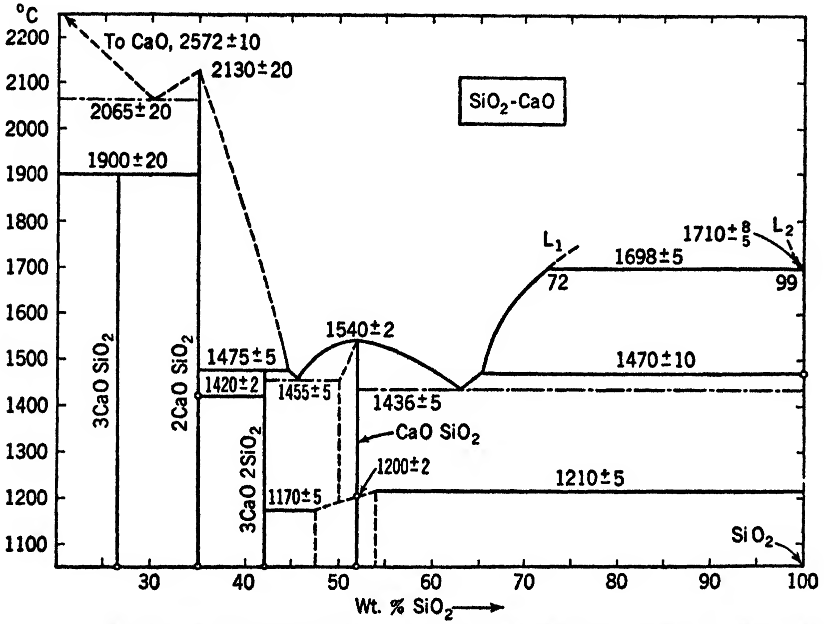
| Silicate Degree | Metallurgical Name | Chemical or Mineralogical Name | Typical Examples Silicate Degree in Parentheses |
|---|---|---|---|
| <1 | Subsilicate | .......... | $4CaO\cdot SiO_2$; $(\frac{1}{2})$<br>$4FeO\cdot SiO_2$ $(\frac{1}{2})$<br>$3FeO\cdot SiO_2$ $(\frac{2}{3})$ |
| 1 | Monosilicate or Singulo-silicate | Orthosilicate | $2CaO\cdot SiO_2$ (1)<br>$2FeO\cdot SiO_2$ (1) |
| 1.5 | Sesquisilicate | .......... | $4CaO\cdot 3SiO_2$ (1.5)<br>$4FeO\cdot 3SiO_2$ (1.5) |
| 2 | Bisilicate | Metasilicate | $CaO\cdot SiO_2$ (2)<br>$FeO\cdot SiO_2$ (2) |
| 3 | Trisilicate * | .......... | $2CaO\cdot 3SiO_2$ (3)<br>$2FeO\cdot 3SiO_2$ (3) |

* Found only in the Bessemer converter.

**Melting Points of Slags.**—All the oxides and silicates found in slags are soluble in one another in the liquid state, and slags are like alloys in that they ordinarily do not have definite melting points but freeze and melt over a range of temperature. Accordingly, the melting point of a slag must be obtained from the temperature-composition plot or equilibrium diagram of its constituents.

When slags solidify, they form solid solutions, mechanical mixtures, etc., and/or amorphous solid or glass. Most slags freeze as glasses, especially when cooled rapidly. However, when crystals separate from slags, they are always definite, recognizable, silicate minerals. The composition of solid slag, however, is not of great interest to the metallurgist, because most furnace operations are so adjusted that the slag is discharged while completely molten, and this molten slag is usually discarded.

The liquidus line or surface is the principal feature to be considered in the equilibrium diagrams of slags, and the melting point of any given slag is defined as the temperature at which it is entirely liquid, or the intersection of the composition ordinate and the liquidus.



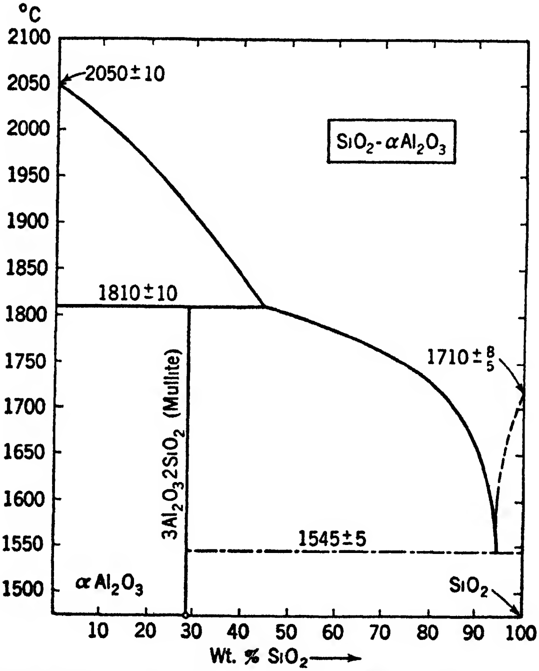
*(From International Critical Tables, Vol. IV, McGraw-Hill Book Co., New York)*

FIG. 5.—The $SiO_2$-CaO Equilibrium Diagram.

To illustrate some typical equilibrium diagrams of slags, those for the following series have been included: $CaO - SiO_2$; $SiO_2 - Al_2O_3$; and $CaO - Al_2O_3 - SiO_2$. Note that the melting point of a properly chosen slag may be much lower than the melting points of the constituent oxides. This is the fundamental reason for fluxing furnace charges.

**Formation Temperatures.**—Since the materials in a furnace charge consist of a mechanical mixture of slag-forming oxides and not of formed slag, the slag will not liquefy at its melting point, but the charge must be heated above this point to the *formation temperature* of the slag before it will liquefy. To illustrate the meaning of formation temperature, let us consider the simple analogy of the lead-antimony eutectic.

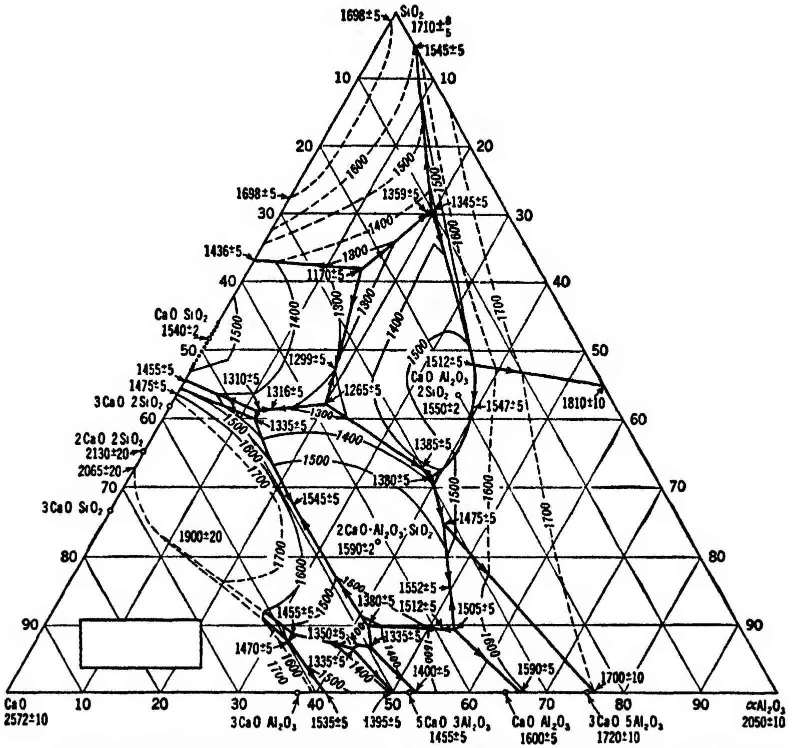
If we have a piece of solid alloy of eutectic composition, it will melt at 247° C. (Fig. III-9), but if we heat 88 grams of pure lead and 12 grams of pure antimony together in a crucible (each metal being in the form of a single large piece), the mixture will not fuse at 247°. It may be necessary to heat to the melting point of lead (327° C.) before any liquid forms. As soon as any liquid of eutectic composition is formed, however, the two metals will begin to dissolve in it, and the rest of the melting *can* take place at 247°, but will not necessarily do so unless enough time is allowed for the two metals to dissolve in the proper proportions. We may sum up the principle involved here by stating that the temperature required to form a liquid lead-antimony alloy containing 12 per cent antimony depends upon the size of the solid particles of the metals and the intimacy of their as-



*(From International Critical Tables, Vol. IV, McGraw-Hill Book Co., New York)*

FIG 6.—The $SiO_2$-$\alpha Al_2O_3$ Equilibrium Diagram.

sociation. The solidified eutectic or formed alloy represents the ultimate in subdivision of lead and antimony particles, and in intimacy of mixing. Accordingly, the formed alloy will melt at the lowest possible formation temperature. Coarser mixtures of lead and antimony will form alloys at temperatures higher than 247°, and the formation temperature is a function of the size of the solid particles.



(*From International Critical Tables, Vol. IV, McGraw-Hill Book Co., New York*)

FIG. 7.—The CaO-$SiO_2$-α$Al_2O_3$ Equilibrium Diagram. (Projection of the Liquidus Surface.)

Precisely similar conditions apply to the formation temperatures of slags. The formation temperature is always higher than the melting point of the formed slag; and the coarser the pieces of the slag-forming oxides, the higher will be the formation temperature. Experiments have determined that the formation temperatures of a given binary series of slags lie on a line above and roughly parallel to the liquidus, the distance between the line of formation temperatures and the liquidus being a function of the particle size of the constituent materials. The locus of the formation temperatures of a series of ternary slags would be a warped surface parallel to the liquidus surface.

When exact information is lacking, it may be assumed that the formation temperature of a slag is about 200° C. above its melting point—for very coarse mixtures as much as 300°.

The formation temperature of any mechanical mixture of oxides may be lowered considerably by adding a small amount of formed slag of the same average composition to the charge. The formed slag will fuse at its melting point and the slag-forming oxides will dissolve in the liquid.

**Thermal Properties of Slags.**—In casting the heat balance of a furnace operation, two factors are of special importance with regard to the slag: (1) the sensible heat in the molten slag at the temperature of discharge, and (2) the heat required to form the slag from the mixture of oxides in the charge.

The first item is the same as the heat required to bring a given weight of the formed slag from 0° C. to the temperature of discharge. Estimation of the value of the second item requires that the formation temperature be either known or assumed. The two examples following illustrate how these quantities are determined.

### EXAMPLE 3

Calculate the amount of heat carried out of a furnace by 100 kg. of $CaSiO_3$ discharged at 1500° C.

Solution: The mean specific heat of solid $CaSiO_3$ between 0° and 1250° (the melting point) is 0.220; hence

$0.220 \times 1250 = 275$ Cal. per kg., the heat required to heat the solid to the melting point.

The heat of fusion of $CaSiO_3$ is 100 Cal. per kg.

The specific heat of liquid $CaSiO_3$ is 0.40.

$0.40 \times 250 = 100$ Cal. to heat 1 kg. of liquid slag from 1250° to 1500°.

Total heat $= 100(100 + 100 + 275) = 47{,}500$ Cal. in 100 kg.

Note: We must consider here whether or not the slag crystallizes or remains amorphous. As far as the furnace operation goes, the entire 47,500 Cal. are lost; but if we are interested in the amount of heat that can be abstracted from the slag (by pouring it into water, for example), we must know whether or not the slag is partly or entirely amorphous. If the $CaSiO_3$ solidifies entirely as a glass, then only 37,500 Cal. will be given off when it cools, for the latent heat of fusion is not liberated unless crystallization takes place. Glassy slags, therefore, require less heat to melt than crystalline slags, and slag samples for chemical analysis are usually poured into water (chilled) because glassy material is decomposed by acids much more readily than crystalline (stony) slags.

### EXAMPLE 4

Calculate the amount of heat necessary to form 100 kg. of liquid $CaSiO_3$ at 1500° C. from CaO and $SiO_2$ at 0°. (The "heat necessary to form" must not be confused with the "heat of formation" of $CaSiO_3$. This latter factor will enter into the solution of the problem.)

Solution: Assuming that the formation temperature of the slag is 1450°, or 200° above its melting point, we must first calculate how much heat is required to bring the solid reagents to this temperature.

Mean specific heat of CaO: 0° to 1450° = 0.202
Mean specific heat of $SiO_2$: 0° to 1450° = 0.270
$0.202 \times 1450 = 293$ Cal. per kg. CaO
$0.270 \times 1450 = 392$ Cal. per kg. $SiO_2$

100 kg. $CaSiO_3$ contains $100 \times \frac{56}{116} = 48.3$ kg CaO and 51.7 kg. $SiO_2$

$293 \times 48.3 = 14{,}150$ Cal. in solid CaO
$392 \times 51.7 = 20{,}250$ Cal. in solid $SiO_2$

At 1450° the oxides will combine with an exothermic reaction:

$$CaO + SiO_2 \rightarrow CaSiO_3 + 22{,}400 \text{ Cal.}$$

$$\frac{22{,}400 \times 100}{116} = 19{,}320 \text{ Cal.} = \text{heat of formation of 100 kg. } CaSiO_3$$

In passing from the solid to the liquid state, 100 kg. of $CaSiO_3$ will absorb $100 \times 100 = 10{,}000$ Cal. as latent heat of fusion. Technically, we should use instead the heats of solution of crystalline CaO and $SiO_2$ in this liquid, but such figures are difficult to obtain. The heat of fusion of $CaSiO_3$ is the same order of magnitude. In all events, the breaking down of crystals, whether $CaSiO_3$ or $CaO + SiO_2$, involves considerable heat energy and cannot be neglected in problems of this type. The heats of fusion of CaO and $SiO_2$ would not do, because the temperature is well below the melting points of both of these substances.

To raise the liquid from 1450° to 1500° requires:

$$100 \times 50 \times 0.40 = 2000 \text{ Cal.}$$

Hence, the total amount of heat required is

$$14{,}150 + 20{,}250 + 10{,}000 + 2000 - 19{,}320 = 27{,}080 \text{ Cal.}$$

Note that the heat required to form the slag is much less than the heat content of the molten slag. This is due to the heat contributed by the formation of $CaSiO_3$. The reverse would be true, however, if the formation reaction were endothermic.

**Thermal Constants of Slags.**—Specific heats and heats of fusion of many common slags and slag-forming constituents may be found in metallurgical handbooks and specialized textbooks. Following are a few approximations which may be of use when more exact information is not available.

The heat of fusion of slags varies from 40 to 80 Calories per kilogram. Glassy slags have no heat of fusion. The average specific heat of solid slags is about 0.25, and of liquid slags 0.4. Specific heats of slags may also be approximated by *Woestyn's rule,* which states that the specific heat of a solid slag is the weighted average of the specific heats of the constituent oxides. The average total heat content of fused slags is about 350 to 400 Calories per kilogram.

**Miscellaneous Properties.**—Slags are commonly black, brown, or dark green in color, the coloration being largely due to the presence of oxides of iron. Iron blast-furnace slags are light colored to white. Most slags have a stony texture and a vitreous luster.

**Uses of Slag.**—Slags from non-ferrous smelting are usually discarded as worthless. Iron blast-furnace slags may be used in the manufacture of portland cement, as ballast for railroad beds, and for road making. High-phosphorus (Thomas) slags from the basic Bessemer or basic open hearth may be used in the manufacture of phosphate fertilizer.

**Viscosity of Slags.**—The viscosity of liquid slag must be determined largely by experience with each particular type. Some slags with low melting points may be very viscous; other slags may melt to a very fluid liquid, although the melting point is high. As a general rule, $SiO_2$, lowers the melting point of a slag but increases its viscosity. Metallic oxides such as FeO and MnO raise the fusing point but tend to lower the viscosity.

**Constituents of Slags.**—The most common oxides in iron blast furnace slags are CaO, $SiO_2$, and $Al_2O_3$, with smaller amounts of MnO, MgO, and FeO. In non-ferrous smelting the most common slag ingredients are CaO, FeO, $SiO_2$, and $Al_2O_3$ with lesser amounts of MnO, MgO, and ZnO (in lead smelting). In slag calculations use is sometimes made of "summated" percentages by means of which oxides of similar chemical properties are grouped together and treated as a single constituent. For example, if a flux contains 30 per cent CaO and 10 per cent MgO, we may wish to consider the two together as "summated lime," written $\Sigma$CaO. Since 10 per cent MgO is equivalent to

$$10 \times \tfrac{56}{40} = 14\%\ \mathrm{CaO}$$

the flux contains 44 per cent $\Sigma$CaO. FeO and MnO may be summated by simple addition, since their molecular weights are almost identical.

Some of the minor ingredients of slags may make considerable trouble by causing the segregation of minerals of high melting points which freeze out in the furnace and form accretions on the furnace walls. The spinels are particularly likely to form in this way. Spinels have the general formula $R''O \cdot R_2'''O_3$, where $R''$ is a divalent metal, and $R'''$ a trivalent metal, and probably the most troublesome of all is the spinel $ZnO \cdot Al_2O_3$, zinc aluminate, formed in the lead blast furnace when the proper (or improper) amounts of ZnO and $Al_2O_3$ are carried on the charge.

Some sulfides, notably CaS, MnS, ZnS, and FeS, will dissolve in slags (especially basic slags) to a considerable extent.

TABLE 4

Typical Analyses of Smelting Slags

| | $SiO_2$ | $Al_2O_3$ | CaO | FeO | MnO | MgO | ZnO |
|---|---|---|---|---|---|---|---|
| Iron blast furnace | 35.0 | 15.1 | 32.9 | ...... | 2.5 | 8.0 | |
| Lead blast furnace | 20.2 | 15.0 | 11.0 | 30.5 | ...... | 6.1 | 1.2 |
| Copper matting furnace | 33.5 | 5.2 | 4.0 | 44.6 | ...... | 2.2 | |

## FLUXES

The preceding discussion has illustrated the reasons for the use of flux in smelting operations, and at this point we shall tabulate the common materials used as fluxes. A barren flux should not be used if it can be avoided. Basic ores should be fluxed with acid ores rather than with barren quartz, and siliceous gold ores are always in demand at smelters requiring acid fluxes.

Classification of Fluxes.

1. Silica:
   Sand, quartz, siliceous ores. Only "free" silica is useful as a flux. Siliceous fluxes are used in (*a*) pyritic copper smelting, (*b*) converting of matte, and (*c*) smelting lead ores with a ferruginous or calcareous gangue.
2. Alumina:
   Seldom used intentionally.
3. Iron oxides:
   These are used principally in smelting copper, lead, and iron itself, and sometimes in the treatment of silver ores. The forms most commonly used are hematite and burnt pyrite. Scrap iron is often added to the lead blast-furnace charge. The iron serves as a reducing agent and contributes FeO to the slag. $Fe_2O_3$ and $Fe_3O_4$ are usually reduced to FeO in smelting, and most of the iron in slags is in the form of FeO.
4. Manganese oxides:
   These are used largely like the iron oxides.

5. Limestone:
   Despite the fact that this is usually a barren flux, it is widely used in the smelting of iron, lead, and copper. Limestone is usually charged into the furnace without calcining, and the $CO_2$ is driven off in the furnace. Of course, the best limestone for flux is that which is free from silica.
6. Dolomite and magnesite:
   These fluxes resemble limestone in properties, and are most commonly used in iron smelting.
7. Others:
   *a.* Fluorspar. This flux melts at 1375° C. and makes a very fluid slag. It increases the solubility of metallic oxides.
   *b.* Barite.
   *c.* Gypsum.
   *d.* Metallic sulfides.
   *e.* Litharge.
   *f.* Sodium carbonate and nitrate.

The term "available" silica or "available" lime in a flux refers to the amount of silica or lime present which is not slagged by impurities in the flux itself. Assume for example, that we wish to use limestone as a flux for a siliceous ore, and that the limestone we have contains 85 per cent $CaCO_3$ (equivalent to 47.5 per cent CaO) and 15 per cent $SiO_2$. If the slag to be formed is to contain $SiO_2$ and CaO in the ratio 2 : 1, then the 15 per cent $SiO_2$ in the flux will tie up $^{15}/_{2}$ or 7.5 per cent of the CaO. Hence, the "free" or "available" lime (CaO) in the flux which can be used to flux the silica in the ore is $47.5 - 7.5 = 40.0$ per cent.

## FURNACE OPERATION

Furnaces of all kinds must be heated up and cooled down slowly. As a rule, the larger the furnace, the slower the process. Small furnaces such as assay muffles may be heated from room temperature to 900° C. in less than an hour. On the other hand, it may take a week or more to "blow in" a cold iron blast furnace.

Smelting furnaces are usually operated continuously, often for several years at a time, without shutting down. Refining furnaces are operated continuously if possible, and often a light fire is kept going when the furnace is idle, so that it does not cool down too far. The practice followed in any case depends upon a great many factors, and to illustrate, we shall briefly consider the "blowing in" and "blowing out" of a lead blast furnace.

**Blowing In.**—When a furnace is being started, it usually has had new lining placed in the hearth and smelting zone. Heating must be done slowly to dry and bake the refractories and prevent their breaking down from too sudden expansion. Accordingly, a fire is usually started with kindling in the hearth to dry out the furnace. After a time cordwood is added. Then the blast is turned on, and coke and slag are fed in from the top. When the slag begins to melt and appear in the crucible, more slag is added, together with small amounts of the regular smelting charge. As the temperature comes up, the amount of slag being charged is gradually diminished until the furnace is operating normally. Such an operation may take several days with a lead blast furnace and even longer with an iron blast furnace.

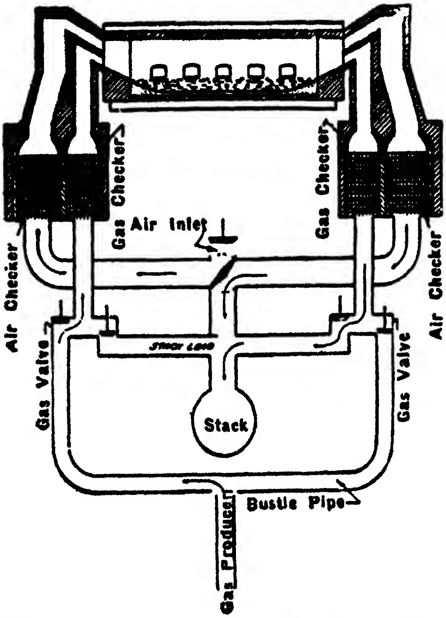
**Blowing Out.**—When it becomes necessary to stop a blast furnace, slag is charged with the regular materials in gradually increasing amounts, and at the same time the stock line is allowed to drop until flame begins to show through on top. Then the liquid material is tapped out, the tuyères are drawn out, and the tuyère holes stopped up. Unless it becomes necessary to stop a furnace because of strikes, market conditions, or lack of material, a blast furnace is never blown out until it needs relining.

## HEAT CONSERVATION

The high heat content of products of combustion from fuel furnaces, both as sensible heat and as combustible gases (principally CO), makes it highly desirable to conserve as much as possible of this heat which would otherwise be lost, and we shall briefly consider some of the most important methods.

**Regenerators.**—The melting of steel requires a higher temperature than ordinary fuel burning with cold air can give. In the open-hearth reverberatory furnace, it is necessary to heat either the air or both air and fuel previous to combustion, so that the flame will attain the proper temperature. The air (or air and fuel, if producer gas is used) are heated by passing through large chambers filled with a checkerwork of refractory brick. There are two sets of these regenerators for each open-hearth furnace—two regenerators, if the air alone is heated, four if both air and gas are heated—and while one set is heating the air and gas for combustion, the other is absorbing heat from the products of combustion. Figure 8 illustrates the flow of furnace gases through a typical open-hearth furnace. Note that the ports at either end are interchangeable and that the one being used as an exhaust port depends upon which of the regenerators is on the heating cycle.

**Recuperators.**—In a recuperative system, the air for combustion is preheated by the sensible heat from the waste gases, but the process is continuous rather than intermittent (as in regenerators). The hot gases pass through a flue surrounding the pipes through which air enters the furnace, and there is a constant interchange of heat between the hot gases and the air. Recuperators are most commonly used with zinc distilling furnaces.



(*From Iron and Steel by H. M Boylston, John Wiley and Sons, Inc., New York*)

Fig. 8.—Diagram of Open-hearth Furnace Showing Checkerworks and Connections.

**Waste-Heat Boilers.**—Waste heat in furnace gases can be converted into a useful form by utilizing these waste gases to heat steam boilers. Waste-heat boilers are standard on all reverberatory smelting furnaces. They are often used with open-hearth furnaces, taking the waste gases as they come from the regenerators.

**Hot-Blast Stoves.**—The blast for an iron blast furnace is heated by burning the relatively cool waste gases from the furnace in hot-blast stoves. The interior of these resembles a regenerative chamber, but the principle involved is different, because they are not heated by the sensible heat content of the waste gas, but by its combustion (blast-furnace gas contains about 25 per cent CO). There are four (three in some modern furnaces) stoves to a furnace. Three are being heated while the fourth is heating the blast. Generally, only about one-third of the blast-furnace gas is so used. The remainder is available for power to run the blowing engine, skip hoist, etc. Heat-saving devices are not used with non-ferrous blast furnaces.

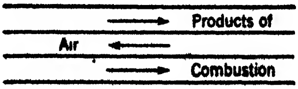
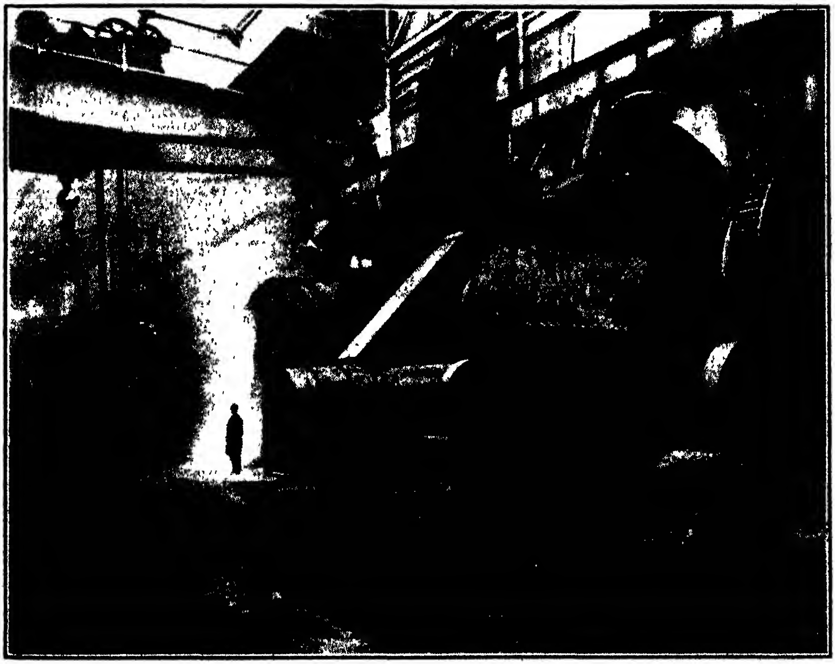


Fig. 9.—The Recuperative Principle.

## CONVERTING

*Converting* is a name given to a special oxidizing process in which a molten charge is oxidized by blowing air through it. The operation is carried out in a converter (Fig. 10). The converter is a steel shell lined with refractory brick and mounted on motor-driven trunnions by means of which the converter can be tilted to any desired angle.



*(Courtesy Anaconda Copper Mining Company)*

Fig. 10.—Great Falls Type Copper Converters.

Converters usually are pear-shaped vessels, but some non-ferrous converters are cylindrical vessels mounted with the axis of the cylinder in a horizontal position. There is a row of tuyères along the bottom of the converter through which air is blown through the charge. One of the trunnions is hollow and serves as a windbox to feed air to the tuyères. Steel converters usually take a charge of about 25 tons, and copper converters vary in capacity from 12 to 75 tons.

Converting has two important applications in metallurgy: (1) the converting of liquid pig iron into steel, or Bessemerizing; and (2) the converting of mattes to form metal by burning out sulfur and iron. The Bessemer converter was first used in steel-making, and the converter was later applied in non-ferrous metallurgy to the treatment of mattes. Steel converting is known as the Bessemer process, and this name is sometimes applied to non-ferrous converting.

**The Bessemer Process.**—In converting pig iron into steel, it is necessary to remove certain impurities such as silicon and manganese and reduce the carbon content from about 4 per cent to 1 per cent or less (generally 0.2 per cent to 0.9 per cent). This may be done by blowing in the Bessemer converter. Liquid pig iron is charged into the converter, and air is blown through the bath by means of tuyères in the converter bottom. When the air strikes the molten material, the iron immediately begins to oxidize to $FeO$; but since the affinity of silicon and manganese for oxygen is much greater than that of iron, these elements rob the $FeO$ of its oxygen so that the effective reactions are

$$2Mn + O_2 \rightarrow 2MnO + 174{,}000 \text{ Cal.}$$

$$Si + O_2 \rightarrow SiO_2 + 201{,}000 \text{ Cal.}$$

The $MnO$ and $SiO_2$ form a slag which rises to the top of the bath. When all the Si and Mn have been oxidized, the first period of the blow is at an end.

The affinity of carbon for oxygen is less than that of silicon and manganese, so that carbon does not burn until the second period after practically all of the Si and Mn are gone. Then carbon burns to CO, thus:

$$2C + O_2 \rightarrow 2CO + 58{,}320 \text{ Cal.}$$

During the first period there is no flame at the converter mouth. However, during the second period the CO burns to $CO_2$ at the mouth of the converter, giving rise to a long flame. When this flame drops, all the carbon is gone and the blow is complete. The air is then turned off, and a *recarburizer* is added to deoxidize the bath and bring the carbon up to the proper percentage.

In American practice the acid Bessemer process is used exclusively. The acid Bessemer converter has a siliceous (acid) lining, and an acid slag is maintained. In some European plants which treat high-phosphorus pig, the basic Bessemer process is used. The converter has a basic lining, and the process carries a basic slag. The blow requires three periods rather than two—the first two are the same as the periods of an acid blow, but in the third period or *afterblow* the phosphorus is oxidized:

$$4P + 5O_2 \rightarrow 2P_2O_5 + 733{,}800 \text{ Cal.}$$

**Converting of Copper-Iron Mattes.**—All non-ferrous converting is done in basic-lined converters. In the converting of copper-iron mattes, the first material to oxidize is FeS:

$$2FeS + 3O_2 \rightarrow 2FeO + 2SO_2 + 223{,}980 \text{ Cal.}$$

The $SO_2$ escapes in the converter gases, and a siliceous flux is added to slag the FeO. After all the iron is oxidized, the slag is poured off, leaving "white metal" (principally $Cu_2S$), which is oxidized in the next stage:

$$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2 + 183{,}980 \text{ Cal.}$$

$$Cu_2S + 2Cu_2O \rightarrow 6Cu + SO_2 - 28{,}019 \text{ Cal.}$$

or, adding these equations:

$$3Cu_2S + 3O_2 \rightarrow 6Cu + 3SO_2 + 155{,}961 \text{ Cal.}$$

After the blow has proceeded for the proper time, the converter contains only impure metallic copper (blister copper) which is ready for refining. The converting of copper is seldom completed on a single charge as is true of steel converting. Usually the iron is slagged and removed, and then more matte is added, and the iron again slagged. This process is continued until a large amount of white metal has accumulated in the converter, and this is then blown to blister copper. The converter slag carries considerable copper and is returned to the reverberatory smelting furnace.

**Converting of Nickel-Iron and Copper-Nickel-Iron Mattes.**—The converting of nickel-bearing mattes is complicated by the fact that nickel oxidizes so readily that the matte cannot be blown down to the metal. Therefore, the converting consists essentially of the oxidation of the iron sulfide and slagging of the iron. The remaining nickel sulfide or copper-nickel sulfides (corresponding to the "white metal" in copper converting) must be poured out of the converter and treated by some other process.

**Converter Characteristics.**—There are two principal ways in which converting differs from most other pyrometallurgical processes. In the first place, the converter requires a molten charge, although small amounts of solid material may be added if it does not chill the bath too much. In the second place, the converter uses no extraneous fuel, the required heat being supplied by the oxidation of such elements as Si, Mn, C, P, Fe, and S.

**Direct Smelting in Converters.**—In the past few years considerable work has been done on the problem of using converters alone for the treatment of high-grade sulfide products (ores and concentrates). It appears that the converter can be used quite successfully for this purpose, provided that the solid materials are added to the liquid converter charge in small amounts so that the charge is not chilled too much.

## DISTILLATION

Zinc and mercury may be recovered from their ores and concentrates by distillation in which the metal is first vaporized and then condensed. Distillation is also applied in certain minor processes such as the removal of zinc from the crust formed in the Parkes process.

**Zinc Distillation.**—The sulfide ores or concentrates are dead roasted to convert all the zinc sulfide to oxide, and the roasted product is then mixed with carbon (anthracite coal or coke) and heated in a fire-clay retort. The temperature must be high enough to promote the reaction (about 1300° C.) but not high enough to fuse the charge. Carbon reduces the zinc oxide:

$$\mathrm{ZnO + C \rightarrow Zn + CO - 54{,}100\ Cal.}$$

Since the temperature is well above the boiling point of zinc, the zinc forms as vapor, and the gases leaving the retort are about 50 per cent Zn and 50 per cent CO by volume. These gases are cooled in a condenser, and the zinc condensed to liquid metal.

**Mercury Distillation.**—The principal ore mineral of mercury is cinnabar, HgS, and the raw ore is usually fed directly into the distilling furnaces without preliminary concentration. When HgS is heated in air, the sulfur burns to $SO_2$; but the mercury does not oxidize because of the high dissociation tensions of the oxides of mercury. The mercury passes out of the furnace as a vapor, and is condensed in water-cooled condensers.

**The Chemistry of Distillation.**—The proper control of temperature is very important in distilling processes, and the following discussion will serve as an introduction to some of the theoretical aspects of the problem.

In zinc distillation the temperature must be high for two reasons: (1) the reduction reaction is endothermic and is promoted by high temperatures (Le Chatelier's principle); and (2), if the vapor is to form continuously, the vapor pressure of the zinc must be greater than the opposing partial pressure of the gaseous zinc. Since the condenser gases are approximately one-half zinc vapor, the partial pressure of the zinc vapor will normally be $\frac{760}{2}$ or 380 mm. The boiling point of zinc under 380 mm. pressure is about 842° C. (the normal boiling point is 930°); and consequently, the temperature of the retort must be well above 842°.

In the condensation of metallic vapors, the two important factors are the temperature and the vapor pressure of the metal, as the following example will illustrate.

### EXAMPLE 5

In a zinc retort the metal is reduced according to the following reaction:

$$ZnO + C \rightarrow CO + Zn$$

The products enter the condenser at 1000° C. and leave the condenser at 400°.

Required: (1) the temperature at which the zinc will begin to condense; (2) the percentage of zinc lost as uncondensed vapor.

Solution: Since the gases are 50 per cent Zn vapor by volume and are at atmospheric pressure, condensation will begin when the partial pressure of the zinc vapor is the same as the vapor pressure of zinc; i.e., when the gaseous mixture becomes saturated with zinc. Since the partial pressure of Zn equals 380 mm., condensation will begin at the temperature at which the vapor pressure of zinc equals 380 mm., or 842° C. (1)

As a basis for calculation, assume that we have 2 cu. m. of gas (S.C.) entering the condenser at 1000° C. When the gas leaves, the 1 cu. m. of CO will still be present but most of the original cubic meter of zinc vapor will have condensed. At 400° the vapor pressure of zinc is about 0.086 mm.; consequently, the ratio of Zn vapor to CO in the discharge gases is $\frac{0.086}{(760-0.086)} = 0.000113$, or there are 0.000113 cu. m. of Zn vapor remaining uncondensed. Since we started with 1 cu. m. of Zn vapor, the zinc lost represents 0.0113 per cent (2).

Attempts to reduce zinc continuously in a blast furnace and condense the zinc from the furnace gases have failed, because, for one thing, under these conditions the zinc vapor would constitute only about one-eighth of the volume of gases instead of one-half, as in the retort process. The partial pressure of zinc vapor would, therefore, be so low that it would be difficult to condense the zinc efficiently.

## METALLIC SMELTER PRODUCTS

**Matte.** A matte is a molten solution of artificial sulfides. In our discussion of matte smelting, we made the assumption that copper matte was a solution of $Cu_2S$ and FeS. Although this assumption usually gives a fair approximation of the composition, the composition of copper-iron mattes is not as simple as this. These mattes are best considered as "alloys" of the ternary system Cu-S-Fe. This means that a given matte need not consist entirely of $Cu_2S$ and FeS, but may contain some excess copper, iron, or sulfur. A small amount of $Fe_3O_4$ is often found in copper mattes.

When a lead blast furnace carries much copper on the charge, enough sulfur is left in the charge to fix the copper in a matte which is immiscible with the crude lead and also with the slag. It is easier to recover the copper from such a matte than to recover it from the liquid lead. If no matte were formed, the copper would be reduced and come down with the lead. These leady mattes contain considerable amounts of PbS and some Pb in addition to $Cu_2S$ and FeS.

The mattes produced in smelting nickel-bearing ores contain the nickel as $Ni_3S_2$, in addition to FeS (and $Cu_2S$ if copper is present.)

**Speiss.**—A speiss is an artificial arsenide (sometimes an antimonide) formed in lead smelting, smelting of oxide copper ores, and in some lead-refining operations. Most speiss is essentially an iron arsenide containing some sulfur, copper, nickel, and cobalt, if these elements are present in the furnace. Speiss is not miscible to any extent with molten copper or lead, matte, or slag.

**The Precious Metals.**—In non-ferrous smelting, usually some of the precious metals, gold, silver, and the platinum metals, are found in furnace charges. Many non-ferrous ores contain these metals. They follow the base metals into the concentrate, and remain in the sinter or calcine so that they eventually reach the smelting furnace. Some of the siliceous fluxes used in smelting and converting are gold ores. All these metals are present as elements or as easily reduced compounds, and they are very soluble in liquid copper or lead, and in molten matte. Any of the precious metals found in copper matte will remain in the blister copper after the matte has been blown. Consequently, the precious metals follow the base metals, lead and copper, through the entire smelting cycle, and are found in the crude metal as impurities. The separation of the precious metals from the base metals is a problem for the refinery.

**Bullion.**—Any metal containing appreciable amounts of the precious metals is known as *bullion.* Copper and lead bullions are *base bullions,* and a bullion containing principally gold and silver is *doré bullion.*

## FIRE REFINING

**Introduction.**—Most of the common processes used for the refining of metals can be classed under pyrometallurgy, electrometallurgy, or hydrometallurgy; but there is a natural distinction between extraction and refining processes in practice. In smelters the refinery is usually a department separate from the extraction plant or reduction department. In many cases the refinery and smelter are separate plants, the crude metal being shipped from the smelter to the refinery. Anode copper produced at the Anaconda smelter is shipped to an electrolytic refinery at Great Falls, Montana; crude lead from the blast furnaces in the Salt Lake district goes to Chicago and the Eastern seaboard for refining; the lead smelter at East Helena, Montana, ships crude lead to a refinery at Omaha; and blister copper produced in central Africa is refined in the United States or Europe.

Hydrometallurgical refining methods are not of great importance. Possibly the most important is the refining of crude bauxite by some method such as the Bayer process. Other hydrometallurgical processes such as the parting of alloys and the fractional crystallization of metal salts are often used in connection with certain fire and electrolytic refining operations. Electrolytic refining is of great importance. It will be discussed in the following chapter.

**Nature of Impurities.**—The choice of methods to be employed in refining a given metal depends upon the nature of the impurities to be removed. There are two principal classes of these: (1) impurities which must be removed because their presence is injurious to the properties of the metal, and (2) impurities which may not be harmful but which have sufficient value to make their recovery profitable (gold, silver, platinum).

**General Considerations.**—Fire-refining processes vary over such a wide range, that it is almost impossible to make a simple classification which will include them all. The simplest way to study the subject is to consider each process as a unit without trying to define its proper classification with respect to other processes. Accordingly, we shall consider several of the most important processes in this fashion. A few general rules applying to all fire-refining processes may be laid down:

1. The crude metal must be liquefied before it can be refined.
2. The chemical reactions involved are usually oxidation reactions.

In a sense, fire refining is the opposite of reducing smelting, because the reducing action of smelting is responsible for most of the impurities found in such metals as iron, lead, and copper, and by reversing the conditions and exposing the metal to oxidizing conditions the impurities can be removed. The basic law of pyrometallurgy applies to refining as well as to smelting—reduced elements remain in the molten metal; oxidized elements enter the slag or form one if a slag is not already present (or volatilize). To be removed by fire refining, impurities must oxidize more readily than the metal to be refined, and for this reason fire methods cannot be used to remove the noble metals such as gold and silver.

**Refinery Products.**—A refinery ordinarily produces refined metal and a number of by-products such as slag, skim, dross, blue powder (impure zinc plus zinc oxide), and litharge. As a rule, the by-products contain large amounts of the principal metal as well as the impurities so that they are too valuable to be discarded. In some cases they are given further treatment to recover certain elements. In other cases they are sent back to the reduction department where they enter the cycle again. Consequently, no waste products are formed in refining operations. Often there is a tendency for some impurities to build up in the closed circuit until they become very troublesome.

**Fire Refining of Copper.**—The three kinds of copper treated by fire-refining methods in order of their purity are cathode copper, blister copper (converter copper), and black copper (produced in the reduction smelting of oxide copper ores). All these are treated in reverberatory refining furnaces. The metal is first charged into the furnace and melted down. Cathodes and black copper cakes are charged while solid and melted in the furnace; but if the converters and the refining furnace are in the same plant, molten blister copper may be charged as it comes from the converters. After the charging and melting are complete, the impurities are oxidized by air which may be introduced by "flapping" the surface of the molten copper or by blowing compressed air into the bath through iron pipes. Under the oxidizing action, such impurities as Fe, Pb, Zn, Sn, Co, Ni, As, Bi, S, Se, and Te are oxidized, and rise to the surface to form a viscous slag which is skimmed from the bath as it forms. After the impurities, copper begins to oxidize; and the $Cu_2O$ formed is soluble in the liquid copper to the extent of about 6 per cent. Oxidation is continued until the bath is saturated with $Cu_2O$ to insure the removal of all impurities. The presence of so much of this brittle compound in the saturated copper or *set copper* makes it necessary to *pole* the copper to reduce the $Cu_2O$ back to metallic copper. In the most common type of poling, long poles of green wood are inserted into the bath; the heat decomposes (destructively distils) the wood, and the reducing gases formed react with the $Cu_2O$ to form CO and $H_2O$, and metallic copper. Poling is continued until the copper arrives at the *tough-pitch* stage, when the bath contains about 0.7 per cent $Cu_2O$. Poling must not be continued until all the $Cu_2O$ is removed, lest some impurities be reduced and re-enter the metal. Perfect skimming of the slag is obviously impossible, and always small amounts of impurities are left in the copper. As mechanically occluded, oxidized particles, these impurities are relatively harmless; but when reduced to the elemental stage, they alloy with the copper and may seriously damage its properties (particularly the electrical conductivity).

The time required for a refining operation depends upon the amount of impurities present; black copper requires a longer refining period than blister copper or cathode copper. Copper is always fire-refined previous to electrolytic refining, in order to take as much of the refining load as possible off the electrolytic plant.

Any precious metals in the crude copper will be found in the fire-refined product, since they are not oxidized.

Cathode (electrolytic) copper is a very pure product. Since the cathodes are unsuited for mechanical fabrication, however, because of their shape and the irregularity of their surfaces, they must be melted down and cast into such forms as wire-bars or billets. Even though these cathodes are washed after being taken from the electrolyte, they still contain a certain amount of occluded electrolyte, together with some slime particles. When the cathodes are melted, these substances contaminate the liquid copper. Such impurities, together with sulfur from the fuel used, make it necessary to fire-refine cathode copper, even though it has already been purified by electrolysis.

**Softening Lead Bullion.**—Crude lead from blast furnaces (bullion, if it contains gold and silver) contains varying amounts of As, Sb, Su, Bi, Sn, Fe, and S. Since these impurities (particularly As and Sb, which are almost always present) make the lead hard, the name *softening* is given to the purification process. Before softening proper, the lead is usually held in the molten state in drossing kettles for a period of time to permit oxidized material to rise to the surface to be skimmed off. The formation of this dross is often assisted by agitating the molten metal with air or steam. Sulfur is sometimes stirred into the drossing kettle to bring up Cu as $Cu_2S$.

After the preliminary drossing which usually removes most of the copper together with smaller amounts of the other impurities, the liquid lead is pumped into a softening furnace. This is a reverberatory furnace which may hold about 300 tons of lead. In it the lead is scorified or oxidized by the action of oxygen in the furnace gases. Impurities such as Sn, As, and Sb are oxidized and skimmed off the bath, together with a certain amount of litharge (PbO). After the lead is completely softened (refined), it is ready for market or for the desilverizing process, if there is silver in the lead. Bismuth is the only one of the harmful impurities found in lead which cannot be removed in the softening operation. Gold and silver remain in the softened bullion. The skim from the softening furnace is worked up to recover tin and antimony as well as the remaining lead. Oxidation of impurities is sometimes hastened by blowing jets of steam into the bath or adding litharge.

In the *Harris process* for softening lead, the liquid lead is brought in contact with a layer of molten fluxes which react with impurities such as Sn, As, and Sb to convert them into the corresponding stannates, arsenates, and antimonates which remain dissolved in the flux. Copper is not removed in the Harris process; and if it is present, a preliminary drossing is necessary to remove the copper. In the operation of this process, the molten lead is pumped up and allowed to fall through the fused fluxes. The lead is kept circulating in this way until it is completely softened. The fluxes used are mixtures of such salts as $NaNO_3$, NaOH, NaCl, PbO, and similar materials, it being essential that the flux contain an oxidizing agent and an alkali salt. Impurities are oxidized, as

$$5PbO + 2Sb \rightarrow 5Pb + Sb_2O_5$$

$$10NaNO_3 + 6As \rightarrow 5Na_2O + 3As_2O_5 + 10NO$$

$$4NaNO_3 + 3Sn \rightarrow 2Na_2O + 3SnO_2 + 4NO$$

and the oxidized impurities form salts which are soluble in the alkali flux

$$Na_2O + Sb_2O_5 \rightarrow 2NaSbO_3$$

$$Na_2O + As_2O_5 \rightarrow 2NaAsO_3$$

$$Na_2O + SnO_2 \rightarrow Na_2SnO_3$$

**Desilverization of Lead Bullion.**—Precious metals are recovered from copper bullion only by electrolytic refining. They may be removed from lead bullion in the same way (Betts process). However, silver (and gold) can also be removed from lead bullion by the *Parkes process.* With the exception of some lead from the Missouri valley mines, most of the lead produced in the United States contains considerable silver, and desilverization is an important stage in most lead-refining operations.

The Parkes process depends upon the strong affinity of metallic zinc for silver (also gold). Zinc is added to the softened lead bullion and stirred into the liquid metal, where it melts and reacts with the silver to form a material which has a higher melting point than the bullion and a lower specific gravity. Consequently, the zinc crust containing the silver rises to the top of the desilverizing kettle and is skimmed off. Most of the silver in the crust is thought to be present as the compound $Ag_2Zn_3$. The zinc crust containing the silver is then squeezed in a press to remove most of the entrained lead and sent to the silver refinery.

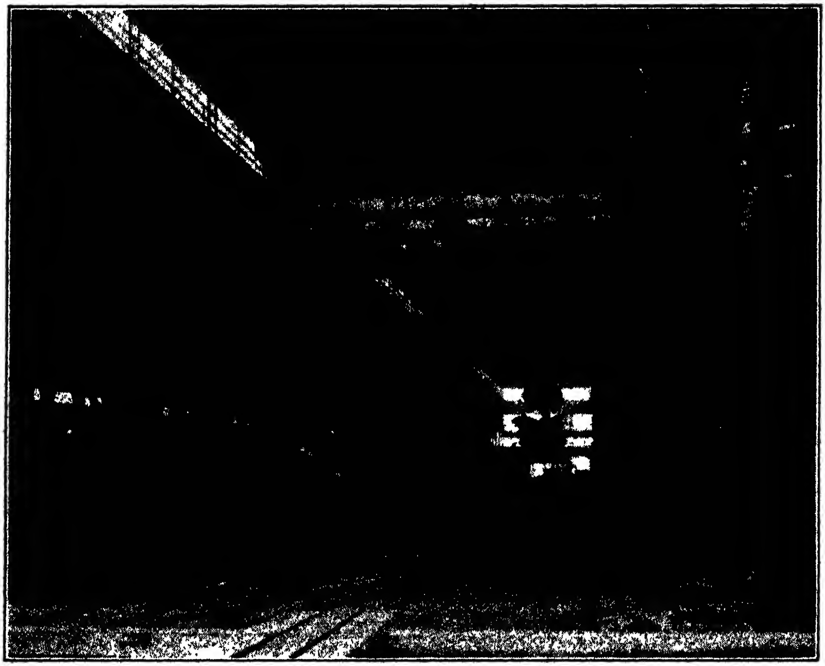
The Parkes process generally requires two stages. The first zinc added is in the form of an unsaturated crust, only enough zinc being used to produce a saturated (high-silver) crust which is ready for refining. The formation of saturated crust, however, leaves some silver in the kettle. A second zincking with pure zinc removes all the silver in the form of an unsaturated crust which is then used for the first zincking of the next kettle of bullion. Gold has a stronger affinity for zinc than silver has, so that any gold in the bullion commonly comes up in the first silver dross. When considerable amounts of gold are present, the first kettle may be a degolding kettle to remove the gold, and the two following kettles the standard desilverizing kettles.

Zinc is only slightly soluble in molten lead (0.5 to 0.7 per cent, depending upon the temperature), but this saturation zinc must be removed after desilverization. Saturation zinc may be removed in a reverberatory furnace resembling a softening furnace, in which the zinc is oxidized to ZnO by blowing air into the bath. The ZnO, together with any litharge formed, is skimmed off. The Harris process can also be used to remove saturation zinc. In the *Betterton process*, zinc is removed by passing chlorine gas through the molten lead. The zinc forms $ZnCl_2$ which appears as the molten salt on top of the liquid lead and is poured off at intervals.

Saturated zinc crusts are first treated in retorts to distil off the zinc, leaving a metal which consists principally of gold and silver dissolved in liquid lead. This high-grade bullion is then cupelled to remove the lead.

The *Pattinson process* is another method for desilverizing lead bullion, but it has been replaced by the Parkes process in practically all cases. The operation of the Pattinson process depends upon the fact that lead and silver form a series of conglomerate alloys with a eutectic containing 3.5 per cent (1020 ounces per ton) silver, melting at 303° C. If a lead-silver alloy is carefully cooled, the silver concentrates in the liquid. If the remaining liquid is poured off after about seven-eighths of the alloy has frozen, the lead can be separated into high-silver and low-silver fractions. By repeated melting and freezing, a desilverized lead (about 0.3 ounce of Ag per ton) and a rich bullion (about 700 to 800 ounces Ag per ton) can be produced. The silver is recovered by cupelling the high-grade bullion. Gold will follow the silver in the Pattinson process.

**Cupellation.**—High-grade lead-silver-gold alloys, such as those obtained from the zinc crusts formed in the Parkes process, are usually treated by cupellation. In principle, this method is exactly the same as the cupellation of the lead buttons obtained in the crucible assay for gold and silver. The alloy is melted in a shallow *cupel* or *test* and exposed to an oxidizing atmosphere. Under these conditions the lead oxidizes to litharge (PbO) and eventually all the lead is oxidized, leaving a gold-silver alloy (doré) in the cupel. The important differences between refining practice and the cupellation used in fire assaying are the size of the charge treated and the nature of the cupel. The bone-ash cupels used by the assayer are porous, and liquid litharge wets the bone-ash and is therefore soaked up by the cupel as



*(Courtesy The Wellman Engineering Company, Cleveland)*

FIG. 11.—Charging Floor of an Open Hearth Plant. Liquid Metal Is Being Charged into the Furnace in the Foreground.

fast as it forms. The high surface tension of the molten alloy prevents it from wetting the cupel; consequently, the liquid alloy remains in the cupel like a drop of water on an oiled surface, while the liquid PbO is absorbed by the cupel. The value of litharge prohibits such practice in large-scale operations, and the cupel used in refining lead bullion is made of a non-absorbing medium such as concrete or clay and limestone. The litharge forms a pool of liquid which may be poured from the cupel or drained out of a channel cut in the hearth material. In lead refineries, the litharge thus formed is usually returned to the softening furnace where it aids in the oxidation of impurities. The doré bullion containing gold and silver may be treated by parting in acid or by electrolytic parting.

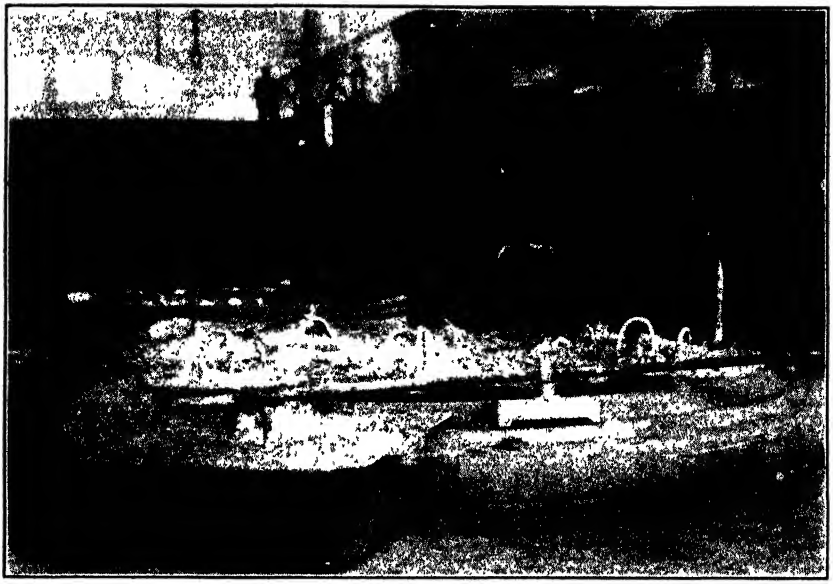


Fig. 12.—Parkes Process Kettles.

Lead is always the principal metal in alloys which are treated by cupellation. If small quantities of copper or other metals are present, however, they will also be oxidized to a certain extent.

**Refining Anode Mud.**—Most of the methods of refining anode mud and similar materials are quite complicated and vary widely, depending upon the composition of the material being treated. Following is a brief outline of one method of treating anode mud from copper electrolysis which will illustrate the type of operations.

The mud is screened to remove coarse pieces of copper and then roasted to convert free copper into CuO. Leaching with strong $H_2SO_4$ dissolves the CuO, and the residue from the leach is charged into a reverberatory doré furnace where it is melted down with oxidizing fluxes (niter + soda ash, for example). Under the oxidizing influences of air and the fluxes, metals such as As, Se, Te, Pb, Bi, Ni, and Fe are oxidized, and either volatilize or dissolve in the slags. These slags are skimmed at intervals and fresh flux added, the process being continued until only the doré remains in the furnace. The various slags or skims and the flue dust from the doré furnace are then treated to recover such elements as Se and Te.

**Distillation.**—Refining by distillation is not very widely used, and is commonly applied only to three metals—zinc, mercury, and cadmium—any of which may also be extracted by distillation. Properly conducted extraction by distilling methods usually gives a metal so pure that further refining is not necessary.

Zinc is sometimes recovered from lead blast-furnace slags by blowing powdered coal through the molten slag in a special reverberatory furnace. The zinc compounds (effectively, ZnO) are reduced to metallic zinc which vaporizes, and then burns to ZnO after escaping from the bath. The finely divided ZnO passes off in the gases and is caught in settling chambers and bag houses.

Repeated distillation is used in refining mercury, and the principles of fractional distillation are sometimes used in separating zinc from cadmium. It is of interest to note that the zinc produced by distillation usually contains small amounts of lead and cadmium. This impure zinc or spelter is preferred by many users (galvanizers and brass-makers) to pure electrolytic zinc. Electrolytic zinc plants manufacture spelter by adding small amounts of lead to the purified zinc.

**The Open-Hearth Process.**—Steel may be made from pig iron (with large or small amounts of steel scrap) by refining in an open-hearth furnace. This is a regenerative, reverberatory furnace in which the pig iron is melted down with suitable fluxes and iron oxides in the form of iron ore or roll scale which is the oxide formed on steel ingots and billets that is dislodged in rolling or forging. Carbon, silicon, manganese, and other impurities are removed about as in the Bessemer process, except that the necessary oxygen is supplied by the oxides. Either acid or basic open-hearth furnaces may be used, depending upon the nature of the furnace lining, which in turn is governed by the chemical nature of the slag formed. Most of the steel produced in this country is basic open-hearth steel.

**Refining of the Chemically Strong Metals.**—The metals aluminum and magnesium are too active chemically to permit any fire-refining

## TABLE 5
### Typical Analyses* of Crude and Refined Metals

**Copper**

| | Cu | Pb | As | Bi | Sb | S | O | Te | Se | Fe | Co+Ni | P | Ag | Au |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Cement copper (precipitate) | 77.45 | 0.63 | 0.04 | 0.006 | 0.15 | 1.93 | ..... | ..... | ..... | 4.7 | 0.03 | ..... | 30.0 | |
| Black copper | 94.55 | 0.012 | 0.126 | ..... | 0.002 | 0.867 | 0.095 | ..... | ..... | 3.04 | 0.29 | 0.01 | 0.60 | |
| Blister copper | 98.8 | 0.150 | 1.10 | ..... | 0.040 | 0.20 | ..... | ..... | ..... | 0.13 | 0.050 | ..... | 30.25 | 0.31 |
| Anode copper | 99.13 | 0.0065 | 0.118 | 0.004 | 0.053 | 0 261 | ..... | 0.017 | 0.009 | 0.011 | 0.043 | ..... | 39.98 | 0.23 |
| Lake copper (wire-bars) | 99.90 | 0.003 | 0.006 | ..... | ..... | 0.0016 | ..... | 0.001 | 0.001 | 0.003 | 0.009 | ..... | 2.80 | |
| Electrolytic "cathode copper" | 99.94 | 0.001 | ..... | ..... | 0.0009 | 0.0026 | 0.04 | 0.000 | 0.001 | 0.003 | 0.003 | ..... | 0.56 | |

**Lead**

| | Pb | Sb | As | Bi | Sn | Zn | Co | Ni | Mn | Ce | Te | Fe | Cu | Ag | Au |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Crude lead from blast furnace | 98.93 | 0.7203 | 0.0064 | 0.0048 | ..... | 0.0028 | 0.0002 | 0.0002 | ..... | Trace | ..... | 0.0064 | 0.1862 | 41.2 | |
| Lead after first drossing | 99.03 | 0.7066 | 0.0053 | 0.0050 | ..... | 0.0017 | Trace | 0.0017 | ..... | ..... | ..... | 0.0042 | 0.1096 | 41.5 | |
| Lead after softening and desilverizing by Parkes process. Market lead of "corroding" grade | 99.958 | ..... | 0.0024 | 0.0030 | 0.004 | 0.003 | ..... | 0.0001 | 0.0008 | Trace | ..... | 0.0027 | ..... | 0.29 | |
| Anode lead | 97.79 | 0.52 | 0.85 | 0.210 | ..... | ..... | ..... | ..... | ..... | ..... | 0.011 | ..... | 0.065 | 139.9 | 1.52 |
| Electrolytic "cathode" lead | 99.98 | 0.0066 | Trace | 0.0024 | ..... | ..... | ..... | ..... | ..... | ..... | ..... | 0.0028 | ..... | 0.29 | |

**Zinc**

| | Zn | Pb | Fe | Cd |
|---|---|---|---|---|
| Spelter— | | | | |
| High grade | 99.83 | 0.07 | 0.03 | 0.07 |
| Intermediate | 99.23 | 0.20 | 0.03 | 0.50 |
| Prime Western | 98.0 | 1.60 | 0.08 | ........ |
| Electrolytic zinc | 99.99 | Total impurities | | <0.01 |

**Iron**

| | Fe | C | Si | Mn | P | S |
|---|---|---|---|---|---|---|
| Pig iron | 91 75 | 3.50 | 2.75 | 0.85 | 1.10 | 0.045 |
| Steel | 99.12 | 0.45 | 0.05 | 0 37 | | 0.01 |
| Wrought iron | 97.0 | 0.10 | (Bulk of impurities as included slag) | | | |

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* Au and Ag in ounces per ton; all others in percentage.

operations. As a result the refining is done on the raw material rather than upon the metal. Crude bauxite, for example, is refined to yield pure $Al_2O_3$, which is then electrolyzed to give commercially pure aluminum. As a general rule, metals produced by pyrometallurgical processes must invariably be refined. Whether or not metals produced by hydrometallurgy need refining depends upon the methods of precipitation. Electrodeposited metals do not need refining (except for the fire-refining of cathode copper), but metals precipitated by chemical methods must be refined.

## METALLURGICAL SMOKE

The various gases produced in pyrometallurgical operations produce large volumes of smoke which consists of the gaseous products of combustion, together with dust and fume carried by the stream of gases. It is the dust and fume that impart color to smoke. All the gases are transparent and colorless.

**Gases in Smoke.**—The gases found in ordinary smokes are $N_2$, CO, $CO_2$, $O_2$, $SO_2$, and $H_2O$. Obviously the relative concentrations of the various gases will depend upon the source of the smoke. Nitrogen is the most abundant, forming from 60 to 87 per cent of the volume. $CO_2$ varies from 3 to 5 per cent in pyritic smelting to 12 to 15 per cent in reducing smelting. Copper converter smoke contains little $CO_2$. CO is unimportant except in iron blast-furnace gases. It forms about 25 to 30 per cent of the total volume of gas discharged from the iron blast furnace.

The most harmful gas in smoke is $SO_2$, and the problem of disposing of smoke laden with $SO_2$ is of considerable importance. In some states it has been decided by law that chimney gases containing more than 0.75 per cent of $SO_2$ are harmful to vegetation. Concentrations of $SO_3$ as low as 0.25 per cent are more harmful than higher concentrations of $SO_2$. Air containing 0.007 per cent $SO_2$ cannot be breathed, and as little as 0.00067 per cent $SO_2$ can be detected by its odor. Smoke from non-ferrous smelting usually contains about 3 per cent $SO_2$.

Many methods have been suggested for the removal of $SO_2$ from smoke, but only two have any important applications.

1. Make $H_2SO_4$ from the $SO_2$. For this purpose the gas should contain at least 9 per cent $SO_2$, and sulfuric acid is usually made from roaster gases because only these have a sufficiently high $SO_2$ content.

2. Dilute the gas with air by means of a high stack aided by fans. Since the rate of diffusion of any gas is proportional to the square

root of its molecular weight, $SO_2$ diffuses more slowly than lighter gases such as $O_2$ and $N_2$. Therefore, the $SO_2$ must be carried to a considerable height if it is to be sufficiently diluted before it can come in contact with vegetation.

**Fume.**—Certain metals and compounds in furnace charges vaporize or sublime, and then condense when the smoke is cooled to form a fume. The most common constituents of fumes are $H_2O$, $As_2O_3$, $Sb_2O_3$, $SnO_2$, $ZnO$, $PbO$, $Te$, $TeO_2$, $CuO$, $Au$, $Ag$, $PbSO_4$, and $H_2SO_4$ (the last formed by the combination of $SO_3$ and $H_2O$). Fume particles may be colloids, i.e., particles so small that they will not settle out of the smoke stream under the influence of gravity, and they will pass freely through filtering media.

Fumes should be avoided as far as possible (except in such processes as the treatment of zinciferous slags where fuming is actually used for extraction), both because they represent a loss of metal and because they may contain materials such as $As_2O_3$ which are harmful to animals and vegetation. Dense clouds of visible smoke also have a bad psychological effect even though the bulk of the fume may consist of condensed water particles.

**Dust.**—The term dust is applied to small solid particles which are mechanically carried in the smoke. Dust may include anything found in the furnace charge. Particles of unburned carbon or soot give the black color to some smokes. After fume has been condensed it is in the form of small solid or liquid particles, and a strict distinction between dust and fume is impossible. However, all the dust and the larger particles of fume may be removed by settling and filtering. Colloidal fume particles can be removed only by electrical precipitation.

**Recovery of Dust and Fume.**—The recovery of dust and fume from smelter smoke is desirable for two reasons: (1) to save the values that would otherwise be lost, and (2) to remove harmful substances. Of the following methods of recovery, the principal difference is that some processes recover finer particles than others. The proper choice of a method or combination of methods is a separate problem for each kind of smoke. Suspended particles (dust and fume) may be removed by:

1. Cooling the stream of smoke. This promotes the condensation of fume and decreases the velocity and hence the carrying power of the smoke stream. It may be effected in one of two ways: (*a*) by admitting cold air; (*b*) by using long flues and expansion chambers.
2. Filtration (in bag houses).
3. Electrical precipitation (in Cottrell treaters).

**Bag Houses.**—The use of a bag filter is one of the most common methods for removing dust and fume from smelter smoke. A bag house contains a number of cotton or woolen bags (from 3000 to 5000, as a rule) 18 inches in diameter and about 30 feet long. The bags are closed at the top, and the open ends are fastened to the intake pipes by means of thimbles. Smoke is forced to enter the bags at the bottom and pass out through the meshes of the cloth, leaving all solid particles except the fine fume inside the filtering bag. After the fume and dust have collected for a certain time, the bags are shaken to dislodge the fume, which is collected in hoppers below the

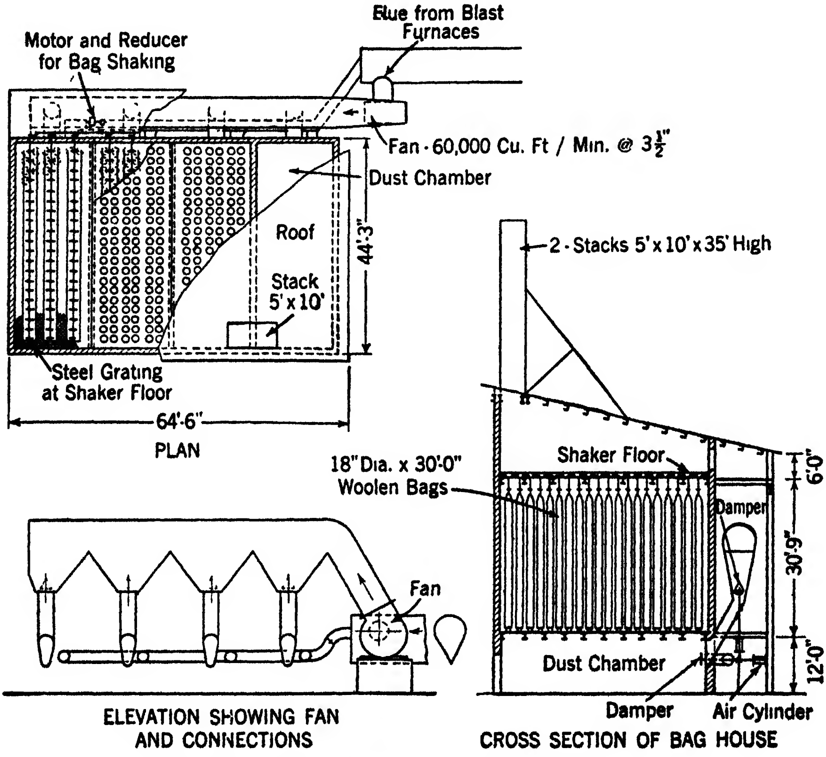
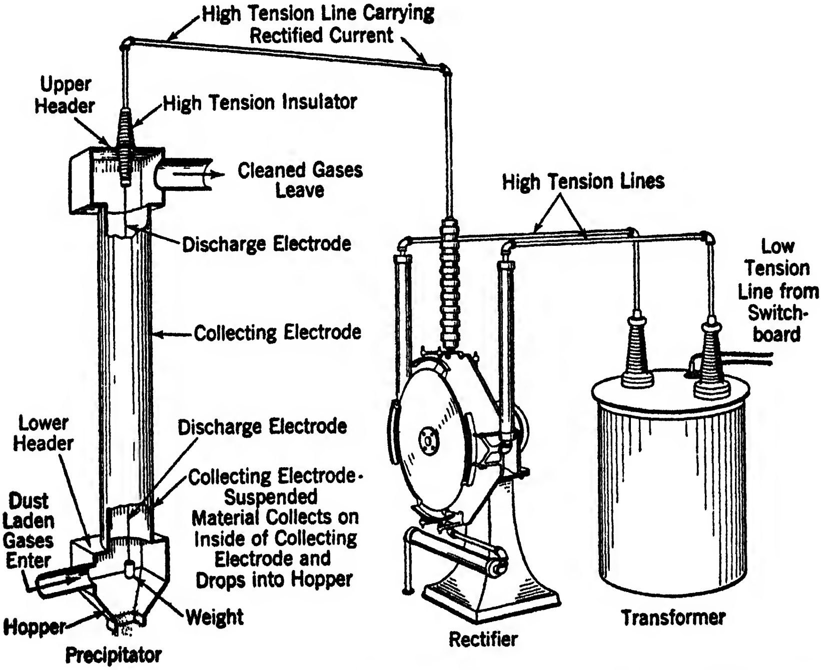


FIG. 13.—General Arrangement of a Bag House.

The resistance of these bags to the passage of gases is quite high, usually representing a head loss of 3 to 6 inches of water. High temperature and acid gases tend to destroy the cloth in the bags. Woolen bags are more resistant than cotton bags, but they are also more expensive. Gases containing free acid cannot be passed through bag houses because the acid rapidly attacks the bags.

**Cottrell Treaters.**—In the Cottrell treater for removal of fine fume, the particles are made to assume an electric charge and are then attracted to an oppositely charged plate. The fume builds up into a layer on the plate, and is dislodged at intervals by pounding on the plates. The material is then collected in hoppers below the Cottrell treater.



*(Courtesy Western Precipitation Company, Los Angeles)*

Fig. 14.—Diagram of a Cottrell Treater Unit.

Most Cottrell treaters consist of large rooms in which a number of vertical plates and chains, or pipes and wires, are placed. A static potential of about 75,000 volts is maintained between the chains and the neighboring plates (or between wires and the encircling pipes). The negative electrode usually has a small cross-sectional area (chain or wire); the positive electrode must have a relatively large area exposed (plate or pipe). The electrical discharge causes the fine particles of fume to assume a negative charge, and they are then attracted to the positive electrode where they adhere as a layer.

The electric "current" flowing between the two electrodes is carried on ionized gas molecules, and it is from these ionized molecules that the solid particles receive their charges. Smokes containing free $SO_3$ and $SO_2$ ("acid smokes") can be passed directly into the Cottrell treater, but smokes containing large amounts of $As_2O_3$ and other metallic oxide fume ("non-conducting," "basic") smokes must first be made *conducting*, either by mixing with a conducting smoke or by humidifying. Smoke is humidified by passing it through a spray chamber where it picks up some water vapor. The term "conducting" smoke refers to the properties of the deposit of fume formed on the positive electrode. A non-conducting smoke will form a non-conducting layer which insulates the electrode and seriously interferes with the flow of the current.

The Cottrell treater is very efficient in removing fume which is too fine to be retained in bag houses, and it is the only method that will recover free $SO_3$. Cottrell treaters are usually located at the base of the stack.

**Treatment of Fume and Dust.**—The treatment given the fume recovered in flues, bag houses, and Cottrell treaters depends upon the nature of the material in it. In many lead smelters the fume is charged on the Dwight-Lloyd machines. In copper smelters the fume often contains so much arsenic that it can be refined to produce commercial "white arsenic." Fume containing large amounts of ZnO is usually sent to a zinc leaching plant for treatment.

**Chimneys.**—The waste gases from pyrometallurgical operations are discharged into the atmosphere by means of *chimneys*, which are vertical flues open at the top and connected at the bottom with the flues which bring the smoke to the base of the chimney. In most large metallurgical plants there are one or more large chimneys, and each of these may discharge the smoke produced from several furnace operations.

The chimney or stack performs two functions: (1) it discharges smoke high into the atmosphere so that the harmful gases are well diluted before they can diffuse back to the earth; and (2) it produces a certain amount of (negative) pressure ("head" or "draft") which aids in drawing the waste gases from the furnaces through the flues, settling chambers, bag houses, etc.

Chimneys for metallurgical plants are commonly made of special radial fire brick faced with common brick, of concrete lined with a glazed tile, or of steel. The design depends upon a number of factors such as the size of the chimney and the temperature and corrosive nature of the gases which are to pass through it. The largest chimneys in the world are found in metallurgical plants, and these include such chimneys as the brick stack at Anaconda, Montana (585 feet high, 60 feet inside diameter), and the reinforced-concrete stack at Selby, California, which, with an inside diameter of 68 feet and a height of 605 feet 9 inches, is the tallest in the world.

When a chimney is in operation it is filled with hot gases which, because of thermal expansion, are lighter than the outside air. The *draft* or *head* of the chimney is due to the difference between the weight of a column of this hot gas and that of a column of outside air of the same dimensions. The theoretical head of a chimney is given by the formula:

$$h = H\left(\frac{T'}{Td} - 1\right) \tag{1}$$

where $h$ = head of the chimney measured in *feet of hot gas* (i.e., a column of gas of the same density and temperature as that in the chimney).

$H$ = height of chimney in feet.

$T'$ = average temperature (Kelvin) of the chimney gas.

$T$ = temperature (Kelvin) of the outside air.

$d$ = density of the chimney gas referred to air at the same temperature and pressure. $d$ ordinarily lies between 1.0 and 1.1.

The value for $h$ may be converted into other units thus:

$$h' = \frac{h \cdot d \cdot 273 \cdot 760}{T' \cdot P} \tag{2}$$

where $P$ is the barometric pressure in millimeters of mercury, gives the head ($h'$) in feet of air at standard conditions; and

$$h'' = \frac{h' \cdot 12}{773} \tag{3}$$

gives the head ($h''$) in inches of water gauge. This last unit is most commonly used in measuring head or draft, and 1 inch water gauge is the pressure which will support a column of water 1 inch high.

Formulas (1), (2), and (3) give the theoretical (*total* or *static*) head of the chimney. When gases are moving through the chimney, however, there is a head loss due to friction, and another head loss due to the velocity head of the moving gas in the chimney. The *available head* ($h_a$) which would be measured by a draft gauge at the breeching opening of an operating chimney is, therefore, always less than $h$, and a safe relation to assume in calculating available head is:

$$h_a = 0.80h \tag{4}$$

From formula (1) we note that the head should increase indefinitely with the height of the chimney and with the temperature of the stack gases. Actually, however, the friction loss becomes so great after the stack exceeds 150 feet in height that little or no additional head is gained by making the stack higher; the primary purpose of higher stacks is to diffuse the smoke farther from the earth. As to the temperature effect, it must be remembered that while higher stack temperatures give a greater head, the increase in temperature expands the gas so that a chimney actually discharges less gas by weight at high temperatures than at lower temperatures. The net result of these two effects is that the best performance of the chimney is obtained when $T' = 2T$, or when the temperature of the stack gases is approximately 300° C. Excessively hot gases also have a pronounced corrosive action on the lining of the chimney.

In some cases the chimney draft alone is sufficient to pull the gases into the chimney. In other cases where the smoke must pass through bag houses, long flues and settling chambers, etc., the natural (chimney) draft is insufficient and must be supplemented by fans or blowers.

## CHARGE CALCULATIONS

In all pyrometallurgical operations it is necessary that the operator adjust the feed to a furnace in such a way that the process will operate at maximum efficiency and that the furnace products will have the desired composition. This is particularly true of smelting furnaces.

Although the metal or matte produced in smelting is the most important product from the economic standpoint, from the point of view of the furnace operator the most important product is the slag. Metals and mattes usually melt at lower temperatures than slags; and, if the slag melts easily and runs freely, there will seldom be any trouble with the metal or matte. Most of the difficulties met in the operation of smelting furnaces result from the fact that the slag does not behave as it should, so that the problem of the furnace operator is to adjust his furnace charge to produce a slag which has the required characteristics.

The first thing to be decided is the composition of the slag to be produced. Past experience, coupled with information about the melting points and viscosity of various slags, will usually show that the operator must aim for a slag with a composition between certain definite limits. This is complicated by the fact that the operator is seldom free to choose his ores and fluxes—he must make his charge of whatever material is at hand and do it in such a way as to use up all the available material. In an iron furnace, for example, it may be necessary to use as much of a certain ore as possible, because it is cheaper than other, more desirable ores. If an iron ore is high in phosphorus, it will usually be necessary to mix it with enough low-phosphorus ore to keep the phosphorus content of the pig iron below a certain prescribed limit.

The operator must know how much fuel will be required by the furnace in smelting a ton of charge, which impurities will enter the matte or metal and which can be held in the slag, which substances will be lost in the stack gases, etc. When he has given consideration to all these questions, he is ready to calculate the composition of the charge to the furnace. The charge without the fuel is known as the *burden* of the furnace, and the combination of fuel and furnace is thought of as being the agent which smelts the burden. The process of selecting a furnace charge is often called burdening the furnace, and the phrase "lighten the burden" of a furnace means to increase the amount of fuel used per ton of burden.

Example 6 is a simple illustration of the principles involved in burdening an iron blast furnace.

### EXAMPLE 6

An iron blast furnace smelts an ore mixture having the following composition:

| | |
|---|---|
| Fe | 60% |
| $SiO_2$ | 10% |
| CaO | 4% |

The flux used contains 92 per cent $CaCO_3$ and 8 per cent $SiO_2$. The coke contains 90 per cent C, 7 per cent $SiO_2$, and 3 per cent CaO.

Required: The weight of ore, flux, and coke to be charged to yield 1000 kg. of pig iron containing 95 per cent Fe, 4 per cent C, and 1 per cent Si, and a slag having the ratio $SiO_2 : CaO = 1 : 2$, assuming that the furnace requires 950 kg. of coke per ton of pig iron.

Solution:

$1000 \times 0.95 = 950$ kg. Fe in pig

$\frac{950}{0.60} = 1582$ kg. ore required

$1000 \times 0.01 = 10$ kg. Si to pig

$10 \times \frac{60}{28} = 21.4$ kg. $SiO_2$ reduced to enter pig

$1582 \times 0.10 = 158.2$ kg. $SiO_2$ from ore

$950 \times 0.07 = 66.5$ kg. $SiO_2$ from coke

$1582 \times 0.04 = 63.3$ kg. CaO from ore

$950 \times 0.03 = 28.5$ kg. CaO from coke

Let $x$ = number of kilograms of flux required; then

$$92\%\ \mathrm{CaCO_3} = 92 \times \frac{56}{100} = 51.5\%\ \mathrm{CaO},$$

and $0.515x$ kg. = wt. of CaO in flux

and $0.08x$ kg. = wt. of $SiO_2$ in flux

$$\text{Hence } \frac{158.2 + 66.6 + 0.08x - 21.4}{63.3 + 28.5 + 0.515x} = \frac{1}{2}$$

$$\frac{203.4 + 0.08x}{91.8 + 0.515x} = \frac{1}{2}$$

$$406.8 + 0.16x = 91.8 + 0.515x$$

$$0.355x = 315$$

$$x = 887 \text{ kg. of flux}$$

and the charge will consist of

887 kg. flux
1582 kg. ore
950 kg. coke.

## THE HEAT BALANCE

In any pyrometallurgical process the sources and distribution of heat are of great importance in determining the performance of the operation. In a heat balance the various amounts of heat are listed in two columns. On the left-hand side are given the various items of heat supply, and on the right-hand side the items of heat distribution. In order to illustrate the principle involved, the following heat balance is given. The calculations necessary to obtain these data are not included here. Note that exothermic reactions contribute heat to

**Summary.—Heat Balance Sheet of Iron Blast Furnace***

| Heat Supplied | Pound Calories | % | Heat Distributed | Pound Calories | % |
|---|---|---|---|---|---|
| Combustion of coke... | 3,643,000 | 83.3 | Formation of pig iron | 37,000 | 0.8 |
| Heat in blast........ | 645,000 | 14.8 | Reduction of oxides | 1,882,000 | 43.1 |
| Formation of slag.... | 84,000 | 1.9 | Decomposition of carbonates | 175,000 | 4.0 |
| | ...... | .... | FeS → CaS | 14,000 | 0.3 |
| | ...... | ... | Evaporation of $H_2O$ | 93,000 | 2.1 |
| | ...... | .... | Decomposition of $H_2O$ | 235,000 | 5.4 |
| | ...... | .... | Heat in gases | 305,000 | 7.0 |
| | ...... | .... | Heat in pig iron | 332,000 | 7.6 |
| | ...... | .... | Heat in slag | 276,000 | 6.3 |
| | ...... | .... | Heat in cooling water | 186,000 | 4.3 |
| | ...... | .... | Loss by radiation, etc. | 837,000 | 19.1 |
| Total....... | 4,372,000 | 100.0 | Total....... | 4,372,000 | 100.0 |

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* Butts, Allison: A Textbook of Metallurgical Problems; McGraw-Hill Book Co., New York, 1932. Reprinted by permission.

the left-hand column. Heat absorbed in endothermic reactions is tabulated in the right-hand column.

**Efficiency of Furnace Operations.**—The efficiency of any furnace operation is the heat expended in doing useful work divided by the total heat input. The difficulty in calculating furnace efficiencies is that it is often hard to decide just what constitutes the useful work; for example, in the above heat balance we may decide that the heat in the gases, the heat lost in cooling water, and the heat loss by radiation are wasted. Then the useful heat is 3,044,000 pound calories, and the efficiency is $\frac{3{,}044{,}000}{4{,}372{,}000} = 69.6$ per cent. However, we might also assume (and very properly) that the furnace would not operate unless (1) it was water cooled, (2) the gases escaped at relatively high temperatures, and (3) the furnace was maintained at a high temperature with inevitable radiation losses. On this basis the efficiency of the furnace is 100 per cent.

The efficiency of an operation is commonly used only for such relatively simple processes as distillation and melting. For complex operations such as roasting or smelting, the heat balance is much more instructive.

## EXERCISES

1. A mixture of hydrogen and oxygen gases will remain indefinitely at room temperature without reacting; but, if heated, they will combine to form water with the liberation of a large amount of energy. Explain this apparent violation of Le Chatelier's principle.

2. Read the discussion on the smelting of the New Caledonia nickel ores in the "Handbook of Non-Ferrous Metallurgy" by Liddell, and explain why it was necessary to employ matte smelting on an ore which contained no sulfur.

3. Explain why certain non-ferrous smelter schedules pay a premium on the silica contained in an ore, while others pay for iron. Why is a premium for silica usually offset by a penalty on iron?

4. Find the weight and grade of a matte produced by smelting 100 pounds of ore containing 25 per cent pyrite and 25 per cent chalcopyrite.

5. In Fig. IV-26 showing the effect of impurities on the conductivity of copper, the curves indicate that the addition of small amounts of oxygen *increases* the conductivity while all other impurities decrease it. Explain.

6. What is the meaning of the expression "985 fine," as applied to silver bullion?

7. Write the chemical equations involved in the removal of Fe, Pb, Sn, Bi, S, and Te in the fire-refining of copper. What happens to each of the compounds formed?

8. Limestone containing 89 per cent $CaCO_3$ and 11 per cent $SiO_2$ is to be used as a flux in a process which forms a slag having the formula $CaSiO_3$. Calculate the percentage of free lime in the flux.

9. Calculate the percentage of free silica in a quartzite containing 86 per cent $SiO_2$ and 14 per cent $Fe_2O_3$. The slag ratio is $SiO_2 : FeO = 40 : 60$.

10. Determine the silicate degree of the following slags, and give their metallurgical names:

*a*. 20% CaO, 30% FeO, 40% $SiO_2$
*b*. $(Fe, Mn)_2 (Ca, Mg)Si_3O_9$
*c*. $SiO_2 : Al_2O_3 : CaO = 20:8:35$ (consider alumina as a base)

11. An ore contains

| | |
|---|---|
| $Fe_3O_4$ | 61.5% |
| $MnO_2$ | 2.0% |
| $SiO_2$ | 14.7% |
| $Al_2O_3$ | 4.3% |
| CaO | 3.6% |
| MgO | 6.8% |

In smelting, all the iron oxide and 60 per cent of the $MnO_2$ are reduced to metal. Determine the rational analysis of the slag formed.

12. Calculate the amount of heat necessary to form 1 kg. of the slag $CaO \cdot Al_2O_3 \cdot 2SiO_2$ from the constituent oxides and heat it to 1800° C. Melting point 1550°. Formation temperature 1700°.

Mean specific heats:

| | |
|---|---|
| $Al_2O_3$ | 0.226 |
| CaO | 0.201 |
| $SiO_2$ | 0.279 |

Heat of formation of slag = 20,000 Cal. per formula weight (from the constituent oxides).

| | |
|---|---|
| Heat of fusion of slag | 100 Cal. per kg. |
| Specific heat of liquid slag | 0.40 |

13. Calculate the mean specific heat of the solid slag given in problem 12 by Woestyn's rule.

14. With the aid of Fig. 7, write the chemical composition of 3 lime-alumina-silicate slags which have melting points below 1300° C.

15. Explain how the temperature of a converter may be controlled by the rate at which air is blown through the charge.

16. In blowing white metal to metallic copper in a converter, the converter must be tilted so that the tuyères are always above the level of the blister copper, for copper will immediately freeze in the tuyères when struck by cold air. Explain why this should be true of copper but not of the steel in the Bessemer converter.

17. During a Bessemer blow, the following substances are burned:

300 kg. of Si to $SiO_2$
540 kg. of C to CO
200 kg. of C to $CO_2$
200 kg. of Mn to MnO
600 kg. of Fe to FeO

The blast pressure (gauge) is 25,000 kg. per sq. m., and the single-action blowing engine makes 120 r.p.m. The internal diameter of the cylinder is 1.5 m., and the stroke is 2 m. long. The efficiency of air delivery is 88 per cent.

If the outside air is at standard conditions, how long is required for the complete blow?

18. Derive equation (1) in this chapter.

19. It is desired to construct a stack for a refining furnace. The stack must handle 5,000.000 cubic feet of gas (measured at standard conditions) per 24 hours. The density of the gas will be 1.03; temperature of gas entering chimney 500°.C.; temperature of gas leaving chimney 300° C. The velocity of gas in the stack shall average 15 feet per second. There shall be a draft gauge (available head) equal to 1.0 inch of water. Outside air 20° C., barometer 760 mm.

How high shall the stack be, and of what diameter?

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# CHAPTER XIV

# ELECTROMETALLURGY

## ELECTROLYSIS

**Second-Class Conductors.**—The flow of electricity through a first-class or metallic conductor is a directed flow of free electrons. *Electrolytes*, which are ionized solutions or fusions of acids, bases, or salts, are also said to "conduct" a current, but the mechanism is entirely different in these *second-class conductors.*

To illustrate the action of electrolysis, let us assume that we have a small direct-current dynamo with a wire attached to each terminal. Connected in one of these wires is an ammeter to indicate the magnitude of the current flowing. If the dynamo is started and the ends of the wires are connected, a current will flow through the circuit, the electrons moving from the negative terminal through the wires to the positive terminal (Fig. 1). If the connection between the wires is broken, the current will cease to flow, but the two terminals will still carry a positive and negative charge respectively. A potential difference will exist between them. If we now insert the two terminal wires into a water solution of NaCl, the ammeter will indicate a flow of current just as if the solution were a metallic conductor.

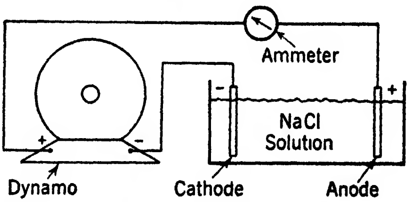


FIG. 1.—Diagram to Explain the Action of Electrolysis.

The crystal lattice of solid NaCl is made up of alternate sodium and chlorine ions. When these crystals are dissolved in water, most of the ions separate and move about as individual particles. There are millions of these ions swimming about in a cubic centimeter of ordinary salt solution. The total number of positive ions (sodium) is equal to the total number of negative ions (chlorine). Each ion carries a single charge, and the concentration of both kinds of ions is kept uniform throughout the solution by the random diffusion of the ions.

When the two terminal wires are dipped into the solution, each wire or electrode comes in contact with both positive and negative ions. The electrode carrying a positive charge (the anode) has a dearth of free electrons so that it immediately seizes upon available electrons, which are those carried by the $Cl^-$ ions in the immediate vicinity of the anode. The cathode, on the other hand, has an excess of free electrons. It gives these up to the only available "electron sink"—the positively charged $Na^+$ ions. If continued, this procedure would result in a concentration of $Na^+$ ions about the anode and of $Cl^-$ ions about the cathode (since the ions of opposite charge are neutralized in each case); but such a segregation of like charges is impossible in an electrolytic solution, and the tendency is immediately counteracted by the diffusion of both species of ions; $Cl^-$ ions move away from the cathode and toward the anode, and $Na^+$ ions move away from the anode and toward the cathode. As the diffusion replenishes the supply of ions at the two electrodes, a continuous neutralization takes place; and the net effect is the same as if a first-class conductor were connecting the two wires—a steady current flows through the ammeter in the external circuit.

Often the explanation is offered that the positively charged anode attracts the negatively charged $Cl^-$ ions because they have opposite charges, and that $Na^+$ ions are attracted to the cathode for the same reason. Although this statement is true, this electrostatic effect is felt for a distance of only a few atom diameters from the electrode. It has practically no effect on the "conduction" of the current. The phenomenon that accounts for the redistribution of ions in an electrolytic cell in such a way as to permit a continuous exchange of electrons at the electrodes is the natural diffusion of ions, atoms, and molecules, caused by thermal agitation.

Let us now consider what has happened to the neutralized ions. The $Cl^-$ ions which lose their charge become neutral Cl atoms. These atoms unite to form molecules of $Cl_2$. The chlorine formed in this way escapes as a gas by bubbling out of the solution immediately surrounding the anode. At the cathode, neutral Na atoms appear. If no secondary reaction took place, they would assemble into crystals and form a metallic deposit on the cathode. However, sodium reacts with water:

$$2Na + H_2O \rightarrow 2NaOH + H_2$$

gaseous hydrogen escapes about the cathode, and NaOH is formed in the *catholyte* (electrolyte surrounding the cathode. The electrolyte surrounding the anode is called the *anolyte*).

Before drawing conclusions about the laws of electrolysis, let us consider two other simple examples.

(*A*) If an aqueous solution of $CuSO_4$ is electrolyzed, the $Cu^{++}$ ions are neutralized at the cathode, and the copper atoms form a crystalline metallic deposit on the cathode. At the anode $SO_4^{--}$ ions are neutralized. The neutral $SO_4$ group cannot exist as such but immediately reacts with the surrounding water:

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

and the oxygen escapes as a gas.

The reaction which takes place at the anode depends upon the material of which the anode is composed. In the case given above, the anode is assumed to be insoluble (lead, for example). If the anode were a copper strip, the Cu atoms would unite with the $SO_4$ groups:

$$Cu + SO_4 \rightarrow CuSO_4$$

and the anode would corrode or dissolve to form $CuSO_4$. Another way of looking at the change is this: The anode carries a positive charge, since electrons are being continually pumped away from it by the dynamo, and accordingly some of the copper atoms at the surface are really ions, since they have lost electrons. When $SO_4^{--}$ ions come in contact with these $Cu^{++}$ ions, $CuSO_4$ is formed, and the $Cu^{++}$ ions are torn from the electrode and enter the solution.

Whether or not a given metal will corrode under certain conditions depends upon the solution pressure of the metal, the osmotic pressure of the ions of that metal in the solution, and the potential difference between the two electrodes.

Let us now write the chemical reactions involved in the electrolysis of $CuSO_4$. The symbol (*e*) denotes a single electron.

In all cases the reaction at the cathode is:

$$Cu^{++} + 2\,(e) \rightarrow Cu \qquad (a)$$

With an insoluble anode, the anodic reaction is:

$$2SO_4^{--} + 2H_2O - 4\,(e) \rightarrow 2H_2SO_4 + O_2 \qquad (b)$$

and the *net reaction* for the cell as obtained by adding (*a*) and (*b*) is:

$$2CuSO_4 + 2H_2O \rightarrow 2Cu + O_2 + 2H_2SO_4 \qquad (c)$$

With a soluble anode (copper), the anodic reaction is:

$$Cu - 2\,(e) \rightarrow Cu^{++} \qquad (d)$$

(*d*) is the reverse of (*a*), so that here there is no net reaction in the cell. Copper is transferred from the anode to the cathode, but there is no change in the composition of the electrolyte.

Finally, if a soluble anode of some other metal (zinc, for example) were used, the anodic reaction would be:

$$Zn - 2\,(e) \rightarrow Zn^{++} \qquad (e)$$

and the net cell reaction:

$$CuSO_4 + Zn \rightarrow ZnSO_4 + Cu \qquad (f)$$

Reaction (*f*) could not continue indefinitely, for after the concentration of $ZnSO_4$ in the electrolyte became high enough, Zn would begin to deposit at the cathode.

(*B*) Consider the reaction of fused NaCl electrolyzed between carbon electrodes. Melting the NaCl results in ionization just as the dissolution in water does. The cathodic reaction is:

$$Na^+ + (e) \rightarrow Na$$

and the anodic reaction:

$$2Cl^- - 2\,(e) \rightarrow Cl_2.$$

Sodium collects at the cathode as a metal (it is liquid at temperatures high enough to fuse NaCl), and the $Cl_2$ gas escapes at the anode.

**The Mechanism of Electrolysis.**—From the preceding illustrations some general rules governing electrolytic reactions may be summarized:

1. Electrolysis consists of two separate and equivalent chemical reactions. At the cathode reduction takes place, and at the anode oxidation.

2. There is no current passing through the electrolyte in the sense of a directed flow of free electrons. The motion of the ions which permits a continuous exchange of electrons is due to diffusion.

3. The change at the cathode must involve a transfer of the same number of electrons as does the change at the anode. The two reactions, therefore, are chemically equivalent. To illustrate, if 23.00 grams of sodium are deposited (Example *B*) at the cathode, 35.46 grams of chlorine will be liberated at the anode.

4. The reaction at anode and cathode may result in a net reaction involving a change in the composition of the electrolyte, or the anodic and cathodic reactions may balance each other so that there is no net

reaction. The latter case results in the transfer of metal from anode to cathode.

**Faraday's Law.**—The statement of this law gives the necessary and sufficient information for all problems concerning the current flowing in electrolysis. It is stated as follows: one gram-equivalent of material is chemically altered at each electrode for every 96,500 coulombs passed through an electrolytic cell.

**Electrical Units.**—An *ampere* is the unvarying electrical current that will deposit 0.00111800 gram of silver per second from silver nitrate solution. Conditions must be such that the current efficiency of deposition is 100 per cent; i.e., all the current must be depositing silver.

An *ohm* is the electrical resistance offered to an unvarying current by a column of mercury at 0° C., 14.4521 grams in mass, of constant cross-sectional area and 106.300 centimeters in length.

A *coulomb* is the quantity of electricity passing a given point in 1 second when a current of 1 ampere is flowing. The coulomb is also called an *ampere-second*. An *ampere-hour* is the quantity of electricity passing a given point in 1 hour when the current is 1 ampere. A *faraday* is 96,500 coulombs.

Current, resistance and voltage are connected by Ohm's law:

$$E = IR \tag{1}$$

where $I$ is the current in amperes, $R$ is the resistance in ohms, and $E$ is the potential in volts. The volt, therefore, is the electrical potential required to drive a current of 1 ampere through a resistance of 1 ohm. The definitions given for the ampere and ohm are their legal definitions. The definition of the volt depends upon the other two.

The *watt* is the unit of electrical power and is the power required to move a current of 1 ampere against a potential of 1 volt. If $W$ is in watts, $I$ in amperes, and $E$ in volts:

$$W = EI \tag{2}$$

and from Ohm's law

$$W = I^2R \tag{3}$$

where $R$ is the resistance in ohms.

A *kilowatt* equals 1000 watts.

The unit of electrical energy is the *joule* or *watt-second*. It may be defined as the energy liberated when 1 coulomb of electricity falls through a potential of 1 volt. If $Q$ is in coulombs, $V$ in joules, and $E$ in volts:

$$V = EQ \tag{4}$$

The *electrochemical equivalent* of an element is its gram-atomic weight divided by its valence.

Electrical power and energy units may be converted to other units by the following relations:

1 kilowatt = 1.341 horsepower.
1 watt = 44.24 foot-pounds per minute.
1 joule = 0.239 gram calorie.
1 kilowatt-hour = 860.3 kilogram calories.

### EXAMPLE 1

How much copper can be deposited from a $CuSO_4$ solution by a current of 30 amperes flowing for 8 hours?

Solution:

$$30 \times 3600 \times 8 = 864{,}000 \text{ coulombs (total)}$$

$$\frac{864{,}000}{96{,}500} = 8.95 \text{ faradays}$$

But 1 faraday will deposit $\frac{63.57}{2} = 31.8$ grams of Cu

$$8.95 \times 31\ 8 = 28\ 4 \text{ grams of Cu deposited.}$$

**Current Efficiency.**—There are no exceptions to Faraday's law of electrolysis, but it may happen that all the current does not deposit the metal desired. For example, if an electrolyte contains $CuSO_4$ and $H_2SO_4$, some $H^+$ ions may be neutralized at the cathode with the result that not all the current is employed in depositing copper. The current efficiency is defined as the ratio of the amount of metal deposited to the theoretical deposit. If, in Example 1, 26.3 grams of copper had actually been deposited, the current efficiency would be:

$$\frac{26.3}{28.4} \times 100 = 92.6\%$$

**Current Density.**—In any process by which a metal is deposited electrolytically, the current density determines the physical character of the deposit. Low current densities usually give fine-grained, adherent deposits; high current densities often produce coarse-grained deposits which adhere loosely to the cathode. Current density is a measure of the intensity of current at the surface of an electrode, and in most metallurgical operations it is expressed in amperes per square foot of cathode surface. If the anode and cathode have the same surface area, then the current density will be the same at each electrode.

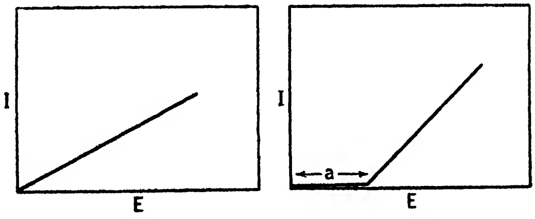
**The Resistance of Electrolytes.**—Although the current flowing in an electrolytic cell is not the same as the current flowing in a metallic conductor, the resistance of an electrolyte obeys the same law (Ohm's law) as the resistance of a first-class conductor with one exception, which will be discussed shortly. If $r$ denotes the resistance of a unit cube (cm.$^3$) of an electrolyte in ohms (specific resistivity), then the resistance of a layer of electrolyte $l$ centimeters in thickness and $s$ square centimeters in cross-section is

$$R = r\frac{l}{s} \tag{5}$$

When varying potentials are impressed across a metallic conductor, the current passing varies linearly with the voltage, since $R$ is constant and according to Ohm's law:

$$E = IR$$

The plot of current against voltage gives a straight line, as shown by Fig. 2*a*. If a current-voltage curve for an electrolytic cell composed of platinum electrodes immersed in $CuSO_4$ is plotted in the same way, a curve is obtained similar to the one shown in Fig. 2*b*. No appreciable current begins to flow until the voltage has reached the value denoted by the point *a* which represents the *decomposition potential* of $CuSO_4$.



*a.* First Class Conductor *b* Second Class Conductor (Insoluble Anode)

Fig. 2.—Conductivity Curves.

The net chemical reaction taking place in the cell is:

$$CuSO_4 + 2H_2O \rightarrow Cu + H_2SO_4 + \tfrac{1}{2}\,O_2 - 55{,}030 \text{ cal.}$$

and the term "$-55{,}030$ cal." means that the reaction is endothermic, and that 55,030 calories of heat are absorbed for every 63.57 grams of copper deposited.

From equation (4) we note that electrical energy $V$ is the product of voltage $E$ and quantity of electricity $Q$. Since 2 faradays or 193,000 coulombs are required to deposit 63.57 grams of copper (Faraday's law), and since the decomposition of $CuSO_4$ is accomplished by means of electrical energy.

$$jE \times 193{,}000 = 55{,}030$$

where $j$ is the factor used to convert joules to calories (0.239).

$$E = \frac{55{,}030}{193{,}000 \times 0.239} = 1.19 \text{ volts}$$

This value is the decomposition potential for this reaction, or the lowest voltage which will supply energy enough to carry out the decomposition. Since the quantity of electricity required for any reaction is fixed by Faraday's law, the electrical energy can be brought up to the proper amount only by increasing the voltage. In the example quoted, 1.19 volts must be impressed across the electrodes before any current will flow; after that the current will increase with the voltage in accordance with Ohm's law. Note that, if copper electrodes were used, the decomposition potential would be zero, because the anode would corrode, and there would be no net cell reaction. Consequently there would be no chemical absorption of energy.

In the Daniell cell the anode is zinc suspended in an anolyte of $ZnSO_4$ and a copper cathode is suspended in a $CuSO_4$ catholyte. The cell reaction is:

$$Zn + CuSO_4 \rightarrow Cu + ZnSO_4 + 53{,}410 \text{ cal.}$$

In this case the reaction is exothermic and gives off heat energy instead of absorbing it. Instead of a certain voltage being required to cause this reaction, it takes place of itself, and the cell generates electricity at a pressure of $E$ volts. To calculate $E$ proceed as before.

$$E = \frac{53{,}410}{193{,}000 \times 0.239} = 1.15 \text{ volts}$$

This equation may be generalized as

$$E = \frac{-\Delta H}{njF}\text{[1]} \tag{6}$$

where $E$ = decomposition potential in volts;
$\Delta H$ = heat of reaction in calories;
$n$ = valence change;
$j$ = 0.239;

and equation (6) reduces to:

$$E = \frac{-\Delta H}{23{,}060n} \tag{7}$$

which is *Thomson's rule.*

---

[1] Using now the convention that $\Delta H$ is negative for an exothermic reaction.

Thomson's rule is useful because its derivation throws light on the meaning of decomposition potentials and because it provides a method of calculating (approximately) the decomposition potential of a given reaction. Thomson's rule, however, is not always accurate for the reason that all the chemical energy need not be converted into electrical energy (as has been assumed), or vice versa. When the energy changes from one form to another, heat energy may be absorbed from or given up to the surroundings, and this is not taken into account by Thomson's rule. The correct expression which takes all factors into consideration is the *Gibbs-Helmholtz equation*:

$$E = \frac{-\Delta H}{njF} + T\frac{dE}{dT} \tag{8}$$

where $T$ is the absolute temperature. Unless the value of the temperature coefficient $\frac{dE}{dT}$ is known, the Gibbs-Helmholtz equation cannot be used for computation; however, for most metallurgical work Thomson's rule is sufficiently accurate. In some cases the term $T\frac{dE}{dT}$ is too large to be neglected, even for an approximation.

The chemical energy which appears as electrical energy is not strictly the heat of reaction but the free energy change, $\Delta F$, and $\Delta F$ and $E$ (voltage) are connected by the simple law

$$\Delta F = -n \times 23{,}074E \tag{9}$$

where $\Delta F$ is the free energy change in calories, and $E$ is the potential of the cell in volts. Equation (9) or its equivalent is used in deriving the Gibbs-Helmholtz equation.

**Overvoltage, Contact Potentials.**—In computing the total voltage, $E_T$, required for a given electrolytic operation, the following equation is used:

$$E_T = E_D + E_C + E_G + E_K$$

These symbols represent decomposition potential ($E_D$); voltage required to overcome the ohmic resistance of the electrolyte ($E_C$); overvoltage required to deposit a metal or liberate a gas ($E_G$); and contact voltage, or the voltage drop due to resistance of the electrode contacts ($E_K$). The values for $E_G$ and $E_K$ must be determined experimentally, but $E_D$ and $E_C$ may be calculated. The application of these quantities to a specific problem is illustrated in Example 2.

**Arrangement of Equipment.**—In large electrolytic plants such as those producing electrolytic copper, zinc, or lead, the electrolytic tank house contains a large number of tanks which serve as electrolytic cells. Each of these contains a number of cathodes and anodes spaced as closely as practicable, so that the electrolyte resistance will be a minimum. Arrangements are made so that all the cathodes or anodes in a given tank may be removed in a group (Fig. 3), usually by means of an overhead crane. In electrodeposition processes, insoluble anodes are used; and since these do not corrode, they do not have to be removed except at relatively long intervals. For electrolytic refining the anodes are cast from the impure metal which is to be refined. Cathodes are of two types, either of which may be used for refining or electrodeposition. The cathode may be a starting sheet of the same metal as that to be precipitated, or it may be of a different metal. Examples of the first type are the starting sheets of copper and lead used in the electrolysis of these two metals. These are cast (lead) or electrodeposited (copper) as thin sheets and are made of refined metal so that, when the cathode has been built up to its maximum

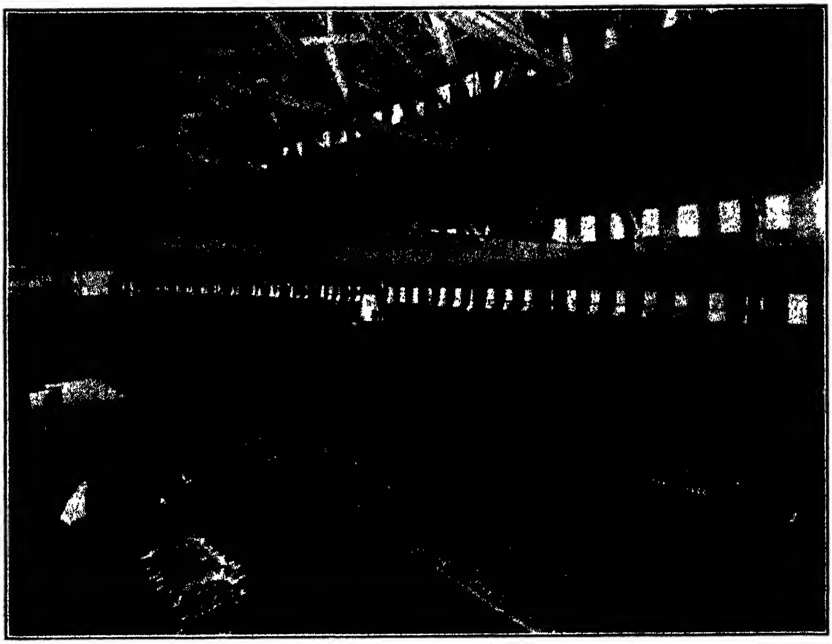


Fig. 3.—Tank Room in an Electrolytic Copper Refinery.

Note the two cranes for handling anodes and cathodes. In the foreground is a carload of anode scrap to be returned to the anode furnaces. Note the tapered bus-bars and the arrangement of cathodes and anodes in the tanks. The men working on top of the tanks are engaged in removing short circuits caused by irregular growths on the cathodes.

thickness, the entire cathode consists of refined metal which can then be melted down and cast. The use of aluminum cathodes in the electrolysis of zinc is an example of the second type of cathode, and in this case the sheets of deposited zinc must be stripped from the aluminum cathode before being melted and cast.

The electrodes in any one tank are connected in parallel (except in the series method of copper refining), and a group of tanks connected in series constitutes a circuit. The fact that the tanks in a given circuit are in series makes it possible to use standard electrical generators. The voltage drop in any tank may be only one or two volts, but by connecting the proper number of tanks in series, the total voltage drop can be brought to whatever figure is necessary for the generator used. Since the anodes and cathodes in a single tank are connected in parallel, the effect is the same as if each tank had only one large anode and one cathode; and the area of this hypothetical cathode would be the same as the total surface area (both sides) of the actual cathodes in one tank. Anodes and cathodes have lugs or ears from which they may be suspended in the tank, and one lug rests on a heavy copper conductor or bus-bar, which conducts the current. Figure 4 is a schematic diagram showing the electrical connections in an electrolytic tank.

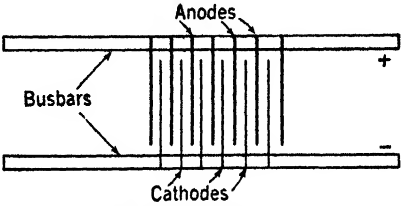


Fig. 4.—Diagram Showing the Arrangement of Anodes and Cathodes in an Electrolytic Cell.

In order to keep the composition of the electrolyte constant at all points in the system, it is circulated through the tanks. Usually a certain number of tanks are arranged in a *circulation cascade* so that the electrolyte flows from one tank to the next by gravity. After passing the last tank the electrolyte is pumped back into the head tank. In some cases it may be purified, heated, or sent through a leaching cycle before it returns to the electrolytic cells.

This discussion will aid in the understanding of Examples 2 and 3. The operating details of other electrolytic processes differ from these, as will be mentioned in a later section.

### Example 2

**The following data apply to an electrolytic extraction operation for producing copper. Electrolyte $CuSO_4$; cathode, copper sheets; lead anodes; average resistivity of electrolyte 5.6 ohms per cm.$^3$; electrodes 4.2 cm. apart; current den-**

sity 175 amperes per square meter; gas overvoltage at anode 0.48 volt; voltage drop cathode to bus-bar 0.06 volt, and anode to bus-bar 0.12 volt. Current efficiency 90 per cent; 1000 amperes current per tank.

Required:

(1) The voltage drop due to ohmic resistance of electrolyte.
(2) The decomposition voltage.
(3) Voltage drop anode to cathode.
(4) Voltage drop bus-bar to bus-bar.
(5) Weight of copper deposited per day per tank.
(6) Kilowatts used per tank.
(7) Kilowatt-hours per kilogram of copper deposited.

Solution:

$r = 5.6$, $l = 4.2$, $s = 10{,}000$ sq. cm. (1 sq. m.), and $I = 175$ amperes

$R = r\frac{l}{s} = 5.6 \times \frac{4.2}{10{,}000} = 0.00235$ ohm

$E_C = IR = 175 \times 0.00235 = 0.41$ volt (1)

The cell reaction is

$CuSO_4 + H_2O \rightarrow H_2SO_4 + Cu + \frac{1}{2}\ O_2 - 55{,}030$ Cal.

$E_D = \frac{55{,}030}{23{,}060 \times 2} = 1.19$ volts (2)

$(E_T - E_K) = E_C + E_D + E_G = 0.41 + 1.19 + 0.48 = 2.08$ volts (3)

$E_T = 2.08 + 0.06 + 0.12 = 2.26$ volts (4)

$\frac{0.90 \times 1000 \times 86{,}400}{96{,}500} \times \frac{63.6}{2} \times \frac{1}{1000} = 25.6$ kg. Cu per day per tank (5)

$2.26 \times 1000 = 2260$ watts $= 2.26$ kw. per tank (6)

$2.26 \times 24 = 54.2$ kw.-hr. per tank per day.

$\frac{54.2}{25.6} = 2.12$ kw.-hr. per kg. Cu (7)

### EXAMPLE 3

A copper refinery has 1080 tanks each containing 24 cathodes and 25 anodes. The cathode plates measure 40 by 30 inches (submerged area). Five 1200-kw. generators are used, each with a circuit of 216 tanks. Current density is 25 amperes per square foot, and the average distance from anode to cathode surface is 5 cm. Current efficiency 92 per cent. Voltage drop due to contacts and other losses is 40 per cent of the total voltage drop.

Required:

(1) Capacity of the plant.
(2) Increase in cathode thickness per day.
(3) Voltage absorbed per tank.
(4) Specific resistivity of the electrolyte.

Solution:

$\frac{2 \times 40 \times 30}{144} \times 24 = 400$ sq. ft. cathode surface per tank

$400 \times 25 = 10{,}000$ amperes per tank

$$\frac{63.6}{2 \times 96{,}500} \times 10{,}000 \times \frac{86{,}400}{1000} \times 1080 = 308{,}000 \text{ kg.}$$

$$308{,}000 \times 0.92 = 284{,}000 \text{ kg. per day} \quad (1)$$

$$\frac{284{,}000}{1080 \times 24} = 10.93 \text{ kg.} = 10{,}930 \text{ grams per cathode}$$

$$\frac{10{,}930}{8.7} = 1260 \text{ cc. per cathode}$$

$$40 \times 30 \times (2.54)^2 = 7750 \text{ sq. cm.} = \text{area of cathode (1 side)}$$

$$\frac{1260}{7750} = 0.163 \text{ cm. increase in thickness} \quad (2)$$

$$\frac{1{,}200{,}000}{10{,}000} = 120 \text{ volts drop per circuit}$$

$$\frac{120}{216} = 0.555 \text{ volts drop per tank} \quad (3)$$

$$0.555 \times 0.60 = 0.333 \text{ volts per tank drop due to resistance of electrolyte.}$$

$$I = \frac{25}{144 \times (2.54)^2} = 0.0269 \text{ ampere per cm.}^2$$

$$R = \frac{E}{I} = \frac{0.333}{0.0269} = 12.4 \text{ ohms}$$

$$r = R\frac{s}{l} = \frac{12.4 \times 1}{5} = 2.48 \text{ ohms per cm.}^3 \quad (4)$$

**Factors Affecting Electrolytic Resistance.**—The resistance of any electrolyte decreases as the number of ions per unit volume increases, and in order to keep the average resistance as nearly constant as possible, the metal is never completely precipitated from the electrolyte. There is always a certain amount of metal tied up in the electrolyte in any operation, and an attempt to remove it all would not only increase the resistance but would cause other dissolved metals to precipitate on the cathode. In many operations there is a certain amount of free acid in the electrolyte which is formed when a salt is decomposed, and the concentration of this acid in the electrolyte must be kept within certain limits. Small amounts of acid aid in reducing the resistance of the electrolyte; but if too much acid is present, it may cause a large loss of metal by chemical corrosion at the cathode. The matter of holding the metal content of the electrolyte above a certain limit applies particularly to electrodeposition. In refining processes the corrosion of the anode replaces the metal plated out on the cathode.

Since diffusion is the principal factor governing the resistance of an electrolyte, an increase in temperature (which speeds up the thermal movement of the ions), will cause a marked decrease in the resistance of an electrolyte. Electrolytes are sometimes heated for this reason; but the advantage gained by decreased resistance may be offset by the following disadvantages:

1. Cost of heating.
2. Evaporation loss.
3. Difficult working conditions caused by heat and humidity.
4. Increased chemical solution of electrodes by free acid in the electrolyte. Rapid corrosion of a soluble anode may cause the electrolyte to become too highly concentrated in the metal salt; corrosion of the cathode lowers the current efficiency.

**Plant Operation.**—In large electrolytic tank houses the principal operations are the removal of cathodes when they have received the proper deposit, stripping cathodes when necessary, replacing cathodes or starting sheets in the tanks, and removing the remnants of corroded anodes (in refining operations), and placing new anodes. Electrolytic deposits tend to form "trees" or accretions which sometimes grow large enough to cause a short circuit between an anode and cathode. The tanks must be inspected at regular intervals so that such accretions can be removed. Anode mud or slime collects in the bottom of electrolytic refining tanks, and this must be cleaned out from time to time.

**Intermediate Electrodes.**—If a metallic electrode is suspended between the anode and cathode in an electrolytic cell, it will conduct a current even though it is not connected to either of the principal electrodes. If we have an electrolytic tank containing a cathode at one end and an anode at the other, as shown by the diagram in Fig. 5, a potential gradient will exist throughout the length of the column of electrolyte between the two electrodes. Now if an intermediate electrode be inserted between the anode and cathode, a potential difference will also exist between the two faces of the intermediate electrode and a current will flow through it. Assume that the original cell consisted of copper electrodes in an electrolyte of $CuSO_4$, and that the intermediate electrode is also a copper strip. The face of the intermediate electrode closest to the anode will be negative with respect to the anode so that copper will dissolve from the anode and plate out on the adjacent side of the intermediate electrode. The other side of the intermediate electrode will be positive with respect to the

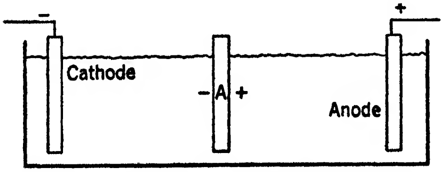


FIG. 5.—An Intermediate Electrode (*A*).

cathode, and copper will dissolve from the intermediate electrode and deposit on the cathode. The net result is that copper is being deposited on one side of the intermediate electrode and being dissolved from the other side. The only important use of intermediate electrodes in electrometallurgy is in the series system of copper refining.

**Behavior of Impurities in Electrolysis.**—In the refining of copper, the anode usually contains less than 0.5 per cent total impurities. This amount is too small to affect the voltage calculations. For such purposes it may be assumed that both anode and cathode consist of pure copper and that there is no chemical voltage (decomposition voltage). In the electrolytic parting of doré bullion (Thum and Moebius processes) the metallic impurities may amount to a considerable fraction of the anode, and the corrosion of such an anode usually produces or consumes a definite chemical voltage.

Impurities may enter the electrolyte in the leaching cycle in electrodeposition processes or be dissolved from the anode in refining. In a well-conducted operation, none of these should deposit on the cathode, and the small amount of impurity found in cathode deposits is usually due to mechanically entrained electrolyte or slime. The following general rules cover the principal facts about the behavior of impurities.

1. When an anode corrodes, impurities less noble than the principal metal will dissolve. The more noble impurities do not dissolve but drop to the bottom of the tank to form part of the anode mud. As an example, in the refining of copper, iron dissolves but gold and silver do not.

2. Some impurities form insoluble salts and are precipitated. If lead is dissolved in a sulfate solution, it precipitates as $PbSO_4$.

3. Dissolved impurities generally will not deposit on the cathode, if the necessary decomposition voltage for the reaction is less than the voltage drop between anode and cathode. The decomposition voltage of $AuCl_3$ is 0.39 volts, and the decomposition voltage of $CuCl_2$ is 1.36 volts. Consequently, gold can be plated from a chloride solution with a potential drop of, for example, 0.50 volt. Any dissolved copper will not deposit since the total voltage is well below 1.36 volts. If two metals form compounds which have approximately the same decomposition voltages, the metals can be plated simultaneously as an alloy.

4. The metals which deposit at the cathode are influenced by the law of mass action; all other things being equal, the metal whose ions are present in greatest amount is most likely to deposit. In refining, and in extraction processes where the leaching agent is regenerated,

the electrolyte remains in a closed circuit, and certain soluble impurities tend to build up to the point where they begin to deposit on the cathode. To keep the concentration of such impurities below the danger point, a certain fraction of the electrolyte is removed for purification. In copper-refining practice about 1 per cent of the total electrolyte is continuously being "bled" from the main circuit and replaced by purified electrolyte or fresh acid solution. The copper in the foul electrolyte may be removed by cementation, and this operation keeps such soluble impurities as Fe, Ni, Bi, As, and Sb from building up in the electrolytic circuit.

Fig. 6.—Section Through Copper Cathode Showing Starting Sheet.

Note that the starting sheet has smaller crystals than the remainder of the cathode. This is due to the fact that the starting sheet is formed by electrodeposition at a lower current density than is used in the refining tanks. The upper (straight) edge of the starting sheet is the edge which was next to the cathode when it was being made.

5. Properly conducted electrolytic refining or electrodeposition yields a very pure metal. In most cases electrolysis produces a metal of greater purity than that produced by any other method.

## APPLICATIONS OF ELECTROLYSIS

Following are brief descriptions of the more important electrolytic processes.

**Copper Refining (Multiple).**—Anodes are cast from fire-refined copper which contains gold and silver, for electrolytic refining of copper is not used unless there are precious metals in the copper. The cathodes are electrolytically deposited starting sheets of pure copper. The electrolyte consists of $CuSO_4$ and 12 per cent free acid.

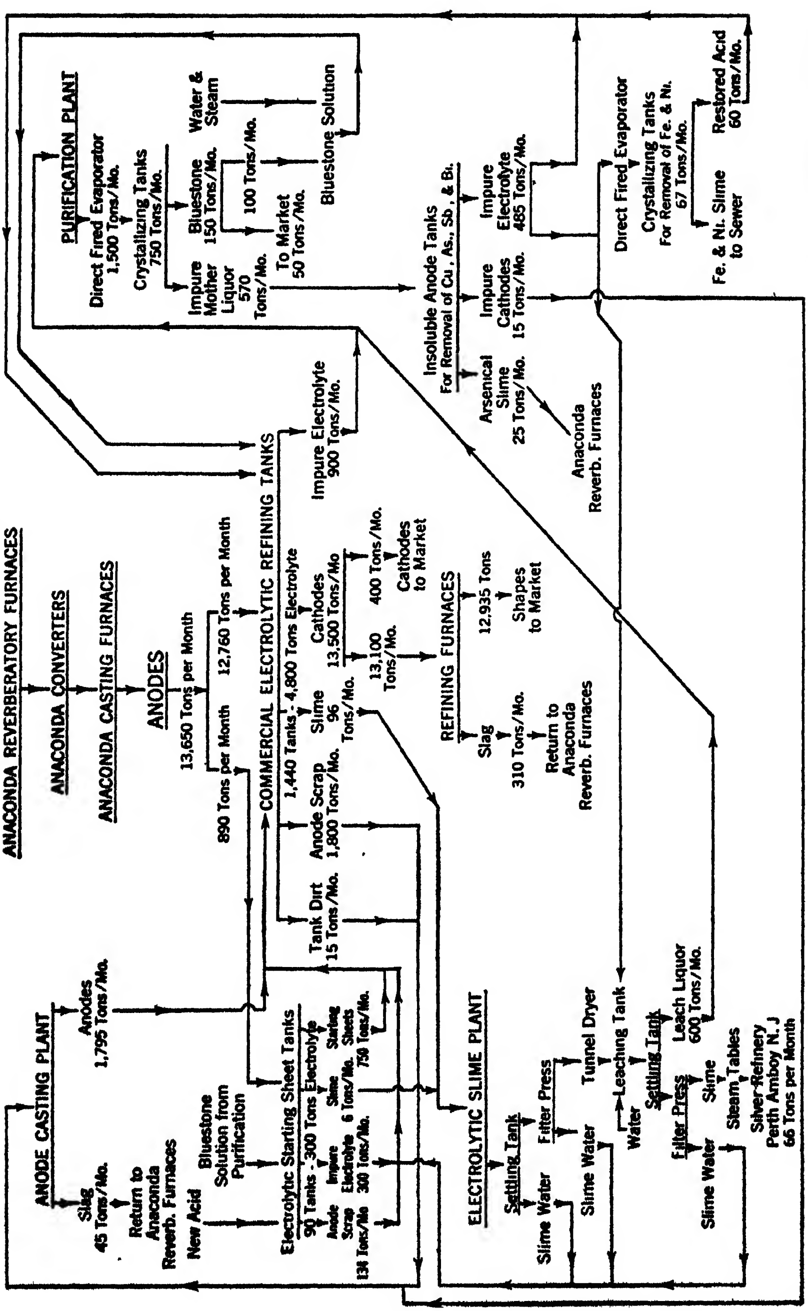
Current density is from 15 to 25 amperes per square foot. Gold, silver, and platinum, together with other impurities, are found in the anode mud. Electrolytic refining is the only method used to remove precious metals from copper bullion.

**Copper Refining (Series.)**—This resembles multiple refining in all respects except the arrangement of electrodes. The electrodes in any tank are in series, and only the two end electrodes are connected with the bus-bar or power line. The rest of the electrodes are intermediate electrodes. Impure copper is dissolved from one side and pure copper is deposited on the other. The process continues until all the copper has been thus refined and transported from one electrode to the next. The electrodes are made of rolled copper rather than cast copper, and there are no separate anodes and cathodes—each electrode serves as both anode and cathode.

**Copper Extraction.**—The anodes are insoluble (lead, antimonial lead, magnetite, silicon cast iron, copper silicide) and the cathodes are built up on pure copper starting sheets. The electrolyte consists of the copper-bearing solution from sulfuric acid leaching. In passing through the tank house the copper content decreases (for example, from 2.70 to 2.30 per cent) and the free $H_2SO_4$ content increases (2.20 to 2.45 per cent, for example). The electrodes in each tank are connected in parallel (multiple). In other respects the extraction process resembles electrolytic refining.

**Zinc Extraction.**—Electrolyte from the leaching of roasted zinc concentrates is agitated with zinc dust to neutralize the free acid and precipitate metallic impurities. The pure $ZnSO_4$ solution is then electrolyzed in tanks which resemble those used to produce electrolytic copper. Anodes are insoluble (usually lead), and cathodes are rolled aluminum sheets from which the deposited zinc is stripped. Electrolyte entering the tanks contains about 10 per cent zinc as sulfate and a trace of $H_2SO_4$. On leaving it contains about 2.5 per cent zinc and 11.5 per cent free acid. The current density may be about 30 amperes per square foot.

**Extraction of Aluminum.**—Purified and calcined $Al_2O_3$ obtained from the treatment of bauxite ore is dissolved in molten cryolite ($3NaF \cdot AlF_3$) and electrolyzed between carbon electrodes. The molten cryolite will dissolve about 25 per cent $Al_2O_3$ and fresh material is added as the electrolysis proceeds. Electrolysis is carried out in a graphite-lined furnace or pot, the lining serving as the cathode. Carbon anodes are inserted in the bath from the top. Aluminum is liberated at the cathode and oxygen at the anode. Since the aluminum is heavier than the electrolyte, it collects in the bottom of the tank



(*Courtesy Anaconda Copper Mining Company*)

FIG. 7.—Flowsheet of the Electrolytic Copper Refinery at Great Falls, Montana.

as molten metal and is tapped at regular intervals. The liberated oxygen consumes the anodes

$$2C + O_2 \rightarrow 2CO$$

so that they must be replaced regularly.

The temperature of the bath is about 900° C. The electric current must provide heat enough to keep the charge molten as well as perform the electrolysis. Current density will be about 650 to 750 amperes per square foot of cathode surface, and about 7 volts are required.

**Extraction of Magnesium.**—Magnesium is most commonly produced by electrolysis of fused, anhydrous magnesium chloride mixed with sodium or potassium chlorides. The electric current keeps the bath molten, and the electrolysis produces metallic magnesium and chlorine. Carbon anodes are used and iron cathodes. The fact that liquid magnesium is lighter than the electrolyte makes special design of the cells necessary to prevent oxidation of the liquid metal.

**Hoopes Refining Process.**—Although the light metals (aluminum and magnesium) are difficult to refine so that the refining is usually done on the raw material (bauxite or magnesium salts), the Hoopes process provides a way of electrolytically refining impure aluminum (usually alloys). The refining furnace has a carbon bottom which serves as the anode connection, and a number of carbon cathodes dipping into the bath from the top. The electrolyte is a solution of fused fluorides which has a specific gravity greater than that of pure aluminum but less than that of the alloy. Accordingly, the impure metal melts, and the molten pool of alloy on the bottom of the tank is the anode. The pure metal separates at the cathodes and forms a liquid layer above the electrolyte.

**The Betts Process.**—Impure lead may be cast into anodes (soluble) and refined by a process resembling the electrolytic refining of copper. The cathodes are thin sheets of pure lead formed by casting, and the electrolyte is an aqueous solution of lead fluosilicate ($PbSiF_6$) and fluosilicic acid ($H_2SiF_6$). Current density is from 14 to 16 amperes per square foot.

**The Hybinette Process.**—Treatment of copper-nickel mattes results in the formation of an impure copper-nickel alloy which is cast into anodes and refined electrolytically in a slightly acid sulfate solution. Anolyte and catholyte are kept separate by means of canvas sacks (diaphragms) surrounding the cathodes. The anodes dissolve uniformly, and the anolyte contains copper and nickel sulfates. This anolyte is run over shot nickel to cement out the copper, and the purified nickel sulfate solution enters the cathode compartment where nickel is deposited on the cathode.

**Electrolytic Refining of Doré Bullion.**—Doré bullion, which is essentially an alloy of silver and gold with lesser amounts of the base metals, may be refined by the Thum or Moebius processes. The anodes are doré bullion either held on a canvas-lined tray (Thum) or in canvas bags (Moebius). The cathode is the carbon bottom of the porcelain parting cell, and a granular deposit of silver is formed on it. The gold slime (containing the base metals and the platinum metals) is retained in the canvas diaphragms, and the deposited silver is melted down into bars. The electrolyte is a practically neutral aqueous solution of silver and copper nitrates.

**The Wohlwill Process.**—Practically pure gold (such as the metal made by melting and casting the slime from Thum or Moebius cells) may be refined by electrolyzing in an aqueous solution of $AuCl_3$ plus HCl. Anodes are impure gold, and cathode starting sheets are rolled from pure gold. The finished cathodes are fine gold which may be melted and cast into bars. Silver is recovered from the slime (AgCl), and the platinum metals concentrate in the electrolyte which must be treated at intervals to remove these metals as well as base-metal impurities.

**Electroplating.**—The electrolytic deposition of a surface coating of a metal upon a finished metallic object is called electroplating. The metal coating is applied either for ornamentation, protection against corrosion, or both; and the metal in the plating is nearly always a more expensive metal than that which composes the body of the object. Electroplating produces an object that has the surface properties of the expensive metal but which is not nearly as costly as an object made entirely of this metal.

In electrolytic refining and extraction the physical character of the deposit is of little importance so long as it is pure and is uniform enough to adhere to the cathode until it can be removed and melted down. Current efficiency, speed of deposition, and purity of deposit are the most important matters to be considered in electrolytic deposition and refining. In electroplating, however, the physical character of the deposit is all-important, and in many cases it is necessary to sacrifice speed and high current efficiency to assure the formation of an even, coherent deposit of metal. Electroplated coatings do not alloy to any extent with the underlying metal.

The chemical composition of the electrolyte is a very important factor in determining the character of the deposit formed, and hundreds of different plating baths have been used in the electroplating of various metals. Other factors which are of great importance are:

1. Metal deposited.
2. Nature of the article to be plated.
3. Current density.
4. Temperature.
5. Circulation of electrolyte.
6. Thickness of deposit.
7. Chemical products of the electrolysis—evolved gases and insoluble precipitates.
8. "Throwing power" of the electrolyte.

The effects of most of the above factors are more or less interdependent, and the proper conditions for electroplating constitute a separate problem for each metal. By the "throwing power" of an electrolyte is meant its ability to deposit a uniform coating in small depressions and crevices on the cathode. The throwing power of various electrolytes shows wide variation, and this factor is very important in the plating of intricate shapes.

Electroplating processes may utilize either soluble or insoluble anodes, and in addition to the pure metals, alloys such as brass may be deposited from suitable electrolytes. Hard metals such as chromium cannot be polished; but if the underlying metal is polished previously, the chrome plate will retain this polish, if a thin coating is used. Thick coatings always tend to become rough and irregular. The following data on the common methods used in electroplating give some idea of the variety of factors which must be considered:

1. Nickel may be plated from nickel ammonium sulfate; nickel sulfate + ammonium chloride; nickel sulfate + sodium citrate + nickel sulfate + ammonium tartrate + tannin; and other solutions. The current density used should be about 0.4 ampere per square decimeter (100 sq. cm.) of cathode surface.

2. Silver is commonly plated from a solution of the double potassium silver cyanide at a current density of about 0.3 ampere per square decimeter.

3. Platinum may be deposited from a solution of platinum chloride containing ammonium phosphate and sodium phosphate; also from platinic chloride solution in citric acid. Current density should be about 1 ampere per square decimeter.

4. Brass may be deposited electrolytically by using a brass anode

in a solution of the soluble double cyanides of potassium and copper, and potassium and zinc.

The principal metals used in electroplating in the approximate order of their importance are nickel, silver, chromium, copper, zinc, gold, cadmium, iron, lead, cobalt, tungsten, and rhodium. Of the alloys, brass is most commonly used in this connection.

Sometimes it is desired to form a shell of metal which corresponds to the outline of some solid object. This process is called *electroforming* and includes *electrotyping.*

## ELECTROTHERMAL PROCESSES

Electric heat is used in a great many cases for smelting, refining, and alloying; and the heating may be done either by resistance or by arcing. Electric heat has many advantages over fuel heating. It permits accurate control of temperature; oxidizing, reducing, or neutral furnace conditions can be maintained at will; and temperatures ranging from a few degrees above room temperature up to 3500° C. can be maintained and controlled. Practically the only disadvantage of electrothermic metallurgy is the high cost of electric power, which restricts the use of electric furnaces largely to the production of quality alloys. At the present time electric heating cannot compete with fuel heating in tonnage processes—at least, not in this country.

The production of electrical heat is based on the fact that the "power loss" or "energy loss" in any electrical circuit appears as heat which is given up to the surroundings. Since from equation (2)

$$W = EI$$

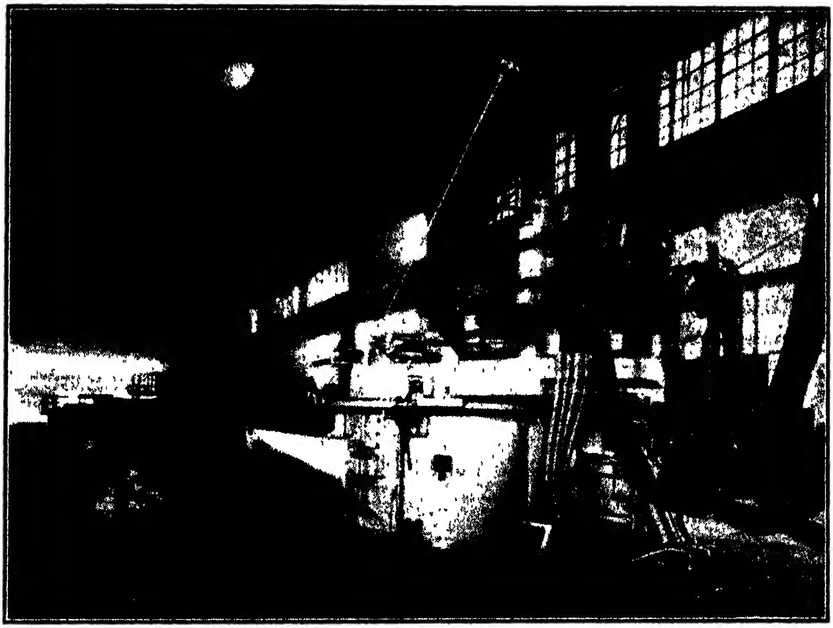
and from equation (3)

$$W = I^2R$$

it follows that the heating current should pass through materials of high resistance, and that currents of heavy amperage should be used, since the energy converted into heat is proportional to the square of the current.

Electric furnaces are of two principal types: (1) those which are heated by means of resistance wire through which the current passes, and (2) high-temperature electric furnaces in which the heat is generated by an arc between two carbon electrodes, by an arc between the charge and one carbon electrode, by the resistance offered by the charge itself to a current, or by currents induced in the charge or container.

Furnaces wound with resistance wire are generally muffle or pot furnaces, and are widely used in alloying and heat-treating operations, because electrical heating of this type permits accurate and positive control of furnace temperatures. These furnaces cannot be used for temperatures above 1000° C. because no commercial resistance wire will stand higher temperatures than this.



*(Courtesy The International Nickel Company, Inc., New York)*

Fig. 8.—The Lectromelt Furnace.

*(Pittsburgh Lectromelt Furnace Corporation)*

High-temperature electric furnaces are used principally in the refining and alloying of high-grade steels and cast irons. They are also used in some foreign countries (Norway, Japan) as iron-smelting furnaces. Some of the most common electric furnaces of this type are:

1. *Induction furnaces.* In this type of furnace, the liquid metal being refined is contained in an annular ring which is essentially the secondary coil—of only one turn—of a transformer. The primary coil has a large number of turns and is wound about the exterior of the furnace. An alternating current in the primary coil induces a heavy current in the secondary coil, and the resistance offered to the passage of the secondary current generates the required heat. In some

high-frequency induction furnaces, a graphite crucible which contains the metal serves as the secondary coil.

2. *Direct arc furnaces.* A heavy current arcs between a carbon electrode and the bath which serves as the other electrode, and the heat generated in this way serves to heat the charge.

3. *Indirect arc furnaces.* An arc is formed by two carbon electrodes placed above the bath, and the heat from the arc is radiated upon the bath.

4. *Combined arc and resistance furnaces.* These furnaces contain two electrodes above the bath, but they dip into the bath (usually into the slag covering above the metal), and the heat is due partly to arcing and partly to the resistance offered by the liquid slag.

Electric furnaces are often made so that they can be tilted to pour out molten slag or metal. One feature of electric furnaces is that their thermal efficiency is quite high, owing to the fact that the principal sources of heat loss are radiation and conduction only. No gaseous products of combustion are formed to carry off large quantities of sensible heat, as necessarily happens in all fuel furnaces.

The chemistry involved in smelting or refining in electric furnaces is no different from that involved in equivalent processes using fuel furnaces, except that there are some reactions which take place only in electric furnaces, because these furnaces can produce much higher temperatures than fuel furnaces.

## EXERCISES

1. How would you define the power efficiency of an electrolytic operation using insoluble anodes? Why would the term "power efficiency" have no meaning if applied to a process using soluble anodes such as the copper anodes used in copper refining?

2. Calculate the thickness of chromium plating deposited in 30 minutes at a current density of 200 amperes per square foot and a current efficiency of 16 per cent. Chromium has a valence of 6 in the plating solution.

3. Why is cementation superior to electrodeposition for "stripping" a solution (removing all the dissolved metal)?

4. Silver (also other metals) is often plated from a cyanide solution in which the silver is in the form of a complex salt such as $NaAg(CN)_2$. Write the complete ionization equation for this salt. Is the bulk of the silver in the form of positive or negative ions? Is the silver plated on the anode or the cathode? Suggest reasons why such a salt should yield a smoother deposit of metal than a silver nitrate solution.

5. If the Daniell cell ($Zn — ZnSO_4 — CuSO_4 — Cu$) has an e.m.f. of 1.0960 volt at 0° C. and 1.0961 volt at 3° C., calculate the heat of the cell reaction by means of the Gibbs-Helmholtz equation. Write the chemical equation and calculate the heat of the reaction from the heats of formation in dilute solution of the compounds concerned.

6. Assuming that the resistance of the electrolyte, overvoltage, etc., are the same in the two cases, which would produce more copper per kilowatt-hour—electrolytic extraction or electrolytic refining? Explain.

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# CHAPTER XV

## SAMPLING AND RELATED TOPICS

### SAMPLING

In all metallurgical processes it is absolutely necessary that the operator know at all times the chemical composition of the material with which he is working. This applies to all the materials involved, whether they be ores, concentrates, copper anodes, gold bullion, alloy steel, or flue dust. The required analysis is obtained by ordinary chemical methods or by the fire assay; but since it is obviously impossible to submit the whole quantity of material to the process of analysis, it becomes necessary to select a portion of the material for analysis in such a way that its composition will represent the average composition of the entire bulk. Such a selected portion is a *sample,* and the art of properly selecting such a sample is called *sampling.* The purchase price of a 100-ton lot of gold ore, for example, may be based on the assay of a 15-gram sample.

Selection of a proper sample depends on a great many factors: the physical state of the material, its moisture content, presence of "metallics" (particles of metal such as gold) in ores, the value of the material, and any number of similar considerations. A few rules for sampling in general are:

1. Take samples frequently; that is, a large number of small samples is much better than a few large samples.
2. Mix thoroughly before the removal of each sample.
3. Crush progressively; that is, reduce the size of the particles proportionally as the size of the sample decreases. The rule is to have the pieces so small that if the largest piece of the richest material were thrown from the sample into the reject, or vice versa, the final result would not be affected.

TABLE 1

PERMISSIBLE MINIMUM WEIGHTS OF SAMPLES OF ORDINARY ORES

| Diameter of Largest Particle, Inches | Minimum Weight of Sample, Pounds |
|---|---|
| 1/25 | 1/16 |
| 1/12 | 1/2 |
| 1/6 | 4 |
| 5/16 | 32 |
| 5/8 | 256 |
| 1 1/4 | 2,048 (1 ton) |

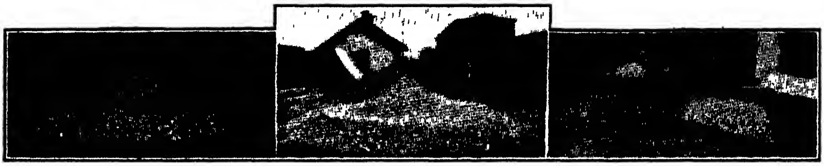
The accuracy of sampling should be comparable with the accuracy obtainable by the analyst. Conversely, no assay is any better than the sample, and a complete report on a small sample means nothing unless the sample has been carefully chosen. People have often been misled by the assay report of a few hand-picked specimens of high-grade ore. The final test of good sampling is the fact that two or more independently chosen samples of the same material will check within the limits of analytical error, if the samples are truly representative. Whenever the value of a substance warrants the expense, two or more independent samples should be sent to different analysts.

**Sampling of Ores and Concentrates.**—Following is an outline of the commoner methods of sampling ores, concentrates, and tailings:

*A. Hand sampling.*

1. *Grab sampling.* This is the least accurate of common sampling methods, yet it is the cheapest and most rapid. By this method small quantities of material are chosen at random from different spots in the large bulk, and these are thrown together to form the base for the final sample. Grab sampling is often used on large piles of ore, or upon tailing or slag dumps; sometimes it is used as a rough check on a sample obtained by more precise methods. If the ore to be sampled is high-grade and spotty, or if the sampler is inexperienced or careless, this method may prove worse than useless.
2. *Trench or channel sampling.* This is merely a slight refinement of grab sampling. The material to be sampled is spread out flat, channeled in one direction with a shovel, and the material for the sample taken at regular intervals along the channel. The procedure is repeated with several other channels in different directions until a sample of the proper size has been secured.
3. *Fractional selection.* When ore is being shoveled out of a railroad car, every fifth or tenth shovelful may be taken for a sample; this is an example of sampling by fractional selection. On large lots of low-grade ores one carload out of every five or ten is taken as the sample. The principle of fractional selection is on the basis of many sampling devices such as the split shovel or the Jones riffle.
4. *Coning and quartering.* This is an old Cornish method which is often used in sampling small quantities (50 pounds to several tons) of ore. The ore is first heaped into a uniform cone by placing each shovelful squarely on the vertex of the cone. After the cone is completed, the operator spreads it into a circular layer of uniform thickness by working around it and removing small shovelfuls from the top and spreading them near the edge. After the layer has been made, it is divided radially into four equal quarters and two opposite quarters are taken as the sample. The portion chosen as the sample may again be coned and quartered, and the process continued until a sample of the proper size has been secured. Two boards fastened in the form of a cross will be found convenient for quartering the pile of ore.

5. *Pipe sampling.* This method consists in running a pipe or grooved bar into the material to be sampled and withdrawing it with a sample in the hole or groove. The process is repeated at a large number of points on the surface of the material, and the many small samples are combined to make the final sample. This method applies only to finely divided substances and is commonly used in sampling carloads of flue dust, concentrates, metallic precipitates, and similar materials. The auger sampler is operated in a similar manner, and the "thief" used in sampling oils and other liquids is a type of pipe sampler.



(*From U. S. Bureau of Mines Technical Paper No. 86: Ore Sampling Conditions in the West. Reprinted from a Textbook of Fire Assaying, by Edward E. Bugbee, John Wiley and Sons, Inc., New York, 1922*)

FIG. 1.—Coning and Quartering.

*B. Mechanical sampling.* Mechanical sampling is very widely used in mills and concentrators in the sampling of large quantities of ore, concentrate, or tailing. Any mechanical method of sampling requires a movement of material, and the principle of the mechanical sampling device is that it systematically removes a portion of the stream of material for a sample. Mechanical samplers are not suited for the sampling of all types of metallurgical products — hand sampling is used practically always except for sampling large amounts of ores or such products of milling operations as concentrates, middlings, or tailings.

Mechanical sampling may be done in one of two ways. In a continuous process, a pipe or similar device is placed in the path of the moving ore (for example, as it discharges from a crusher), so that a certain portion of the stream is continuously deflected into a sample bin; in the intermittent process a moving machine diverts the entire cross-section into the sample bin at regular intervals.

The *whistle-pipe sampler* and the *bank* or *combination riffle* are the most common stationary (continuous) sampling devices, and the method of their operation may be seen in Fig. 2. Although these samplers are mechanically simple, they are not as accurate or reliable as the moving mechanical samplers, and are no longer used to any considerable extent.

Moving mechanical samplers are designed so that a sample cutter moves through the stream of ore at regular intervals and deflects a portion of the ore into a sample chute or sample bin. The *Snyder sampler* consists of a cast-iron plate revolving in a vertical plane on a horizontal axis, and having an inclined sample spout passing through the flange. The ore to be sampled comes to the sampler by way of an inclined chute and impinges upon the flange of the sampling disk. Whenever the sample spout comes in line with the ore stream, the ore passes through the plate and into the sample; at all other times the ore is deflected from the plate and drops into the reject. Generally, the sampler makes from 10 to 30 revolutions per minute, and the size of the cut (generally one-fifth) depends upon the width of the sample spout.

The *Vezin sampler* is made in several types: the sample cutters revolve about a vertical axis, and pass under the delivery spout. The sample passes through the central spout in the sampler and the reject falls outside Vezin samplers usually make from 10 to 40 revolutions per minute and cut from 5 to 20 per cent of the stream.

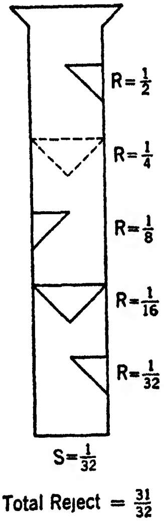
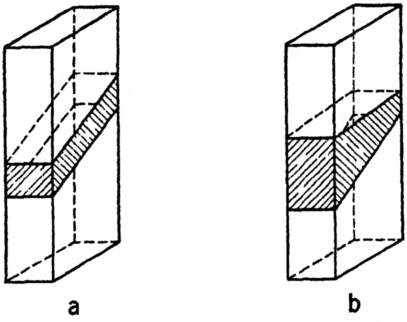


Fig. 2—Whistle-Pipe Sampler.



*a*—Correct *b*—Incorrect

Fig 3.—Cuts Taken by Moving Sample Cutters

The *Brunton oscillating sampler* consists of an oscillating divider swinging back and forth in a vertical plane beneath the feed spout. This cutter or divider is suspended on a horizontal shaft and swings through a 120° arc. The size of the cut made by a Brunton sampler can be changed by changing the speed of the cutter. With the Vezin and Snyder samplers (sector samplers), the cut made by the sampler cannot be varied except by changing the cutter used.

In all moving mechanical samplers the cutter must be so designed that it cuts the same amount from all portions of the stream; and if the stream of ore to be sampled is regarded as a rectangular ribbon, then the sample cut should be in the form of a parallelepiped (Fig. 3).

When ore falls freely or slides through an inclined chute, it generally shows segregation with respect to particle size; i.e., the coarse pieces are thrown farther than the fine, or the coarse material tends to ride on top. Now, the valuable minerals (sulfides, oxides) generally break more readily than gangue minerals (quartz, siderite, silicates), so that the fines usually show a higher assay value than the coarse material. These facts account for the fundamental defect of all continuous or stationary samplers. A stream of ore is seldom uniform throughout its cross-section, and samples taken by such devices as single splitters or whistle-pipe samplers have a tendency to produce a systematic error in the sample, so that the sample consistently shows either a higher or lower value than the ore actually has.

On the other hand, the variation in the composition of an ore stream throughout its cross-section does not affect the accuracy of a sample taken with a well-designed moving sample cutter. The source of error in this case is the variation in composition throughout the length of the ribbon of ore. Errors of this type, however, tend to be compensating rather than systematic, and the accuracy of the sampling operation may be increased by increasing the frequency of the sample cutter (number of cuts made per minute).

**Errors in Ore Sampling.**—The major source of error of all hand-sampling operations is the personal equation, and many of the discrepancies found in samples cut by hand are due to the carelessness, ignorance, or dishonesty of the operator. In many ores the "high-grade" is easily distinguishable, and for most men (depending upon their psychological trends and personal interest in the sample) the tendency is to include either too little or too much of the high-grade ore in the sample. The same statement applies to the selection of fine and coarse material. Many inexperienced samplers are prone to regard the proper precautions as unnecessary. As a result they are careless about such details as coning and quartering carefully; taking every fifth or tenth shovelful, and no more or less, when unloading a car; or mixing material thoroughly before cutting the sample. Of course, there is no limit to the amount of "doctoring" that can be done if the sampler is dishonest. Often the operator can manipulate the sample in such a way that the average observer would not suspect anything; for example, since the coarse particles tend to segregate near the outside of a cone, by "drawing the center" either toward the sample or the reject in coning and quartering, the sampler can produce a sample which is either richer or poorer than the true sample. Unintentional "drawing" of the center in the coning operation may be avoided by placing an upright stick in the center to indicate the spot where each shovelful of ore should be placed.

In mechanical samplers the personal equation is largely eliminated, and a well-designed moving mechanical sampler in good condition will generally produce a very accurate sample. However, if the cutter edges are worn or bent, if the ore chutes are partially blocked, or if ore "hangs up" at any point in the sampling system, the sample delivered will probably be incorrect. The fact that a sample is cut by mechanical means is not always a guarantee of its accuracy, for even the best mechanical sampler can be so manipulated that it will deliver a false sample.

Mill products such as tailings and concentrates are ordinarily more easily sampled than raw ore, principally because the milling operations yield products which are relatively uniform both with respect to assay values and particle size. It may be necessary to make an initial sample cut of one-fifth on crude ore, while on well-mixed, low-grade tailings a sample cut of one-five-thousandth may be satisfactory.

**Pulp Sampling.**—A suspension of solid material in water is called a *pulp;* the word "pulp" is also applied to the finely divided dry material which represents the last step in the reduction of a large sample. It is from this assay pulp that the material for the fire or wet assay is weighed out. The question of sampling pulps applies, of course, to the sampling of solid-liquid mixtures.

If the pulp is thoroughly agitated, a grab or dip sample will give a fair representation of the mixture. If the pulp is in a large tank or thickener, some type of pipe sampler or "thief" may be used to advantage, and specially designed devices permit the sampling of the pulp at various depths. If the pulp is flowing in a launder, it is possible to use a mechanical sampling device which will cut a sample from the stream at regular intervals (*vide* Fig. IX-16).

**Sampling of Liquids.**—The sampling of liquids is relatively simple. A well-mixed liquid is so homogeneous that a small grab or dip sample taken from any part of the bulk constitutes an accurate sample of the material. In the case of liquid metals, the sample is taken in a small ladle and poured into a mold where it solidifies into a sample bar. In other cases, the liquid sample is "shotted," or poured into cold water, and the resulting metal shot is taken as the sample. The ladle must be heated to the temperature of the molten metal before the sample is withdrawn, or a skull of frozen metal will remain in the ladle. Since in most alloys some of the constituents segregate on freezing, the separation of the solid metal in the skull will alter the composition of the sample. Liquid lead bullion is often sampled by removing small "gum-drop" samples, especially when the precious metals are to be determined. The molds are of such a size that the gum-drop sample can be cupelled directly after weighing. Liquid metal flowing from a furnace may be sampled by shotting directly—metal from the stream is batted into a container of water by means of a wooden paddle. The shot or pellets solidify so rapidly that there is little opportunity for segregation, and the pellets so formed will represent a fair sample of the metal.

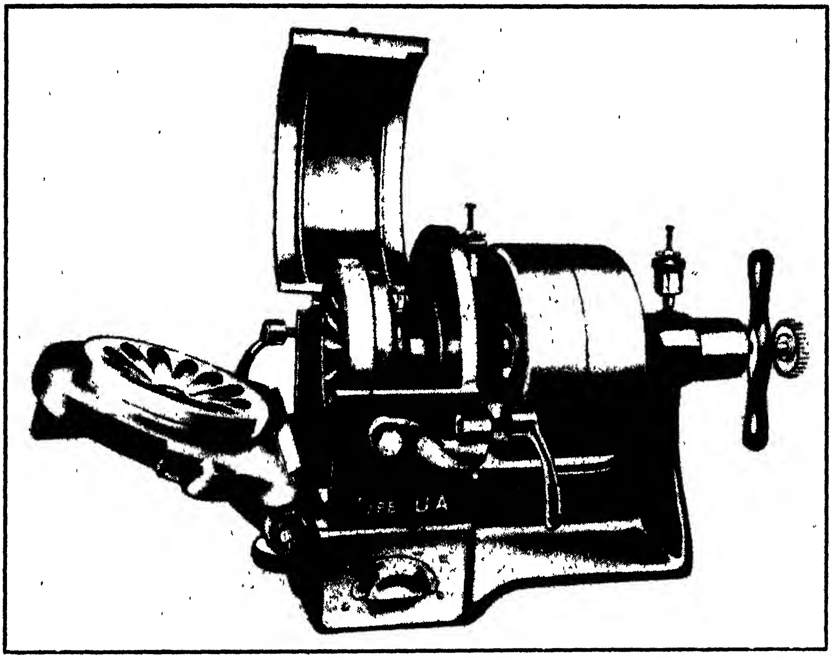
**Sampling of Gases.**—The sampling of gas very often presents many difficulties in spite of the fact that gaseous substances diffuse readily and a mixture of gases rapidly attains a homogeneous composition. A grab sample of gas in a quiescent state gives good results; but most gases must be sampled while in motion, and the temperature, pressure, velocity, and composition of a moving gas all change from time to time and from place to place in the conduit. The sampling of gases becomes a separate problem for almost every type of flue or conduit, and many special devices have been employed to sample moving gases. In general, the following rules apply:

1. Take small samples at frequent intervals.
2. Sample a large number of points over the entire cross-section of the stream of gas.
3. Use a sampling device that will not interfere too much with the normal flow of the gases.

**Sampling of Solid Metals.**—Most metals and alloys cannot be crushed, and the sample from a solid metal must be obtained by punching, filing, sawing, drilling, or chipping. The filings, chips, borings, etc., are taken as the sample. Owing to the segregation that takes place when alloys solidify, care must be taken that the sample includes a representative portion of the metal. In the case of a bar this is best done by making several cuts across the entire cross-section of the bar, since the greatest variation in composition is usually between the outside layers and the center of the bar. If punching or drilling is used, the holes should pass entirely through the metal. Care must also be exercised that an undue amount of scale or crust on the outside of the bar does not get into the sample. *Templets* are often used when a large number of metal products of the same shape are to be sampled. For example, in a refinery treating anode copper, a composite sample may be taken by drilling one hole in each anode;

a templet is used to mark the spot to be drilled, and the holes in the templet are used in succession.

**Laboratory Sampling.**—Samples of ore or concentrate reaching the assay laboratory may weigh from 5 to 100 pounds, and these must be crushed and cut to about 50 grams before a charge can be weighed out by the assayer. In the laboratory, small jaw crushers are generally used to break ore down to ¼-inch diameter, and a pulverizer is used to grind the ¼-inch product. A common type of disk pulverizer is shown in Fig. 4. Here the ore is pulverized between a rotating and a stationary disk, and the machine will reduce ¼-inch ore to −100 mesh in a single pass. Finely divided ore is generally mixed on a rolling cloth and cut with a mechanical splitter such as the Jones riffle (Fig. 5). Larger samples of coarse ore may be coned and quartered.



*(Courtesy Braun Corporation, Los Angeles)*

Fig. 4.—A Laboratory Pulverizer.

Laboratory treatment of metal samples of pulps and liquids, and samples of special products, will vary widely; but whatever the method, the purpose is to obtain a final sample which is small enough to be treated by the chemical process used, and is still representative of the larger sample from which it was cut.

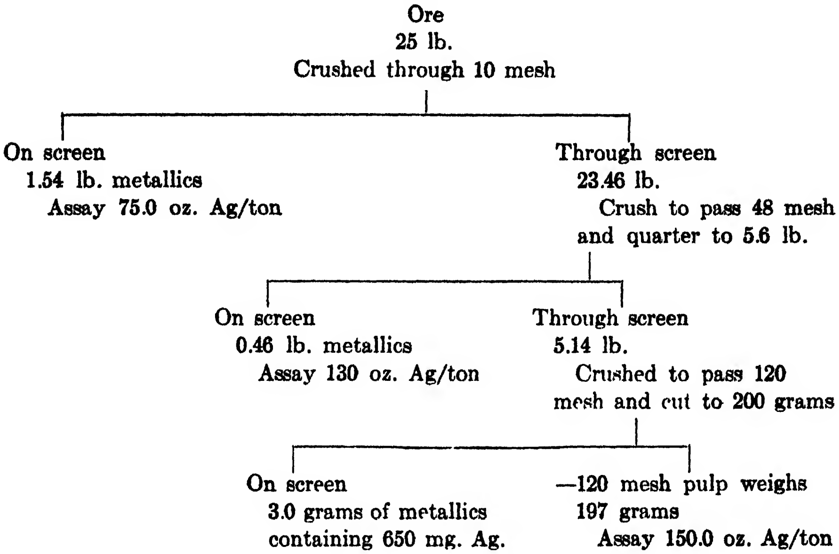
If an ore contains "metallics" or materials such as free gold or silver, these substances will not crush like the ordinary ore minerals, but will flatten out or roll up into cylinders or spheres. If such materials are present in an ore, a special sampling technique is required. Since the size of these malleable particles cannot be reduced in the same ratio as the brittle minerals, the procedure is to reduce the sample in several stages and screen out the metallics each time. Each batch of metallics and the final pulp are assayed, and the initial assay is calculated. A simple method for making this calculation is to average the assays of metallics and pulp from the finest screen to obtain the average assay of the undersize from the previous screen, and then work backwards through the entire set of screens used. This method of calculation is illustrated in Examples 1 and 2. If some of the material is lost in screening, it is usually assumed that this has the same value as the final pulp, and a correction is made on this basis. If the presence of metallics is suspected in an ore, the laboratory sampling must be done carefully; and no coarse particles remaining on a screen should ever be discarded without careful examination.

*(Courtesy Braun Corporation, Los Angeles)*

FIG. 5.—Laboratory Sample Splitter (Jones Riffle).

### EXAMPLE 1

An ore containing metallics is sampled according to the following scheme:



Ore
25 lb.
Crushed through 10 mesh

On screen
1.54 lb. metallics
Assay 75.0 oz. Ag/ton

Through screen
23.46 lb.
Crush to pass 48 mesh and quarter to 5.6 lb.

On screen
0.46 lb. metallics
Assay 130 oz. Ag/ton

Through screen
5.14 lb.
Crushed to pass 120 mesh and cut to 200 grams

On screen
3.0 grams of metallics
containing 650 mg. Ag.

—120 mesh pulp weighs
197 grams
Assay 150.0 oz. Ag/ton

Required: the silver assay of the original ore.
Solution:

650 mg. in 3000 (3 grams) represents

$$\frac{29{,}167 \times 650}{3000} = 6319 \text{ oz./ton}$$

$$\begin{aligned} 6319 \times 3 &= 18{,}957 \\ 150 \times 197 &= \underline{29{,}550} \\ &\phantom{=} 48{,}507 \end{aligned}$$

$$\frac{48{,}507}{200} = 242.5 \text{ oz./ton} = \text{average assay of } -48 \text{ mesh material}$$

$$\begin{aligned} 242.5 \times 5.14 &= 1246.5 \\ 130 \times 0.46 &= \underline{\phantom{0}59.7} \\ &\phantom{=} 1306.2 \end{aligned}$$

$$\frac{1306.2}{5.60} = 233.2 \text{ oz./ton} = \text{average assay of } -10 \text{ mesh material}$$

$$\begin{aligned} 233.2 \times 23.46 &= 5472 \\ 75.0 \times 1.54 &= \underline{\phantom{0}115} \\ &\phantom{=} 5587 \end{aligned}$$

$$\frac{5587}{25} = 223.5 \text{ oz./ton} = \text{assay of original ore } (+10 \text{ mesh})$$

### Example 2

A sample of gold ore weighing 25.04 kg. was crushed to pass a 35-mesh sieve. On the 35-mesh sieve were retained 25.00 grams of metallics which yielded 6.3866 grams of gold. The undersize weighed 24,855 grams (loss = 160 grams). This was quartered to yield a sample weighing 6036 grams and crushed to pass 120 mesh; 3.075 grams of metallics yielding 1.7770 grams of gold remained on the 120-mesh screen, and the undersize weighing 6009 grams (loss = 24 grams) assayed 1.35 ounces of gold per ton.

Assuming that the material lost as dust had the same assay value as the —120 mesh pulp, calculate the initial gold assay.

Solution:

$$29{,}167 \times \frac{1.7770}{3.0750} = 16{,}855 \text{ oz./ton} = \text{assay of } +120 \text{ mesh metallics}$$

$$29{,}167 \times \frac{6.3866}{25.000} = 7451 \text{ oz./ton} = \text{assay of } +35 \text{ mesh metallics}$$

$$\begin{aligned}
16{,}855 \times 3.075 &= 51{,}830 \\
1.35 \times 6009 &= 8{,}112 \\
1.35 \times 24 &= 32 \\
\hline
&\phantom{=}\ 59{,}974
\end{aligned}$$

$$\frac{59{,}974}{6036} = 9.936 \text{ oz./ton} = \text{assay of } -35 \text{ mesh product}$$

$$\begin{aligned}
7451 \times 25.00 &= 186.275 \\
9.936 \times 24.855 &= 246.960 \\
1.35 \times 160 &= 216 \\
\hline
&\phantom{=}\ 433{,}451
\end{aligned}$$

$$\frac{433{,}451}{25{,}040} = 17.31 \text{ oz./ton} = \text{initial assay}$$

Note that the omission of the dust losses would make very little difference in these calculations. However, in sampling material of this kind, every effort must be made to remove all the material from the grinding machinery, pans, and splitters, for although the loss of a few grams as dust does not appreciably affect the accuracy of sampling, the loss of half a gram of the valuable metallics would be serious.

**Salting.**—The introduction of high-grade material into a sample, whether intentionally or unintentionally, is called *salting*. Salting is especially likely to occur after the sample has been reduced to a small bulk, and it must be guarded against in all laboratory operations. If a small pulverizer is used to grind a high-grade gold ore, enough gold may be retained on the disks to salt a low-grade sample crushed in the same machine. The same statement applies to laboratory ball-mills, bucking boards, flotation machines, etc. Accidental salting may be prevented by keeping all crushers, riffles, pans, and other equipment clean by brushing thoroughly and blowing with compressed air.

Intentional salting is probably most common in samples of gold ores, because a small bulk of gold will produce a high assay on the average sample. The gold used to salt the sample may be introduced in the form of a high-grade ore or concentrate, as metallic gold, or as a solution of gold chloride. Many methods have been evolved in attempts (often successful) to salt samples without detection, such as impregnating samples with gold chloride solution—the use of a hypodermic needle permits the salting of a sample even when sealed in a sample sack; rolling gold dust into a cigarette and allowing the ashes to drop into the gold pan being used by the operator; and introducing filings from a gold ring into a pan of placer gravel. Of course, a salted sample is worthless except as evidence of attempted fraud.

If salting is suspected, the following precautions will help to detect it:

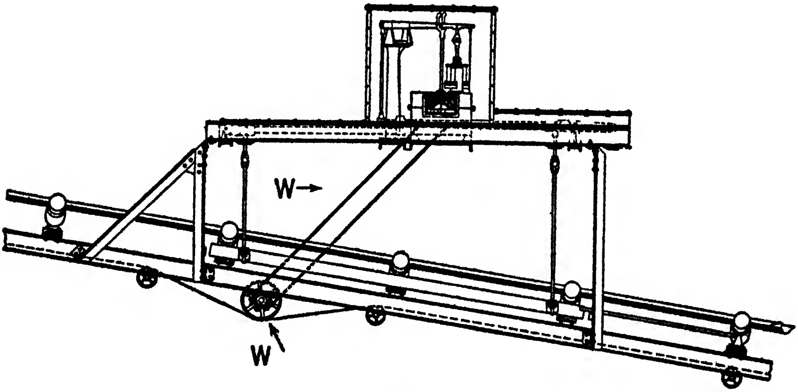
1. Introduce some samples which are known to be barren with the regular samples; and if the samples are being salted, there is a strong likelihood that values will be reported in this barren material. It goes without saying that these blank samples must be numbered or lettered in the same way as the regular samples.
2. Introduce a number of duplicate samples, but mark them so that an outsider would have no way of telling which pair of samples are duplicates. It is very seldom that exactly the same amount of "salt" can be introduced into two different samples. If one of these samples is larger than the other, the difficulty of salting without detection is increased.
3. Examine the valuable "minerals" to see if they are of the type which would be expected in the sample. Gold filings can readily be distinguished from true placer "colors" under the microscope.
4. If possible, never let valuable samples out of the sight of a trustworthy caretaker, unless they are safely under lock and key.

**Moisture Samples.**—Samples for the determination of moisture content are usually grab samples weighing from 100 to 1000 grams. The sample is weighed, placed in a drying oven, dried at 105° C., and weighed again, the loss in weight representing the moisture content. Moisture samples should be weighed as soon as possible after they are taken. If this is impossible, they must be sealed in an air-tight container to prevent evaporation loss.

The moisture sample is taken to determine the net dry weight of a consignment from the gross weight, since all settlements are based on the dry weight of ore or concentrate. Moisture samples should be taken immediately after the gross weight has been determined; and grab sampling is commonly used, since this method is the most rapid of all, and errors involved are usually less than the error that would result from evaporation if the sample were taken by a mechanical sampler or by such slow hand methods as coning and quartering. The grab sample should include representative portions from the top, bottom, and center of the car of ore, for if the sample is taken from the top only, it will usually be too high in wet weather and too low in dry weather.

## WEIGHING

The weighing of metallurgical products is equally as important as sampling, and the weighing must be done in conjunction with sampling in such a way that the operator can always compute the total weight of any constituent of the material in question. In any continuous process, samples are always taken often enough so that the operation process may be guided by the samples and weights of the materials involved. Samples of this kind (whether taken by hand or mechanically) are *control samples.*



*(Courtesy Merrick Scale Mfg. Co., Passaic, N. J.)*

Fig. 6.—The Merrick Weightometer.

**Note that a definite portion of the conveyor belt is suspended and balanced. The integrating mechanism is driven by the pulley and sprocket chain.**

Weighing may be done either continuously or intermittently. In the latter method, the material is weighed in batches; for example, the output of a lead blast furnace may be found by weighing each ladleful of lead that is tapped. In any continuous method of weighing, the material must pass over some sort of integrating weightometer which automatically records the total weight of material passing

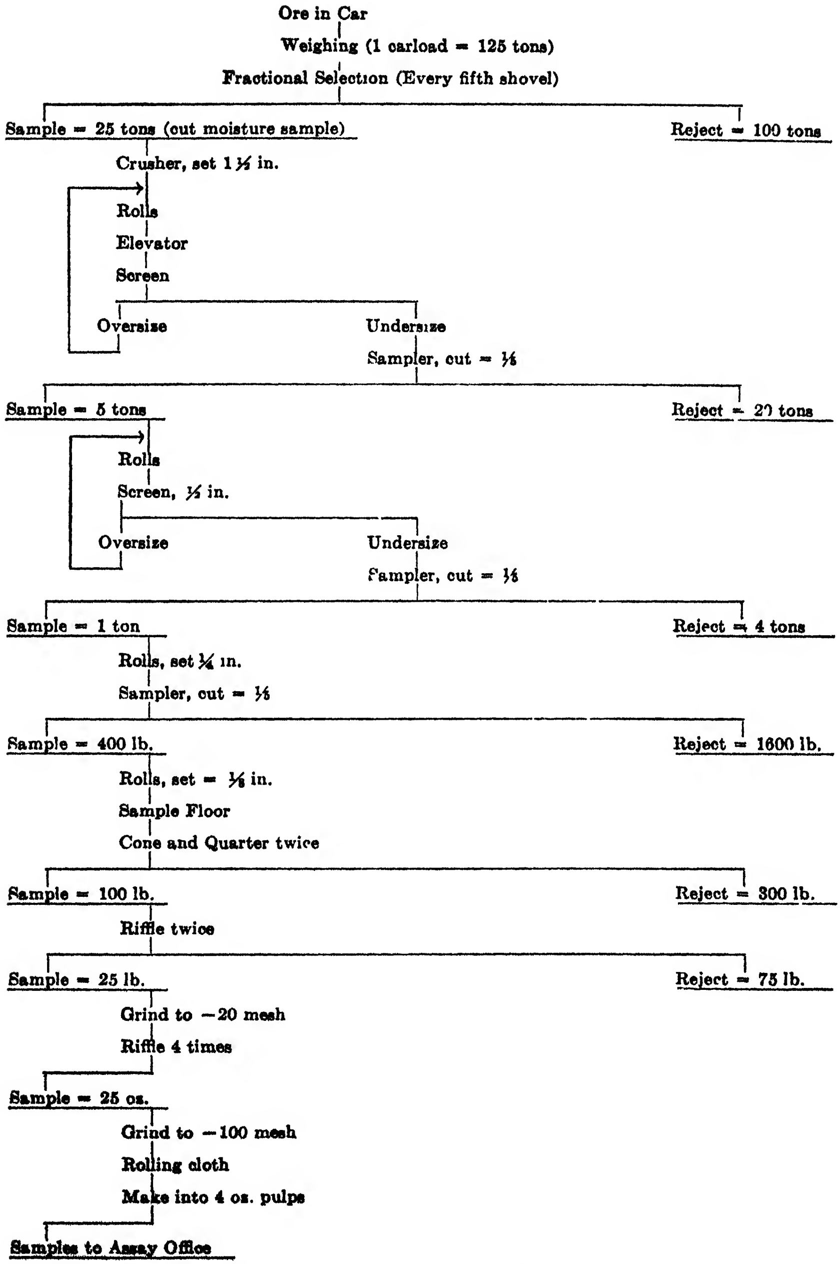
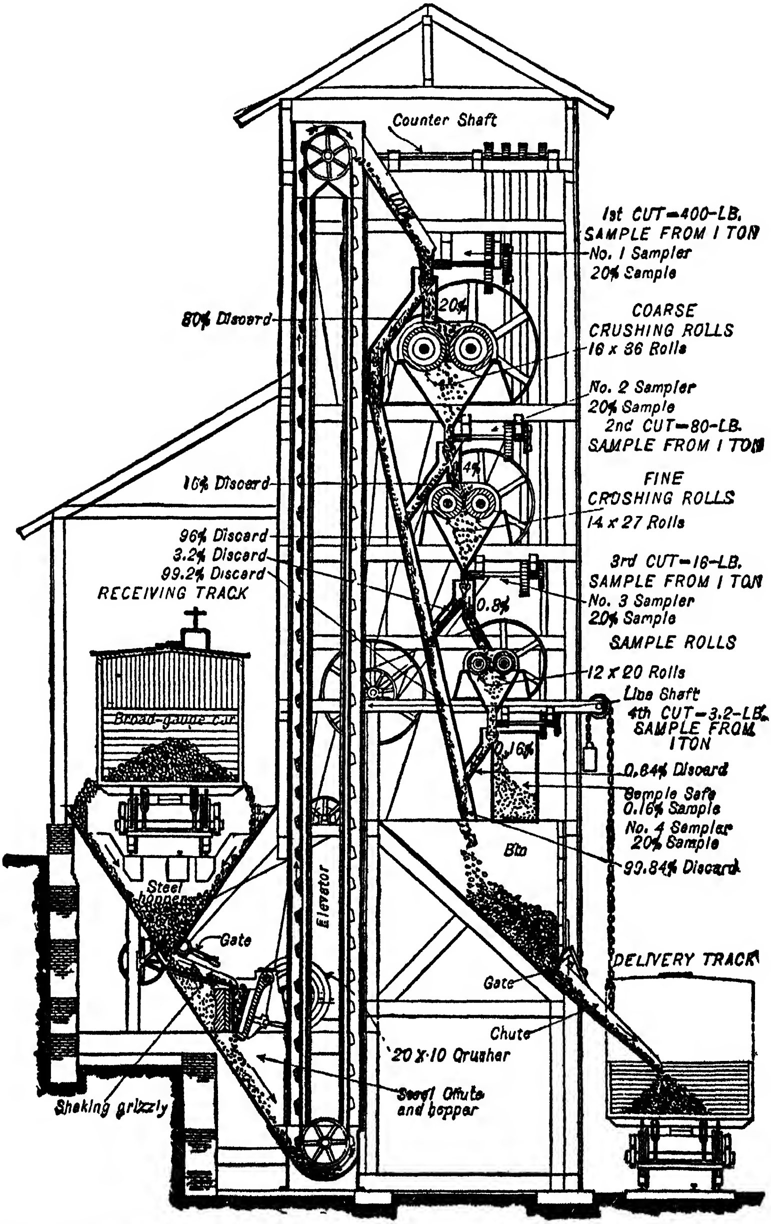


FIG. 7.—Typical Flowsheet of Operations Used in Sampling a Car of Ore.



(*From a Textbook of Fire Assaying by Edward E. Bugbee, John Wiley and Sons, Inc., New York.*)

FIG. 8.—Taylor and Brunton Sampling System.

in a given time. Devices of this sort usually operate on material being transported on conveyor belts.

Waste materials such as slag and tailing may not be weighed directly, but their weights can be calculated by differences if the need arises.

### PURCHASING OF ORES AND CONCENTRATES

The purchasing of ores and concentrates (also fluxes, fuels, scrap, and other raw materials) is quite involved, and is usually governed by policies which are characteristic of individual companies. Whenever these materials are purchased in large amounts, they are contracted for in an agreement between buyer and seller, and the contract covers in detail such points as price, permissible limits of variation in chemical analysis, shipping, and similar considerations. If a seller has a large amount of ore or concentrate which can be supplied at a steady rate, he will in general obtain a separate contract or *schedule* from the smelter to cover the purchasing of his ore or concentrate. For small shipments of ore or concentrate, smelters usually maintain a public or open schedule. Unless the shipper has a separate contract, he will be paid according to the terms of the open schedule.

A smelter does not recover the metal from an ore, and then reimburse the original owner for this metal. The ore is sampled, and after buyer and seller have agreed upon the assay value of the ore, the ore is ordinarily purchased outright by the smelter. The metals produced are then the property of the smelting company, and the profit from them depends upon the difference between the price obtained for the metal products of the ore and the cost of the ore plus operating expenses. In some cases the mine and smelter are owned by the same company, and the output of one mine or group of mines makes up the entire supply for the smelter. Even in this case, however, the ore is "sold" from mine to smelter so that the cost accounting of mine and smelter operations may be kept in order.

A smelter which purchases ores from independent mining companies is called a custom smelter, and the ore so purchased is called custom ore. Some smelters are independently owned and are entirely custom smelters. Others do very little custom work, treating almost entirely the output from the mines of their own company. However, almost any smelter will buy custom ore if it is of such a type that it can be readily treated with the regular ore supply. The system whereby the smelter computes the purchase price for a given lot of ore is called a schedule, and the following are examples of open, or public, schedules. Purchases of ore made by a concentrating plant would be based on analogous schedules.

## DOMESTIC LEAD ORES AND CONCENTRATES[1]

The following terms are subject to the general clauses and are subject to prompt acceptance. Unless shipments are begun within 30 days this quotation is automatically cancelled.

### PAYMENTS

**Gold:** If 3/100 of an ounce per dry ton or over, pay for all at the rate of $20.00 per troy ounce, plus 90 per cent of the realized gold premium in excess of $20.67 per troy ounce. Under present Government net realized price ($34.9125), this is equivalent to $32.81825 per troy ounce.

**Silver:** Pay for 95 per cent (minimum deduction of one-half ounce) at the average Handy and Harman New York silver quotations for the calendar week, including date of arrival of last car of each lot at plant of Buyer; or, if higher, at the realized Mint price, provided silver qualifies for Government purchase and affidavit is furnished, less a deduction in either case of 1½ cents per ounce. Present Mint price is 77 cents per ounce.

**Lead:** Deduct from the wet-lead assay 1.5 units and pay for 90 per cent of the remaining lead at smelter quotation less 1.425 cents per pound of lead accounted for. Nothing is paid for lead if less than 5 per cent by wet assay.

**Copper:** Deduct from the wet-copper assay 8 pounds and pay for 95 per cent of the remaining copper at the daily net refinery quotations for electrolytic cathodes as published in the Engineering and Mining Journal of New York averaged for the calender week including date of arrival of last car of each lot at the plant of the Buyer less a deduction of 5.025 cents per pound of copper accounted for. Nothing is paid for copper if less than ½ per cent by wet assay. No payment will be made for any metal or content except as above specified.

### DEDUCTIONS

**Base Charge:** $3.70 per net dry ton of 2000 pounds; provided the sum of payments for gold, silver, lead and copper does not exceed $25.00 per ton. Add to the base charge 10 per cent of the excess over $25.00 to a maximum charge of $6.70 per ton.

**Insoluble:** Allow no units free; charge for all at 5 cents per unit, fractions in proportion.

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[1] Reprinted from U. S. Bureau of Mines Information Circular 6926, by Gardner and Allsman.

**Zinc:** Allow 5 units free; charge for the excess at 30 cents per unit, fractions in proportion.

**Sulphur:** Allow 2 units free; charge for the excess at 20 cents per unit, fractions in proportion. Maximum charge $2.00 per dry ton of material.

**Arsenic:** Allow 2 units free; charge for the excess at $0.50 per unit, fractions in proportion.

**Antimony and Tin (Combined):** Allow 1 unit free; charge for the excess at $1.50 per unit, fractions in proportion.

**Bismuth:** One-tenth of one per cent (0.1 per cent) of the lead content by wet assay will be allowed free. The excess will be charged at fifty cents (50c) per pound, fractions in proportion.

**Moisture:** A minimum deduction of one per cent will be made from wet weight; when over one percent is contained the actual moisture will be deducted.

**Delivery:** F. O. B. unloading bins.

**Taxes:** Deduct Federal or State taxes, import duties, stamps, and/or other charges now or hereafter imposed.

**Freight:** All railroad freight and delivery charges for account of shipper. Deduct from settlement freight and other advances made by Buyer.

## GENERAL CLAUSES GOVERNING ALL OPEN SCHEDULES

1. Weighing, moisture, and ore sampling (at which seller or a representative may be present) as done by Buyer according to standard practice, promptly after receipt of product, will be accepted as final. The absence of seller or a representative shall be deemed a waiver of the right in each instance. After sampling, the product may be placed in process, comingled, or otherwise disposed of by Buyer. In case of disagreement on assays, an umpire shall be selected in rotation from a list mutually agreed upon, whose assays shall be final if within the limits of the assays of the two parties; and if not, the assay of the party nearer to the umpire shall prevail. Losing party shall pay cost of umpire. In case of Seller's failure to make or submit assays, buyer's assays shall govern.

2. All schedules on ore not under contract for a definite period of time are subject to change without notice.

3. The rates quoted herein are for carload lots. On any lot containing one ton or less there will be a sampling and handling charge of $10.00. This charge will be decreased by $1.00 for each ton in excess of one ton.

4. The rates quoted apply only to ore in bulk. Fifty cents per ton additional will be charged for ore in sacks to cover extra cost of handling.

5. In the event quotation date should fall on a legal holiday or one upon which no quotation is issued, the next succeeding quotation will be used in settlement.

6. In this schedule where the word "ton" is used it is understood to be a ton of 2000 pounds avoirdupois; where the word "ounce" is used, as referring to gold and silver, it is understood to mean the troy ounce; and where the word "unit" is used it is understood to mean one per cent of a ton, or 20 pounds avoirdupois.

7. In order that delivery of the ore at our plant may not be unnecessarily delayed we make it a general rule that *the freight charges must be prepaid or guaranteed by the shipper.*

8. The rates quoted herein are based on present existing scale for common labor at the Smelting Works, and present published all rail freight rates on lead and copper bullion from smelter to New York City. Any increase or decrease is for account of Seller, and proper deduction or credit shall be made accordingly.

## EXAMPLE OF CALCULATIONS

The method of calculating returns based on the foregoing schedule follows:

Wet weight of lot, 137.2 tons.
Moisture, 3.0 per cent.
Dry weight of lot, 137.2 (1.00 − 0.03) = 133.1 tons.

Chemical analysis:

| | | |
|---|---|---|
| Gold | 0.53 | ounces per ton. |
| Silver | 1.65 | do. |
| Lead | 2.6 | percent. |
| Copper | .82 | do. |
| Zinc | 6.7 | do. |
| Arsenic | 2.4 | do. |
| Antimony | 1.4 | do. |
| Tin | 0 | do. |
| Bismuth | .08 | do. |
| Iron | 15.0 | do. |
| Sulphur | 19.7 | do. |
| Insoluble | 28.0 | do. |
| Lime | 5.6 | do. |
| Magnesia | 4.8 | do. |
| Loss on ignition | 9.6 | do. |
| Total | 96.7 | do. |

| | | |
|---|---|---|
| Payments: | | |
| Gold, 0.53 × 32.81825 = | $17.39 | |
| Silver, 1.65 × .95 (0.77 — 0.015) | 1.18 | |
| Lead, Less than 5 percent. | None | |
| Copper, Quotation 9.5 cents per pound<br>0.95 [(0.82 × 20) — 8] × (0.095 — 0.05025) = | .36 | |
| Gross payments per dry ton | | $18.93 |
| Deductions: | | |
| Treatment charge: | | |
| On ore between $0 and $25 gross value, | $3.70 | |
| Penalties: | | |
| Insoluble 28.0 × 0.05 = | 1.40 | |
| Zinc, (6.7 — 5) × 0.30 = | 0.51 | |
| Sulphur, (19.7 — 2) × 0.20 = $3.54; maximum = | 2.00 | |
| Arsenic, (2.4 — 2) × 0.50 = | .20 | |
| Antimony and tin, (1.4 — 1) × 1.50 = | .60 | |
| Bismuth, [0.08 — (0.001 × 2.6)] 20 × 0.50 = | .77 | |
| Total deductions per dry ton | | $ 9.18 |
| Net payments per dry ton | | 9.75 |
| Total returned by the smelter to the shipper 133.1 × $9.75 = | | $1297.73 |

## TABLE 2

### Copper and Lead Smelters in Western States *

| State | Company | Smelter | Location | Ores Treated |
|---|---|---|---|---|
| Arizona... | Phelps Dodge Corp. | Copper Queen Branch | Douglas | Gold, silver, copper, and lead ores and concentrates |
| | do. | United Verde Branch | Clarksdale | Gold, silver, and copper ores and concentrates |
| | do. | Morenci Branch [1] | Clifton | do. |
| | United Verde Extension Mining Co. | | Clemenceau | do. |
| | Magma Copper Co. | | Superior | do. |
| | International Smelting Co.[2] | | Miami | do. |
| | American Smelting & Refining Co. | Hayden [1] | Hayden | do. |
| California | American Smelting & Refining Co. | | Selby | Gold, silver, and lead ores and concentrates |
| Colorado | American Smelting & Refining Co. | Arkansas Valley | Leadville | Gold, silver, lead, and copper ores and concentrates |
| | do. | Durango plant [1] | Durango | Gold, silver, and lead ores and concentrates |
| Idaho | Bunker Hill & Sullivan Mining & Concentrating Co. | Bunker Hill | Bradley | do. |
| Montana | Anaconda Copper Mining Co. | Anaconda Reduction Works | Anaconda | Gold, silver, copper, and zinc ores and concentrates |
| | American Smelting & Refining Co. | | East Helena | Gold, silver, and lead ores and concentrates |
| Nevada | Nevada Consolidated Copper Co. | | McGill | Gold, silver, and copper concentrates and ores |
| Texas | American Smelting & Refining Co. | | El Paso | Gold, silver, copper, and lead ores and concentrates |
| Utah | International Smelting Co.[2] | | Tooele | do. |
| | American Smelting & Refining Co. | | Murray | Gold, silver, and lead ores and concentrates |
| | do. | | Garfield | Gold, silver, and copper ores and concentrates |
| | U. S. Smelting, Refining & Mining Co. | | Midvale | Gold, silver, lead, and zinc ores. Zinc concentrates shipped |
| Washington | American Smelting & Refining Co. | | Tacoma | Gold, silver, and copper ores and concentrates (copper refinery) |

[1] Idle June 1936. [2] A subsidiary of Anaconda Copper Co.

* Reprinted from U. S. Bureau of Mines Information Circular 6926, by Gardner and Allsman.

## TABLE 3

## SCHEDULES FOR GOLD AND SILVER ORES AT COPPER SMELTERS (JULY 1936)*

| Plant | Payments | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Gold[1] | | | Silver[2] | | | Copper[3] | | | Lead[4] | | |
| | Minimum Paid for, Ounces per Ton | Payments | | Minimum Paid for, Ounces per Ton | Minimum Deduction, Ounces per Ton | Percent Paid for | Deductions | | Percent of Quotation After Deduction, | Deductions | | Percent of Quotations After Deduction |
| | | Classes of Ore, Ounces per Ton | Rate per Ounce | | | | Pounds per Ton[5] | Cents per Pound | | Units | Cents per Pound | |
| El Paso...... | 0.03 | All | $32.31825 | ... ..... | 0.5 | 95[6] | 8 | 2.525 | 95[7] | 1.5 | 3.0 | 60[8] |
| Garfield[9]...... | .03 | 0 to 3<br>Over 3 | 31.81825<br>32.31825 | 1.0 | .5 | 95 | 15 | 2.5 | 100 | 0 | 3.5 | 50[10] |
| Midvale...... | .02 | 0 to 5<br>Over 5 | 31.81825<br>(11) | 1.0 | .5 | 95 | 15[12] | 3 | 90 | . ... . | ......... | ....... . |
| Anaconda.... | .01 | All | 31.81825 | .. ....... | 1.0 | 95[13] | 10[12] | 2.5 | 90 | .. . . | . ... | 0 |
| Tooele[15]...... | .02 | All | 31.85 | 1.0 | ......... | 95 | 15 | 2.775 | 100 | .. .. . . | 3.525 | 50[10] |
| Tooele[16]...... | .02 | 0 to 3<br>3 to 6<br>6 to 10<br>Over 10 | 31.85<br>32.20<br>32.90<br>33.25 | 1.0 | . ...... . | 95 | 15 | 2.775 | 100 | ...... . | 3.525 | 50[10] |
| Miami....... | .03 | All | 32.20 | 1.0 | .. ...... | 95 | 10[17] | 2.5 | 90 | .. | ... . .. | 0 |
| Superior[18]... | .03 | All | 32.20 | 1.0 | ......... | 95 | 8[19] | 2.5 | 90 | . ...... | ..... ... | 0 |
| Superior[20].... | .03 | All | 32.20 | 1.0 | ......... | 95 | 8[19] | 2.5 | 90 | ......... | ......... | 0 |

*(Footnotes for Table 3 on page 487.)*

## TABLE 3—*Continued*

### SCHEDULES FOR GOLD AND SILVER ORES AT COPPER SMELTERS (JULY 1936) *

| Plant | Deductions | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Treatment Charge | | | | Penalties | | | | | | |
| | Base | | Add for Excess Gross Value Over Base Percent | Maximum | Zinc | | Arsenic (As), Antimony (Sb), and Tin (Sn). | | | Bismuth | |
| | Per Ton | Gross Value | | | Units Free | Charge per Unit for Excess | Element or Combination | Units Free | Charge per Unit for Excess | Units Free | Charge per Pound for Excess |
| El Paso...... | $3.50 | $ 0 to $ 20<br>Over 20 | 10 | $6.00 | 5 | $0.30 | Arsenic<br>Sb + Sn | 2<br>1 | $0 50<br>1.50 | 0 1 | $0.50 |
| Garfield[9]..... | 3.50 | $ 0 to $ 20<br>Over 20 | 10 | 5 50 | 6 | 30 | As + Sb | 2 | 0 50 | ....... | 0 |
| Midvale...... | 5.00 | $ 0 to $ 30<br>Over 30 | 10 | 7 00 | 6 | .30 | .... | ...... | 0 | ...... | 0 |
| Anaconda.... | 4 00 | $ 0 to $ 15<br>Over 15 | 10 | 5.50[14] | .... | 0 | .. | ...... | 0 | ....... | 0 |
| Tooele[15]...... | 4.00 | $ 0 to $ 25<br>Over 25 | 10 | 6.00 | ...... | 0 | ..... | ...... | 0 | ....... | 0 |
| Tooele[16]...... | 4.00 | $ 0 to $ 25<br>Over 25 | 10 | 6 00 | ..... | 0 | ....... | ..... | 0 | .... | 0 |
| Miami....... | 3.50<br>6.00 | $ 0 to $ 15<br>15 to 40<br>40 to 100<br>Over 100 | 10<br>5 | 6.00<br>8.00 | ...... | 0 | ..... | ..... | 0 | ...... | 0 |
| Superior[18].... | 3.50 | $ 0 to $ 15<br>15 to 100<br>Over 100 | 10<br>5 | 6.00<br>15 00 | ...... | 0 | ..... | ..... | 0 | ....... | 0 |
| Superior[20].... | 2.50 | $ 0 to $ 15<br>15 to 100<br>Over 100 | 10<br>4 | 5.00<br>...... | ....... | 0 | .... | ...... | 0 | ....... | 0 |

*(Footnotes for Table 3 on page 487.)*

[*] Reprinted from U. S. Bureau of Mines Information Circular 6926, by Gardner and Allsman.

[1] Payments on gold are based on the new mint price of $35 per ounce (net $34.9125).

[2] Payments on silver are based on the new mint price for American mined ore at $0.77 per ounce.

[3] Payments on copper are based on the Engineering and Mining Journal quotations.

[4] Payments on lead are based on the New York quotation for common desilverized lead.

[5] When assay is less than the deduction the shipper is charged with the deficiency, except as further noted.

[6] Less a deduction of 1½ cents per ounce.

[7] Nothing paid for copper less than ½ percent.

[8] Nothing paid for lead less than 5 percent by wet assay.

[9] Siliceous ore open schedule.

[10] Nothing paid for lead less than 2 percent by wet assay.

[11] On direct smelting ores containing over 5 ounces gold per ton, the price per ounce for the excess will be to the mutual agreement between the buyer and shipper.

[12] Minimum deduction.

[13] Less a deduction of 2 cents per ounce

[14] To the base treatment charge also add 12 cents for each unit of iron and deduct 2.5 cents for each unit of silica in excess of alumina; treatment charge is not to exceed maximum.

[15] Dry-ore rate.

[16] Gold-concentrate rate.

[17] Minimum deduction 10 pounds and maximum deduction 20 pounds per ton. No payment or deduction will be made when copper is less than 0.8 percent.

[18] Crude-ore open schedule for carload lots

[19] Minimum deduction 8 pounds per ton and maximum deduction 20 pounds per ton.

[20] Concentrate open schedule for carload lots.

## TABLE 4

### Schedules for Gold and Silver Ores at Lead Smelters (July 1936) *

| Plant | Payments | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Gold[1] | | | Silver[2] | | | Lead[3] | | | Copper[4] | | | Iron and Lime |
| | Minimum Paid for, Ounces per Ton | Payments | | Minimum Paid for, Ounces per Ton | Minimum Deductions, Ounces per Ton | Percent Paid for | Deductions | | Percent of Quotation after Deduction | Deductions | | Percent of Quotation after Deduction | |
| | | Classes of Ore, Ounces per Ton | Rate per Ounce | | | | Units | Cents per Pound | | Pounds per Ton | Cents per Pound | | |
| El Paso........ | 0.03 | All | $32.81825 | ......... | 0 5 | 95[5] | 1.5 | 1.425 | 90[6] | 8 | 5.025 | 95[7] | |
| Murray........ | .02 | All | 31.81825 | 1.0 | .5 | 95 | 1.5 | 1.5 | 90[6] | 15 | 5 5 | 100 | Iron[10]<br>Lime[11] |
| East Helena[13].. | .03 | .03 to 3<br>3 to 5<br>5 to 10<br>Over 10 | 31.81825<br>32.31825<br>32.6743<br>33.0304 | ..... ... | 1 0 | 95 | 1 5 | 1 5 | 90[6] | 20 | 6 0 | 100[14] | Iron[15] |
| Selby[16]........ | .03 | Under 5<br>5 to 15<br>Over 15 | 31.81663<br>32.31663<br>32.81663 | 1.0 | 1 0 | 95 | . . | .. .. . | 0 | ...... | .. .. | 0 | |
| Selby[18]........ | .03 | Under 5<br>5 to 15<br>Over 15 | 31.81663<br>32 31663<br>32.81663 | 1 0 | 1 0 | 95 | ... .. | ....... | 0 | . . | ... .. | 0 | |
| Leadville[20].... | .03 | 0 to 1<br>Over 1 | 31.81825<br>32.31825 | ...... . | 1 0 | 95 | 1 5 | 0 | 90 | 20 | 6.5 | 100 | Iron[21] |
| Leadville[22].... | .03 | 0 to 1<br>Over 1 | 31.81825<br>32 31825 | ......... | 1 0 | 95 | 1 5 | 1 5 | 100[23] | 20 | 6 5 | 100[24] | Iron[25]<br>Lime[26] |
| Leadville[29].... | .03 | 0 to 1<br>Over 1 | 31.81825<br>32.31825 | ........ | 1.0 | 95 | 1 5 | 1.5 | 90 | 20 | 6 5 | 100 | |
| Midvale....... | .02 | 0 to 5<br>Over 5 | 31.81825<br>[30] | 1 0 | .5 | 95 | 1 5 | 1.5 | 90[31] | 15[32] | 5 5 | 90 | Iron[33] |
| Kellogg[36] ..... | .05 | Under 5<br>5 to 10<br>Over 10 | 31.81825<br>32.17431<br>32.53037 | 1.0 | ........... | 95[37] | 1 25 | 0 | 90[6] | 20 | 8.0 | 100[38] | |
| Kellogg[41]...... | .05 | Under 5<br>5 to 10<br>Over 10 | 31.81825<br>32.17431<br>32.53037 | 1.0 | ........... | 95[37] | ......... | ......... | 0 | 20 | 8.0 | 100[38] | |

*(Footnotes for Table 4 on page 490.)*

## TABLE 4—*Continued*

## SCHEDULES FOR GOLD AND SILVER ORES AT LEAD SMELTERS (JULY 1936)*

| Plant | Deductions | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Treatment Charge | | | Penalties | | | | | | | | | | | | | | |
| | Gross Value | Base per Ton | Maximum | Insoluble | | Zinc | | Arsenic (As), antimony (Sb), tin (Sn) | | | Bismuth | | Sulphur | | | Moisture | | |
| | | | | Units Free | Charge per Unit | Units Free | Penalty per Unit for Excess | Element or Combination | Units Free | Penalty per Unit for Excess | Units Free | Penalty per Pound for Excess | Units Free | Penalty per Pound for Excess | Maximum Penalty | Units Free | Penalty per Pound for Excess | Maximum Penalty |
| El Paso...... | $0 to $25<br>Over 25 | $3.70<br>[8] | $6.70 | 0 | $0.05 | 5 | $0 30 | As<br>Sb + Sn | 2<br>1 | $0.50<br>1.50 | [9] | $0.50 | 2 | $0.20 | $2.00 | | 0 | |
| Murray...... | [12] | 2.50 | . ... | 0 | .10 | 6 | .30 | As + Sb | 2 | 0.50 | | 0 | 2 | 0.25 | 2 50 | | 0 | |
| East Helena [13] | 0 to 30<br>30 to 40<br>Over 40 | 6.00<br>5.50<br>5.00 | 6.00 | .... | 0 | 5 | 0.30 | As<br>Sb | 2<br>1 | 0 50<br>2.00 | [9] | .50 | | 0 | | | 0 | |
| Selby [16]...... | All | 6.00 | 6.00 | [17] | 0 | ... | 0 | As<br>Sb<br>Sn | 1 | 0 50 | 0 | .50 | | 0 | .. . | | 0 | |
| Selby [18]...... | 0 to 35<br>Over 35 | 6.50<br>[19] | 10.00 | ..... | 0 | .. | 0 | As<br>Sb<br>Sn | 1 | 0.50 | 0 | .50 | . | 0 | . | .. | 0 | |
| Leadville [20]... | All | 6.00 | 6.00 | .... | 0 | 5 | .50 | As<br>Sb<br>Sn | 0 5 | 1.00 | 0 05 | .50 | . | 0 | . . | 10 | $0 05 | 0 |
| Leadville [22]... | 0 to 8<br>8 to 10<br>10 to 50 | 4.00<br>[27]<br>[28] | ..... | 0 | 0.05 | 8 | .30 | As<br>Sb<br>Sn | 0.5 | 1.00 | 0.05 | .50 | 1 | 0.25 | 2.50 | 10 | 0.05 | 0 |
| Leadville [29]... | All | 8.50 | 8.50 | ..... | 0 | 8 | .30 | As<br>Sb<br>Sn | 0.5 | 1 00 | 0 05 | .50 | | 0 | .. . | 10 | .05 | 0 |
| Midvale..... | [34] | 2.50 | ..... | 0 | 0.10 | 6 | .30 | ....... | .... | 0 | [35] | . | 2 | 0.25 | 2.50 | ..... | 0 | |
| Kellogg [36].. .. | [38] | 12.00 | ..... | .... | 0 | 5 | .30 | As<br>Sb | 0 | 1.00 | 0 | 2.50 | 4 | 0.25 [40] | 2.00 | 6 | .20 | $2.00 |
| Kellogg [41].... | 0 to 20<br>[42] | 6.50 | 9.00 | ..... | 0 | 5 | .30 | As<br>Sb | 0 | 1.00 | 0 | 2.50 | 4 | 0.25 | 2.00 | 6 | .20 | 2.00 |

(*Footnotes for Table 4 on page 490.*)

[*] Reprinted from U. S. Bureau of Mines Information Circular 6926, by Gardner and Allsman.

[1] Payments on gold are based on the new mint price of $35 per ounce (net $34.9125).

[2] Payments on silver are based on the new mint price for new American mined ore at 77 cents per ounce.

[3] Payments on lead are based on the New York quotation for common desilverized lead.

[4] Payments on copper are based on the Engineering and Mining Journal quotations.

[5] Less a deduction of 1½ cents per ounce.

[6] Nothing paid for lead less than 5 percent wet assay.

[7] Nothing paid for copper less than ½ percent.

[8] Add 10 percent to the base charge for the excess value over $25 per ton.

[9] 0.1 percent of the wet-lead assay free.

[10] Pay for all at 6 cents per unit.

[11] Pay for all at 5 cents per unit if 5 percent or over.

[12] Add 10 cents to base charge for each unit of lead under 30 percent and deduct 10 cents for each unit of lead over 30 percent.

[13] Siliceous ore schedule; schedule for ores and concentrates with an excess of iron are identical except that treatment charge is a flat $5 per ton.

[14] Nothing paid for copper less than 1 percent.

[15] No credit.

[16] Schedule for gold concentrates.

[17] Add 10 cents per ton per unit of iron short of 25 units excess over insoluble.

[18] Schedule for crude siliceous gold ore.

[19] Add 10 percent to the base charge for the excess value over $35 per ton.

[20] 1934 schedule for iron ores and concentrates; applies only on ores and concentrates containing 20 percent or more of iron excess over insoluble.

[21] Excess over insoluble all at 10 cents per unit not to exceed $3 per ton.

[22] Crude-ore open schedule.

[23] When lead is over 9 cents per pound deduct 25 percent of the excess.

[24] When copper is over 15 cents per pound deduct 25 percent of the excess.

[25] Pay for iron plus manganese at 5 cents per unit but credit is not to exceed charge for insoluble.

[26] All at 8 cents per unit if 10 percent or over.

[27] Add 25 percent of gross value to the base treatment charge when it is between $8 and $10.

[28] Add 10 percent of the gross value to the base charge when it is between $10 and $50.

[29] 1934 siliceous ore special for ores with 50 percent excess insoluble.

[30] On direct smelting ores containing over 5 ounces gold per ton the price per ounce for the excess will be to the mutual agreement between the buyer and shipper.

[31] No payment for lead under 3 percent dry assay.

[32] Minimum deduction.

[33] All at 6 cents per unit.

[34] Based on 30 percent dry lead assay. Debit 10 cents for each unit of lead under 30 percent and credit 10 cents for each unit of lead above 30 percent.

[35] The Midvale smelter reserves the right to reject any shipment containing in excess of 0.1 percent bismuth.

[36] Lead ore open schedule.

[37] Ore over 35 ounces per ton deduct 2 cents per ounce.

[38] No payment for copper under 1 percent or when quotation is 8 cents per pound or less.

[39] Based on 50 percent lead. Add 10 cents per unit when over 50 percent and deduct 10 cents per unit when under 50 percent.

[40] Penalty only applies to ore under 20 percent lead; no penalty for ore 20 percent lead or over.

[41] Siliceous ore open schedule; ores containing no lead or under 5 percent for which no payment is made (lead determined by wet method less a deduction of 1¼ units).

[42] Between $20 and $35, $7.00 per ton; between $35 and $50, $7.50 per ton; between $50 and $75, $8.00 per ton; between $75 and $100, $8.50 per ton; over $100, $9.00 per ton.

## EXERCISES

1. Examine the figure showing the steps involved in the cone and quarter method of sampling. What can you say about the segregation of sizes of material in the cone? What precautions must be taken in order that this segregation shall not affect the sample? Why is the coning operation essential?

2. An ore containing metallics is sampled by the following scheme: The

original sample weighed 10 pounds. This was crushed to pass a 40-mesh screen, and ⅛ pound of metallics remained on the screen. The 9⅞ pounds of —40-mesh material were ground to pass a 120-mesh screen and cut to 200 grams. The —120-mesh pulp was assayed by the regular method. Two grams of + 120-mesh metallics were obtained from the 200 grams of pulp.

Assays:

| | |
|---|---|
| Metallics on 40 mesh | 1000 oz. Ag per ton |
| Metallics on 120 mesh | 1000 mg. Ag in 2 grams |
| Minus 120 mesh pulp | 200 oz. Ag per ton |

Required: The silver assay of the original sample.

3. An ore is sampled according to the following scheme:

25 kg. ore crushed through 40 mesh

On screen: 8.060 grams of metallics yielding 6.505 grams of gold

Through screen. 24.85 kg. crushed to 120 mesh and cut to 5300 grams

On screen: 3.000 grams of metallics yielding 1.583 grams of gold

Through screen: 5288 grams of pulp assaying 35.00 oz. Au per ton

Calculate the gold assay of the ore making allowances for the dust losses in screening.

4. An ore is sampled according to the following scheme:

50 lb. of ore crushed to pass 6 mesh

On screen: 7.00 lb. of metallics. Assay 961 oz. Ag per ton

Through screen: 43.00 lb. Cut to 10.00 lb. and crushed to pass 12 mesh

On screen: 1.00 lb. of metallics. Assay 745 oz. Ag per ton

Through screen: 9.00 lb. Cut to 2.00 lb. and crushed to pass 25 mesh

On screen: 1.00 oz. of metallics. Assay 621 oz. Ag per ton

Through screen: 31.00 oz. Crushed to pass 120 mesh and cut to 90.00 grams

On screen: 4.00 grams of metallics containing 22 mg. of Ag

Through screen: 86.00 grams of pulp assaying 1132 oz. Ag per ton

Calculate the original silver assay of the ore. Of the "ounces" used above, which are troy ounces and which are avoirdupois ounces?

5. An ore contains Pb, 25 per cent; As, 1.0 per cent; S, 12.0 per cent; Ag, 5 oz. Calculate the value of 1 ton of this ore at the smelter, using the schedule and prices given in the example in this chapter.

6. Give reasons for the various deductions, charges, penalties, and premiums shown in smelter schedules.

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# CHAPTER XVI

## PRODUCTION OF THE INDUSTRIAL METALS

### IRON AND STEEL

Iron was known and used in prehistoric times. The metal was first produced on a small scale by reducing iron ore in a wood or charcoal fire. The temperature was usually not great enough to cause melting of the metal nor much adsorption of carbon. The metal produced was in the form of a small plastic lump of iron, low in carbon and containing some mechanically entrained slag. By hammering, this hot mass of metal could be formed into the shape desired. Several small lumps could be welded together to form larger pieces. For centuries this was the only method known for the production of iron, and the metal produced resembled in properties and method of manufacture the material which we know today as wrought iron.

From a simple open fire, the early ironmakers passed to a fire built in a hole in the side of a hill to take advantage of natural draft; later they built crude furnaces with forced draft and used charcoal as fuel rather than natural wood. Improvements in furnace design and the use of a better fuel and forced draft made it possible to obtain higher temperatures and more efficient reduction of the iron ore. Eventually, however, the higher temperature caused the iron to absorb enough carbon to lower its melting point below the temperature of the furnace. When this point was reached, the operators found that when they broke open the furnace to remove the pasty mass of iron, they had instead a liquid alloy which ran freely out of the furnace. This liquid cast iron was first made in Germany early in the fourteenth century—because of its high carbon content it was too brittle to be hammered or rolled and was at first thought to be worthless.

Centuries before man had been able to make cast iron, he had known how to make the relatively low-carbon steel by heating wrought iron in contact with carbon (*cementation*) until sufficient carbon had been absorbed. This steel was much harder and stronger than the wrought iron but was still malleable enough to be forged and welded. CO gas evolved from oxygen in this cemented steel caused blisters to form on its surface, and it was therefore called "blister steel." Often these blister steel bars were piled, heated to welding temperature, and rolled down to give "shear steel" or "single shear steel." If the piling and rolling operation was repeated, the process produced "double shear steel." In 1740, Benjamin Huntsman, an English watchmaker, made the first crucible steel or "cast steel" by remelting blister steel in a crucible. This was the first time that a true steel had been produced in the liquid state.

Thus, up to about 1740 two classes of ferrous metals were available —the brittle cast iron produced in blast furnaces which were the outgrowth of the earlier iron furnaces, and steels and wrought iron which were malleable and which were produced with considerable difficulty directly from iron ore. Meanwhile, the blast furnace was increasing in size and efficiency. In 1735 Abraham Darby at Shropshire, England, first used coke in a blast furnace instead of charcoal. The blast furnace was undoubtedly the most rapid and efficient instrument available for the reduction of iron ores, and the next step required was to find a cheap and rapid method for converting the brittle cast iron into malleable steel.

The puddling furnace for the manufacture of wrought iron was the first method of purification of cast iron. In the puddling process the cast iron was melted down in a small reverberatory furnace, and the carbon, silicon, manganese, phosphorus, and other impurities were oxidized and removed as gas (CO) or in a slag. As the carbon content of the iron was lowered, its melting point was raised until at the end of the operation the iron was in a pasty solid condition. This was worked up into a ball, removed from the furnace, and rolled or hammered down to shape—at the same time the rolling or hammering expelled most of the mechanically entrained slag. The finished wrought iron was essentially pure iron containing about 3 per cent of mechanically entrained slag which was in the form of long fibers parallel to the direction of rolling. The puddling process was probably first used about the twelfth century; and, until the Aston process was invented and applied commercially (1930), it was the only method available for the production of wrought iron. In the Aston process, wrought iron is made by "shotting" iron from the Bessemer converter by pouring it through a bath of slag—this produces a bloom of solid, pasty, wrought iron comparable to the ball withdrawn from the puddling furnace.

Steel could be made from wrought iron by the crucible process by melting the wrought iron down with the proper amount of carbon. This produced a high-grade, but expensive, crucible steel.

In 1855, Sir Henry Bessemer was granted a patent on his converting ("pneumatic") process, and at approximately the same time the process was developed independently by William Kelly in the United States. These processes were at first unsuccessful; but after Robert Mushet had succeeded in deoxidizing the blown bath by the addition of manganese, the Bessemer process became the first tonnage process for the production of steel. About 1868 the Siemens-Martin open-hearth process, employing the Siemens gas producer and the regenerative furnace, was first operated at Crewe, England. From that time to the present, the open-hearth and Bessemer processes have been the principal methods for making steel.

Without these cheap, large-scale methods of manufacturing steel, the modern "Age of Steel" would not have been possible. It is interesting to note that the original process of producing malleable iron direct from ore has been supplanted by a two-stage process which requires that the iron be first produced as non-malleable cast iron. No direct process has as yet been invented which can compete with the blast furnace. Except for small amounts of ore used as an oxidizing agent in open-hearth and puddling furnaces, all the iron ore mined today goes to the blast furnaces to produce pig iron. (Some ore is smelted in electric smelting furnaces, but these also produce pig iron.)

*Pig iron* or *cast iron* is produced by smelting iron ores in a blast furnace to yield an iron alloy containing about 4 per cent carbon and lesser amounts of silicon, manganese, sulfur, and phosphorus. Various commercial grades of pig are produced, each intended for a specific purpose. The important types of pig iron classed according to uses are listed in Table 1.

The ferroalloys contain elements (manganese, chromium, tungsten, etc.) in addition to those found in ordinary cast iron. They are used principally in recarburizing carbon steels and in the manufacture of alloy steel. They may be made in blast furnaces or electric furnaces.

In 1934, 15,632,619 gross tons of pig iron were shipped from American furnaces together with 428,798 tons of ferroalloys. Tables 2 and 3 show the distribution of these according to grades.

In the United States there were 268 iron blast furnaces in 1934; the geographical distribution of these and the number in blast are shown in Table 4.

The world production of pig iron in 1934 was 61,049,000 metric tons, of which the United States produced about 27 per cent. In 1934, 4096 gross tons of pig were exported, and 114,488 gross tons imported for use. The production of the ten leading countries for 1934 is shown in Table 5.

TABLE 1*

| | |
|---|---|
| 1. Foundry or remelting iron (For iron castings and malleable castings) | Foundry pig<br>Malleable pig<br>Charcoal iron |
| 2. Puddling, forge, or mill iron (For making wrought iron) | |
| 3. Steel-making irons | Bessemer pig<br>Low phosphorus pig<br>Basic iron |
| 4. Ferroalloys | Spiegeleisen<br>Ferromanganese<br>Ferrosilicon<br>Ferrophosphorus<br>Ferrovanadium<br>Ferrotungsten<br>Ferrochromium, etc. |

* Boylston, H. M.: Iron and Steel; John Wiley & Sons, New York, 1936. Reprinted by permission.

TABLE 2 *

PIG IRON SHIPPED FROM BLAST FURNACES IN THE UNITED STATES IN 1934

| Grade | Gross Tons | Average Value per Ton |
|---|---|---|
| Charcoal | 56,753 | $19.88 |
| Foundry | 1,326,861 | 16.04 |
| Basic | 10,204,967 | 16.50 |
| Bessemer | 3,045,365 | 18.22 |
| Low-phosphorus | 148,817 | 21.05 |
| Malleable | 805,686 | 17.78 |
| Forge | 14,587 | 17.49 |
| All others | 29,583 | 22.74 |
| *Totals* | 15,632,619 | 16.93 |

* Minerals Yearbook, 1935; U. S. Bureau of Mines.

## TABLE 3 *

### Ferroalloys Shipped from Furnaces in the United States in 1934

| Variety of Alloy | Gross Tons | Average Value per Ton† |
|---|---|---|
| Ferromanganese | 147,947 | $83.50 |
| Spiegeleisen | 45,769 | 24.10 |
| Ferrosilicon (Si 7% or more) | 181,209 | 40.80 |
| Ferrotungsten | 1,188 | 2,050.00 |
| Ferrovanadium | 864 | 215.00 |
| Other Varieties‡ | 51,821 | |
| *Totals* | 428,798 | |

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* Minerals Yearbook, 1935; U. S. Bureau of Mines.

† Calculated from data in original table.

‡ Ferrochromium, ferromolybdenum, and calcium-molybdenum compounds, ferrophosphorus, ferrotitanium, ferrozirconium, silicomanganese, and silicospiegeleisen, and zirconium-ferrosilicon.

## TABLE 4 *

### Blast Furnaces (Including Ferroalloy Blast Furnaces) in the United States in 1934

| State | In Blast June 30, 1934 | December 31, 1934 | | |
|---|---|---|---|---|
| | | In | Out | Total |
| Alabama | 10 | 6 | 16 | 22 |
| Colorado | 1 | | 3 | 3 |
| Illinois | 6 | 5 | 20 | 25 |
| Indiana | 6 | 5 | 13 | 18 |
| Kentucky | 2 | 1 | 1 | 2 |
| Maryland | 3 | 3 | 3 | 6 |
| Massachusetts | | | 1 | 1 |
| Michigan | 6 | 5 | 3 | 8 |
| Minnesota | | | 3 | 3 |
| Missouri | | | 1 | 1 |
| New York | 7 | 4 | 15 | 19 |
| Ohio | 26 | 19 | 36 | 55 |
| Pennsylvania | 26 | 17 | 73 | 90 |
| Tennessee | 1 | | 5 | 5 |
| Utah | 1 | 1 | | 1 |
| Virginia | | | 6 | 6 |
| West Virginia | 3 | 2 | 1 | 3 |
| *Totals* | 98 | 68 | 200 | 268 |

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* Minerals Yearbook, 1935; U. S. Bureau of Mines.

TABLE 5 *

PIG IRON (INCLUDING FERROALLOYS) PRODUCED IN 1934
(Metric Tons)

| Country | Metric Tons | Per Cent of Total |
|---|---|---|
| 1. United States | 16,398,077 | 26.9 |
| 2. Germany<br>(Including the Saar) | 10,567,326 | 17.4 |
| 3. U. S. S. R. | 10,400,000 | 17.0 |
| 4. France | 6,155,000 | 10.1 |
| 5. Great Britain | 6,074,455 | 10.0 |
| 6. Belgium | 2,307,289 | 3.6 |
| 7. Luxemburg | 1,955,258 | 3.2 |
| 8. Japan | 1,720,000 | 2.8 |
| 9. British India | 1,100,000 | 1.8 |
| 10. Italy | 600,000 | 0.9 |
| All Others | 3,771,595 | 6.3 |
| *Totals* | 61,049,000 | 100.0 |

* Minerals Yearbook, 1935; U. S. Bureau of Mines.

*Steel* is produced by refining pig iron, by remelting steel scrap, or by a combination of these methods. The refining may be done in one of the following ways:

1. Refining pig iron and steel scrap by the basic open-hearth process to produce basic open-hearth steel.
2. Refining pig iron by the acid Bessemer process to produce Bessemer steel.
3. Refining pig iron and scrap in the acid open-hearth furnace to make acid open-hearth steel.
4. Duplexing—refining by the duplex process in which the product of the acid Bessemer is given additional refining in a basic open-hearth furnace.
5. Refining high-phosphorus pig in the basic Bessemer converter (not used in the United States).

These five processes represent the important tonnage process for steel making. Higher-quality steels are made by one of the two processes:

6. Crucible process, in which high-grade wrought iron is melted down with carbon in small crucibles. At present the amount of crucible steel produced in the United States is almost negligible.

7. Refining pig or scrap in electric furnaces. This is the most important method of producing high-quality steel, and the larger part of the electric steel output is alloy steel.

TABLE 6*

Production of Steel Ingots and Castings in the United States for 1934

| Process | Long Tons | Per Cent of Total |
|---|---|---|
| Basic open-hearth | 23,256,417 | 89.2 |
| Acid Bessemer | 2,162,357 | 8.3 |
| Electric steel | 361,296 | 1 4 |
| Acid open-hearth | 274,688 | 1.1 |
| Crucible | 531 | |
| *Totals* | 26,055,289 | 100.0 |

* Minerals Yearbook, 1935; U. S. Bureau of Mines.

The importance of steel scrap as a raw material is shown by the fact that steel production exceeded the pig-iron production in 1934 by more than 9,000,000 long tons.

*Wrought iron* is a slag-bearing malleable iron containing very little carbon. It is manufactured (1) by refining pig iron in a puddling furnace, or (2) by shotting metal from the Bessemer converter through a bath of siliceous slag (Aston process). *Ingot iron* is commercially pure iron, with total impurities $< 0.10$ per cent, which is made by a special basic open-hearth process.

## COPPER

Copper was known to prehistoric peoples, and probably both copper and iron were first obtained from native metals. Copper occurs in some ore deposits as native copper; and although iron does not occur native as an ore mineral, it is sometimes found as metallic iron in the form of meteorites. The early metallurgists probably smelted the oxidized ores to get black copper. Later they learned to roast the sulfide ores and smelt the roasted product. Water leaching of oxidized copper was also known in ancient and medieval times. Two important processes which had a great influence on the metallurgy of copper are modern developments—the adaptation of the Bessemer converter to the treatment of copper matte, and the use of electrolytic refining and precipitation.

At the present time the following four methods are used for recovering copper from its ores and concentrates:

1. Matte smelting of sulfide ores and concentrates, converting the matte to blister copper, followed by fire and electrolytic refining of the blister copper. Electrolytic refining is employed only for copper which contains precious metal.

2. Leaching of copper ores with (*a*) dilute sulfuric acid, (*b*) ferric salts and sulfuric acid, or (*c*) ammonia and ammonium carbonate, followed by chemical or electrolytic precipitation of the dissolved metal. The copper in ammoniacal solution is precipitated as $CuO$ by simply heating the solution to drive off $NH_3$ and $CO_2$, and the precipitate is treated in a copper smelter. Chemical precipitation, or cementation, produces impure cement copper which is usually sent to a smelter for melting and refining. Electrolytic precipitation produces high-grade copper which is of the same quality as that produced by electrolytic refining.

3. Reverberatory smelting of native copper ores and concentrates. This is essentially a simple melting process in which the copper is liquefied and the accompanying gangue minerals are fluxed and removed in a slag. Generally, the impure copper is fire refined (to

TABLE 7 *

WORLD'S COPPER PRODUCTION IN 1934

| Country | Short Tons | Per Cent of Total |
|---|---|---|
| Africa | 292,525 | 21.2 |
| Chile | 282,303 | 20.4 |
| United States | 232,299 | 16.8 |
| Canada | 183,415 | 13.3 |
| Other Europe | 124,536 | 9.0 |
| Japan | 66,100 | 4.8 |
| Mexico | 52,116 | 3.8 |
| U. S. S. R. | 48,587 | 3.5 |
| Peru | 30,373 | 2.2 |
| Germany | 26,455 | 1.9 |
| Elsewhere | 43,220 | 3.1 |
| *Totals* | 1,381,929 | 100.0 |

* Mining Outlook for 1936; Engineering and Mining Journal, Vol. 137, No. 2, February, 1936. Reprinted by permission.

produce "Lake copper"), since the copper does not usually carry enough precious metals to warrant electrolytic refining.

4. Blast furnace smelting of oxidized copper ores to produce black copper. The black copper may be refined by fire refining or fire refining and electrolysis. The blast-furnace smelting of copper sulfides to produce matte is practically obsolete in the United States.

In 1932 [1] the apparent consumption of copper in the United States was 250,000 metric tons, production 216,000 tons, imports 178,000 tons, and exports 144,000 tons. The imports were principally in the form of refined copper from Chile and Canada, and crude copper from Chile, Peru, Mexico, and Africa. Practically all the export copper, both refined and crude, went to Europe.

## LEAD

Lead is another metal which was known in ancient times. Because of the low melting point of the metal and the ease with which its ores can be reduced, the metallurgy of lead had a comparatively early development. The metallurgy of lead has always been very closely connected to that of silver, because most lead ores contain considerable amounts of silver. In many instances the problem of removing the silver from lead bullion has been of more importance than the reduction of the metal itself.

The reduction smelting of oxidized lead ores and the roast-reaction treatment of sulfide ores were the first methods used for the recovery of lead. Today there are a few *ore hearths* for the treatment of high-grade silver-free ores, but practically all lead comes from the lead blast furnace.

Lead concentrates are sintered and roasted in Dwight-Lloyd machines and smelted in the lead blast furnace (reduction smelting). The crude lead may be refined or softened by one of a number of fire-refining operations. Lead bullion which is refined by fire methods must be desilverized by the Parkes process. The Betts electrolytic refining process removes both base metal impurities and precious metals.

In 1932 [2] the apparent consumption of lead in the United States was 275,000 metric tons, and production was 265,000 tons. Exports

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[1] Mining Outlook for 1936; Engineering and Mining Journal, Vol. 137, No. 2, February, 1936. Reprinted by permission.

[2] Mining Outlook for 1936; Engineering and Mining Journal, Vol. 137, No. 2, February, 1936.

amounted to 21,000 tons, principally to Japan, and imports were 31,000 tons. Imported lead came largely from Mexico and Newfoundland, with a little from Canada and Europe.

TABLE 8 *

World's Lead Production in 1934

| Country | Short Tons | Per Cent of Total |
|---|---|---|
| United States | 330,911 | 22.2 |
| Australia | 226,336 | 15.1 |
| Mexico | 193,547 | 12.9 |
| Canada | 159,833 | 10.7 |
| Other Europe | 154,425 | 10.3 |
| Germany | 132,276 | 8.9 |
| Spain | 82,516 | 5.5 |
| Burma | 80,437 | 5.4 |
| Italy | 46,241 | 3 1 |
| U. S. S. R. | 29,954 | 2 0 |
| Elsewhere | 58,267 | 3.9 |
| *Totals* | 1,494,743 | 100.0 |

* Mining Outlook for 1936; Engineering and Mining Journal, Vol. 137, No. 2, February, 1936 Reprinted by permission.

## ZINC

Zinc was not known as a separate metal until 1746, although brass had been made much earlier than this by smelting together oxidized zinc and copper ores, or by adding oxidized zinc ore and carbon to molten copper. The extraction of zinc by distilling the metal from a mixture of zinc oxide and carbon in a heated retort was the first successful method for producing zinc metal, and today is still the most important process.

Zinc smelting, as it is often called, consists of heating dead-roasted sulfide concentrates mixed with carbon in a closed refractory retort. The zinc is reduced to metal, vaporized, and the vapor is then condensed to liquid metal. The second method of recovering zinc is by the electrolysis of a purified sulfate solution obtained by leaching roasted zinc concentrates with sulfuric acid. This process yields a remarkably pure metal, and commercial electrolytic zinc is being produced today which is guaranteed to contain 99.9975 per cent Zn.

In 1932[3] the United States apparently consumed 255,000 metric tons of zinc, and produced 259,000 tons. About 2000 tons were imported from Mexico, and 6000 tons exported to Europe and Asia.

TABLE 9 *

WORLD'S ZINC PRODUCTION FOR 1934

| Country | Short Tons | Per Cent of Total |
|---|---|---|
| United States | 366,933 | 28.2 |
| Belgium | 192,885 | 14.8 |
| Canada | 134,926 | 10 4 |
| Poland | 102,522 | 7.9 |
| Germany | 80,358 | 6.2 |
| Australia | 59,353 | 4.6 |
| Great Britain | 57,344 | 4.4 |
| France | 56,410 | 4.3 |
| Mexico | 40,354 | 3.1 |
| Rhodesia | 21,882 | 1.6 |
| Elsewhere | 188,628 | 14.5 |
| *Totals* | 1,301,595 | 100.0 |

* Mining Outlook for 1936; Engineering and Mining Journal, Vol. 137, No. 2, February, 1936. Reprinted by permission.

## GOLD

Gold was one of the first metals known to man. Undoubtedly the first recovery of gold was from placer deposits, but apparently the mining of vein ores of gold also was carried out in prehistoric times. Gold practically always occurs as native metal, and the metallurgical treatment for free milling ores containing coarse gold is extremely simple. The ancients dealt entirely with this type of ore and were not concerned with the problems of treating base ores and ores containing finely disseminated gold.

Today, gold is recovered (1) by the dressing, cyanidation, and amalgamation of dry gold ores; (2) by the washing of placer gravels; and (3) by the refining of base bullion. Table 10 lists the production of gold in 1934 by the various countries of the world.

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[3] Mining Outlook for 1936; Engineering and Mining Journal, Vol. 137, No. 2, February, 1936.

TABLE 10 *

World Production of Gold in 1934

| Country | Fine Ounces | | Per Cent of World Total | |
|---|---|---|---|---|
| North America | 6,385,246 | | 22.8 | |
| United States | | 2,742,161 | | 9.8 |
| Canada | | 2,969,680 | | 10.6 |
| Mexico | | 661,405 | | 2.4 |
| Newfoundland | | 12,000 | | |
| Central America | 130,000 | | 0.5 | |
| South America | 1,120,517 | | 4.0 | |
| Europe | 4,886,627 | | 17.5 | |
| Russia and Siberia | | 4,312,770 | | 15.4 |
| Other Europe | | 573,857 | | 2.1 |
| Asia | 1,861,061 | | 6.7 | |
| British India | | 322,193 | | 1.2 |
| East Indies | | 66,295 | | 0.2 |
| Japan and Chosen | | 841,385 | | 3.0 |
| Philippines | | 340,316 | | 1.3 |
| China and others | | 290,872 | | 1.0 |
| Oceania | 1,256,918 | | 4.3 | |
| Australia | | 870,678 | | 3.1 |
| Fiji | | 1,833 | | |
| Tasmania | | 5,622 | | |
| New Guinea | | 211,099 | | 0.7 |
| Papua | | 7,438 | | |
| New Zealand | | 160,248 | | 0.5 |
| Africa | 12,340,549 | | 44.2 | |
| Transvaal | | 10,479,857 | | 37.5 |
| Rhodesia | | 693,265 | | 2.5 |
| West Africa | | 384,268 | | 1.4 |
| Congo, Egypt, etc | | 783,159 | | 2.8 |
| *Totals* | 27,980,918 | | 100.0 | |

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* Mining Outlook for 1936; Engineering and Mining Journal, Vol. 137, No. 2, February, 1936. Reprinted by permission.

## SILVER

Silver is another metal which has been known since prehistoric times. Originally most of the silver was obtained from lead-silver ores, and today the bulk of the world's silver is still produced from base-metal ores.

Silver is produced principally by the refining of base bullion, although some silver is produced by the cyanidation or amalgamation of dry ores. Table 11 gives the world's silver production for 1934.

TABLE 11 *

WORLD'S SILVER PRODUCTION IN 1934

| Country | Fine Ounces | Per Cent of Total |
|---|---|---|
| Mexico | 74,142,000 | 40.8 |
| United States | 26,441,000 | 14.6 |
| Canada | 16,441,361 | 9.0 |
| Europe | 14,902,458 | 8.2 |
| Australia | 11,900,404 | 6.5 |
| Peru | 9,000,000 | 5.0 |
| Other America | 7,982,000 | 4.4 |
| Japan | 6,920,000 | 3.8 |
| India | 6,850,000 | 3.8 |
| Africa | 5,233,771 | 2.9 |
| Other Asia | 1,775,000 | 1.0 |
| *Totals* | 181,587,994 | 100.0 |

* Mining Outlook for 1936; Engineering and Mining Journal, Vol. 137, No. 2, February, 1936. Reprinted by permission.

## NICKEL

Metallic nickel was discovered in 1751, but there is reason to believe that it was used before this time as an alloying ingredient. The reduction of nickel from its ores is a more difficult problem than the reduction of the other common metals. This fact has retarded the use of this metal until quite recently.

Nickel may be produced by roasting the sulfides to the oxide, and reducing the oxide to a metal with C or CO. The present practice is to smelt to a matte in either a blast furnace or a reverberatory furnace, and then blow the matte to "white metal" in a converter. The matte (which usually consists principally of $Ni_3S_2$ and $Cu_2S$) is then cast into solid pieces. The subsequent treatment of the matte to recover metallic nickel and separate it from the copper is quite complex, and several different methods have been developed. Three important types of treatment are:

1. *The Orford ("tops-and-bottoms") process.* If copper and nickel sulfides are fused with sodium sulfide, the melt separates into two layers; the upper layer consists principally of copper and sodium sulfides, and the lower layer consists primarily of nickel sulfide. The fused sulfides are allowed to solidify, and the two layers are then broken apart. The fusion is repeated with the $Ni_3S_2$ to remove all

the copper. The "tops" may be leached with water to remove the $Na_2S$ and the residual $Cu_2S$ (which carries the gold and silver) melted and blown in a converter. The $Ni_3S_2$ "bottoms" are roasted to NiO, leached to remove impurities, and heated with carbon to reduce the oxide to metallic nickel.

2. *The Mond process.* The copper-nickel matte is crushed and dead roasted. The calcine is then leached with dilute sulfuric acid to leach out the copper. The residual NiO is heated to 350° C. in an atmosphere of water gas to reduce the oxide:

$$NiO + H_2 \rightarrow Ni + H_2O$$

Then CO gas at 50° to 100° C. is passed over the reduced nickel. The reaction produces volatile, gaseous, nickel carbonyl which passes out in the gases

$$Ni + 4CO \rightarrow Ni(CO)_4$$

When this gas is heated to 180° C. and passed over shot nickel, it decomposes into Ni and CO, and the metallic nickel is deposited on the surface of the nickel pellets, causing them to grow in size.

3. *The Hybinette process.* The copper-nickel matte is granulated and roasted to about 5 or 10 per cent S. This roasted matte is then leached with sulfuric acid to remove the bulk of the copper and leave a residue containing about 65 per cent Ni, 3 to 8 per cent S, 20 to 25 per cent Cu, and the rest Fe. This residue is melted and cast into anodes. When these anodes are electrolyzed, both copper and nickel are dissolved at the anode, and the anolyte is then passed over shot nickel or granulated matte to cement out the copper. The purified nickel sulfate solution (catholyte) then enters the cathode compartment where the nickel is deposited on the cathode. Anolyte and catholyte are kept separate by means of canvas bags which surround the cathodes and serve as porous diaphragms.

Impure nickel produced by processes 1 or 2 may be refined electrolytically, if it contains appreciable quantities of precious metals.

The bulk of the world's nickel is produced from the copper-nickel sulfide ores of the Sudbury, Ontario, district. Deposits in Norway, New Caledonia, and India have produced nickel on a commercial scale, but they are not so important as the Canadian deposits.

Practically all the nickel consumed in the United States is imported, and American production of primary nickel is negligible. In 1932 Canada produced 14,600[4] metric tons of nickel, of which 7500

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[4] Mining Outlook for 1936; Engineering and Mining Journal, Vol. 137, No. 2, February, 1936.

tons were exported to the United States, 6900 tons to Europe, and 200 tons to Japan. In the same period New Caledonia produced 2900 tons, all of which was exported to Europe, and India produced 700 tons which also were shipped to Europe. Norway did not show any production for 1932.

## TIN

Tin was known to the ancients, and it probably was used as an alloying ingredient in copper alloys long before it was known as a separate metal.

The only commercial ore mineral of tin is $SnO_2$, cassiterite, which is found both in vein ore and placer deposits. Tin concentrates are treated by reduction smelting in either blast or reverberatory furnaces, and the impure tin is fire-refined.

The United States is a large consumer of tin, but no primary tin is produced in the United States, all of it being imported. Tin differs from nickel, however, in that commercial tin deposits are widely scattered over the globe.

TABLE 12 *

WORLD'S TIN PRODUCTION IN 1934

| Country | Long Tons | Per Cent of Total |
|---|---|---|
| Malaya | 34,127 | 29.9 |
| Bolivia | 20,634 | 18.1 |
| Netherland East Indies | 18,418 | 16.1 |
| Siam | 10,587 | 9.4 |
| China | 8,500 | 7.5 |
| Nigeria | 4,935 | 4.3 |
| Congo | 4,602 | 4.0 |
| Burma | 3,600 | 3.2 |
| Australia | 3,000 | 2.6 |
| Great Britain | 1,812 | 1.6 |
| Elsewhere | 3,821 | 3.3 |
| *Totals* | 114,036 | 100.0 |

* Mining Outlook for 1936; Engineering and Mining Journal, Vol. 137, No. 2, February, 1936. Reprinted by permission.

In 1932 [5] the United States imported 35,400 metric tons of tin; about 8700 tons from Europe, 3900 tons from China, and 22,800 tons

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[5] Mining Outlook for 1936; Engineering and Mining Journal, Vol. 137, No. 2, February, 1936.

from British Malaya. In this period all the Bolivian and African production was shipped to Europe as ore or concentrate.

### ALUMINUM

Aluminum was first discovered in 1827, but not until about 1885 was a commercial method discovered for its extraction. In 1856 the price of aluminum was $90 a pound; in 1886, $5 a pound; and in 1933, 23 cents a pound.

Aluminum is produced by refining crude bauxite to give pure anhydrous $Al_2O_3$, dissolving the $Al_2O_3$ in molten cryolite, and electrolyzing between carbon electrodes. A considerable quantity of aluminum is produced in the United States, and in addition some is imported.

TABLE 13 *

WORLD'S PRODUCTION OF ALUMINUM IN 1934

| Country | Metric Tons | Per Cent of Total |
|---|---|---|
| Germany | 37,158 | 22.0 |
| United States | 33,646 | 20.0 |
| France | 16,300 | 9.6 |
| Canada | 15,500 | 9.2 |
| Norway | 15,500 | 9.2 |
| U. S. S. R | 14,400 | 8.5 |
| Great Britain | 12,500 | 7.4 |
| Italy | 12,400 | 7.3 |
| Switzerland | 8,100 | 4.8 |
| Austria | 2,100 | 1.2 |
| Others | 1,396 | 0.8 |
| *Totals* | 169,000 | 100.0 |

* The Mineral Industry in 1934; McGraw-Hill Book Co., New York. Reprinted by permission.

In 1934 the United States[6] imported about 9100 short tons of aluminum, largely from Norway, Canada, Switzerland, and Germany. In the same period the United States exported about 4400 tons of aluminum, practically all of which went to Japan. It has been estimated that about 1 pound of secondary aluminum is used in the United States for each pound of primary aluminum consumed.[7]

Production of aluminum requires cheap and abundant electric power, which accounts for the large production by Norway, Italy, and Switzerland.

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[6] The Mineral Industry in 1934; McGraw-Hill Book Co., New York.

[7] The Mineral Industry in 1934; McGraw-Hill Book Co., New York.

## ANTIMONY

Antimony was discovered in 1450. Some antimony is found in lead and copper ores and is recovered in softening and refining operations. Often the antimonial material which collects about a lead smelter will be smelted with lead ore to produce antimonial "hard" lead. Most of the straight antimony ores contain stibnite, $Sb_2S_3$, as the economic mineral. Relatively pure $Sb_2S_3$ may be obtained by liquating (melting) the stibnite away from the associated minerals. Crude antimony ore may be smelted directly in a blast furnace; rich ores may be fused with iron in crucibles or reverberatory furnaces to produce metallic antimony:

$$Sb_2S_3 + 3Fe \rightarrow 2Sb + 3FeS$$

In other cases the sulfides are roasted under carefully controlled conditions to produce $Sb_2O_3$ which is volatilized and condensed. The oxide is then reduced by reduction smelting.

TABLE 14 *

WORLD'S PRODUCTION OF ANTIMONY IN 1933

(Exclusive of antimonial lead ores)

| Country | Metric Tons of Recoverable Metal | Per Cent of Total |
|---|---|---|
| China | 13,933 | 74.0 |
| Mexico | 1,950 | 10.4 |
| Bolivia | 1,896 | 10.1 |
| United States | 533 | 2.8 |
| Italy | 370 | 2.0 |
| Others | 133 | 0.7 |
| *Totals* | 18,815 | 100.0 |

* The Mineral Industry in 1934; McGraw-Hill Book Co., New York. Reprinted by permission.

In 1932[8] the United States consumed about 3000 metric tons of antimony, of which 300 tons were domestic production. About 1700 tons were imported from China, 900 tons from Mexico, and 100 tons from Bolivia. About 200 tons of the Chinese production went to Japan, and the remaining 7200 tons to Europe. Most of the Bolivian production and some of the Mexican production was exported to Europe.

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[8] Mining Outlook for 1936; Engineering and Mining Journal, Vol. 137, No. 2, February, 1936.

## CHROMIUM

Chromium was first produced in metallic form in 1798. Little, if any, chromium is ever produced in a form corresponding to the ingots of other metals, and most of the chromium flows through trade channels as chromite or chrome ore. Chromite is used principally in: (1) blast furnace or electric furnace charges when smelting for ferrochromium; this is then used for introducing the metal into alloy steels or alloy cast irons; (2) the manufacture of chromite refractories; and (3) the production of chromium salts for chromium plating. Chromium is another metal which is not produced in the United States to any great extent, although large quantities of it are consumed.

TABLE 15 *

PRODUCTION OF CRUDE CHROMITE IN 1933

| Country | Metric Tons | Per Cent of Total |
|---|---|---|
| U. S. S. R. | 112,728 | 28.5 |
| Turkey | 75,374 | 19.0 |
| New Caledonia | 49,886 | 12.6 |
| Rhodesia | 35,066 | 8.9 |
| Union of South Africa | 34,079 | 8 6 |
| Jugoslavia | 25,463 | 6.4 |
| Cuba | 24,154 | 6.1 |
| Japan | 19,897 | 5.0 |
| British India | 15,775 | 7.0 |
| Others | 3,304 | 0.9 |
| *Totals* | 395,726 | 100.0 |

* The Mineral Industry in 1934; McGraw-Hill Book Co., New York. Reprinted by permission.

In 1932 [9] the United States consumed 90,800 metric tons of chromite, of which only 200 tons were produced domestically. The principal imports were:

| | |
|---|---|
| From Europe | 30,200 tons |
| Turkey | 20,100 tons |
| Africa | 15,700 tons |
| New Caledonia | 11,700 tons |
| India | 8,000 tons |
| U. S. S. R. | 4,900 tons |
| *Total imports* | 90,600 tons |

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[9] Mining Outlook for 1936; Engineering and Mining Journal, Vol. 137, No. 2, February, 1936.

## MANGANESE

Manganese was discovered in 1774. The metal is used principally as ferromanganese (a ferroalloy containing about 80 per cent Mn, 5–6 per cent C, and iron) and spiegeleisen (15–30 per cent Mn, 4.5–5.5 per cent C, and iron). These ferroalloys are manufactured by smelting iron and manganese ores in blast furnaces or electric furnaces, and are used for recarburizing carbon steel and in the manufacture of manganese alloy steel. Minor applications of manganese are the use (1) of manganese dioxide in battery manufacture, and (2) of manganese compounds in the chemical, ceramic, and glass industries. There is no production of manganese metal as ingots. Manganese is another metal which is not produced commercially in the United States to any great extent—most of the manganese used is imported. Manganese usually is transported in the form of ore or concentrate, or as ferroalloys.

TABLE 16 *

WORLD PRODUCTION OF HIGH-GRADE MANGANESE ORE IN 1932

| Country | Metric Tons | Per Cent of Total |
|---|---|---|
| U. S. S. R. | 833,000 | 64.0 |
| British India | 216,009 | 16.6 |
| Africa (Gold Coast) | 51,501 | 4.0 |
| Japan | 20,895 | 1.6 |
| United States | 18,062 | 1.4 |
| Cuba | 9,800 | 0.8 |
| Others | 150,733 | 11.6 |
| *Totals* | 1,300,000 | 100.0 |

* The Mineral Industry in 1934; McGraw-Hill Book Co., New York. Reprinted by permission

In 1932 [10] the United States consumed 133,000 metric tons of manganese ore, of which 18,000 tons were domestic production. Approximately half of the imported ore came from Russia, and the rest from the African Gold Coast, Brazil, Cuba, India, and Puerto Rico.

## MERCURY (QUICKSILVER)

Mercury was known in prehistoric times and is the last on our list of the seven "prehistoric" metals—the others are iron, copper, lead,

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[10] Mining Outlook for 1936; Engineering and Mining Journal, Vol. 137, No. 2, February, 1936.

gold, silver, and tin. The only ore mineral of mercury is cinnabar, HgS, and the metal is extracted by simple heating of the ore which breaks up the compound and distils the metallic mercury. Usually the ore is heated directly without preliminary dressing or other treatment.

TABLE 17 *

WORLD PRODUCTION OF QUICKSILVER IN 1932

| Country | Metric Tons | Per Cent of Total |
|---|---|---|
| Italy | 1,016 | 37.7 |
| Spain | 816 | 30 2 |
| United States | 435 | 16.1 |
| Mexico | 235 | 8.7 |
| Others | 198 | 7.3 |
| *Totals* | 2,700 | 100.0 |

* The Mineral Industry in 1934; McGraw-Hill Book Co., New York. Reprinted by permission

In 1932[11] the United States consumed 720 metric tons of mercury, of which about 440 tons were imported from Europe. The rest was domestic production.

## TUNGSTEN

Tungsten was discovered in 1783. Tungsten passes through trade channels principally as ore or concentrates. The steel industry consumes[12] about 90 per cent of the tungsten used in the United States for the manufacture of alloy steels and high-speed steels. Most of the tungsten used for this purpose is obtained from smelting furnaces as ferrotungsten, an iron-carbon-tungsten alloy containing 75 to 80 per cent tungsten.

Metallic tungsten is used for lamp filaments and similar purposes. The metal is produced by the reduction of chemically purified $WO_3$ in a current of hydrogen, and the resulting metallic powder is sintered and mechanically worked to give a coherent bar of metal.

In 1932[13] about 4600 metric tons of 60 per cent $WO_3$ concentrates were consumed in the United States, of which 3600 tons were domestic

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[11] Mining Outlook for 1936; Engineering and Mining Journal; Vol. 137, No. 2, February, 1936.

[12] The Mineral Industry in 1934; McGraw-Hill Book Co., New York.

[13] Mining Outlook for 1936; Engineering and Mining Journal, Vol. 137, No. 2, February, 1936.

and the rest imported from China and Australia. China and India are the largest producers of tungsten, and most of their product is exported to Europe.

## MAGNESIUM

Magnesium was first prepared as a coherent metallic mass in 1831, and its commercial production has been developed quite recently. The first commercial magnesium produced in the United States cost $10 per pound, and in 1933 the price was down to 30 cents per pound. In 1928 the United States' production of new ingot magnesium was 530,782 pounds as compared with 4,249,838 pounds[14] in 1934. The principal use of magnesium is in the field of light metal alloys where it is a strong competitor of aluminum.

Magnesium is extracted by the electrolysis of purified, anhydrous $MgCl_2$ in a bath of molten NaCl and KCl, or by the electrolysis of purified MgO dissolved in a bath of molten alkali fluorides.

Imports of metallic magnesium into the United States are negligible, only 661 pounds having been imported in 1934.[15]

## OTHER METALS

**Cobalt.**—The metallurgy of cobalt is rather complex, principally because cobalt is usually found in complex ores and must be separated from other metals and non-metals. The United States produces no cobalt, and most of the world's supply comes from the Belgian Congo, Rhodesia, Morocco, Sweden, and Canada. The Canadian cobalt is associated with the copper-nickel ores of Ontario.[16]

**Cadmium.**— Cadmium is practically always found in zinc ores, and the metal is a by-product from zinc smelters, electrolytic plants, and refineries. In 1934[17] the United States produced over 2,700,000 pounds of cadmium, as compared with 500,000 pounds produced by France, the next largest producer.

**Molybdenum.**—Molybdenum is of importance in the manufacture of alloy steels, and its importance is increasing. The United States is the leading producer of molybdenum, producing[18] 85 per cent of the world's total in 1934.

**Arsenic.**—The production and use of metallic arsenic is of very little importance. Most arsenic is used in the form of chemical com-

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[14] The Mineral Industry in 1934; McGraw-Hill Book Co., New York.

[15] The Mineral Industry in 1934; McGraw-Hill Book Co., New York.

[16] The Mineral Industry in 1934; McGraw-Hill Book Co., New York.

[17] The Mineral Industry in 1934; McGraw-Hill Book Co., New York.

[18] The Mineral Industry in 1934; McGraw-Hill Book Co., New York.

pounds as insecticides, weed killers, wood preservatives, and in the glass industry. Practically all arsenic is a by-product from the smelting of copper and lead ores. The United States is the largest producer of arsenic in the world.

**Platinum.**—Platinum is usually associated with smaller amounts of the platinum group of metals—palladium, rhodium, iridium, osmium, and ruthenium; and these metals are obtained in the refining of platinum. Most of the platinum produced in the United States is a by-product from gold and copper ores, and placer gold deposits. Most of the deposits which produce only platinum metals are placer deposits. In 1933 [19] the U. S. S. R. produced 100,000 troy ounces of platinum metals; Canada, 55,700 ounces; Colombia, 44,500 ounces; South Africa, 9000 ounces; and the United States, 3000 ounces.

## EXERCISES

1. Prepare various statistical tables and/or graphs showing the production of certain metals over a period of years:

(*a*) by countries (political units);
(*b*) by continents (geographical units);
(*c*) by various states of the United States.

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[19] Minerals Yearbook, 1935; U. S. Bureau of Mines.

# INDEX

# ANSWERS TO EXERCISES

II.— 1—$8.55 \times 10^{18}$; $8.55 \times 10^{12}$
III.— 1—65% and 35%; 50.3% and 49.7%
IV.— 1—134,000 p. s. i.
— 2—1 to 8.17
— 5—54.7% Pb; 45.3% Sb
— 7—61,820 pound-calories
VIII.— 1—0.0498%; 498; $508.55
IX.— 1—28.6 to 1; 91.9%; 2.025% Pb
— 2—354 cm./sec.; 1.99 mm.; 1.99 to 1
X.— 2—99.48%; 0.4449 pounds per ton of ore
XI.— 1—70.6
— 2—11.2
— 3—6425
— 4—158
— 5—39.5 liters $N_2$; 5.5 liters $O_2$; 4.0 liters $CO_2$
— 6—$Fe_2O_3$ – 81.9%; $SiO_2$ – 6.7%; $FeS_2$ – 11.4%
— 7—3,260,000; 2560; 4480; 1630
— 8—9.1%
— 9—36,800,000; 763,000; 2,750,000; 4
XII.— 2—6100 Cal. per Kg:
— 3—1052 Cal./cu. m., 118.3 B.t.u./cu. ft.; 2807, 316
— 4—2280° C.
— 6—25.2%
— 8—586
— 9—2031 Cal./cu. m.; 50% CO. 20% $H_2$, 30% $N_2$
—10—5480° C.
—12—1.096
—13—0.0000875; 19.8; 11%
—14—0.00392; −0.000000588
—15—227.3°
—16—0.645
—17—0.695°; 7.1°
—18—2.38
—19—0.851
—21—1828° C.

## ANSWERS TO EXERCISES—*Continued*

XII.—22—12.1
—23—491° R.; 29.9 in.
—24—335° C.
XIII.— 4—41.1; 21.2%
— 8—39.5%
— 9—77.6%
—10—1.72; 2; 0.775
—11—$SiO_2$ – 48.7%; $Al_2O_3$ – 14.4%; CaO – 12.0%; MgO – 22.6%; MnO – 2.3%
—12—483 Cal.
—13—0.244
—17—16.3 min.
—19—157 ft.; 3.5 ft.
XIV.— 2—0.00785 mm.
— 5—50,158
XV.— 2—352
— 3—51.2
— 4—1030
— 5—$13.01