PRINCIPLES OF METALLURGY

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PRINCIPLES OF METALLURGY

AN INTRODUCTION TO THE
METALLURGY OF THE METALS

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To his Wife
MARION CUNNINGHAME FULTON
THIS BOOK IS DEDICATED BY
THE AUTHOR

PREFACE

THERE is published in the United States no work which covers the subject of introductory or general metallurgy. The classic on this subject, "An Introduction to the Study of Metallurgy," by the distinguished late Sir William Roberts-Austen, has not been revised for a number of years.

The author in his work in teaching metallurgy has frequently felt the lack [illegible] suitable reference and text-book on the important subject of [illegible]troductory metallurgy, and knows that this want is shared by others. This volume endeavors to supply this want.

The subject is treated from the modern view-points, and metallurgists in general will probably find something of interest in the volume, particularly in the chapters on alloys, measurement of high temperatures, slags, and mattes. The sources of information are fully covered by references in foot-notes, by means of which the author acknowledges his indebtedness to the many workers in the scientific fields which have a bearing on the subject in hand. For material for the chapter on "Metals from the Historic Point of View" is derived in part from the works of Roesing and Neumann, to whom the author expresses his indebtedness. For material in the chapter on "Slag" the author has drawn largely on the invaluable work of J. H. L. Vogt, which has been so far unrecognized in this country. The following firms and individuals have kindly assisted by the loan of photographs and drawings: Mr. Edward S. Shephard of Denver; The Allis Chalmers Company of Milwaukee; The United-Otto By-product Coke Oven Company of New York; The Colorado Iron Works Company of Denver; The Crosby Manufacturing Company of Boston; and the Wellman, Seaver, Morgan Company of Cleveland.

The author also desires to express his indebtedness to Mr. H. M. German for certain drawings in connection with the iron blast furnace; to Mr. O. A. Anderson for drawings of alloy curves, and to Miss Lucretia Charlotte Quist and Miss Della Haft for invaluable aid in the preparation of manuscript.

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CHARLES H. FULTON.

RAPID CITY, *July 19, 1910.*

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CHAPTER I

THE METALS AND METALLURGY FROM THE HISTORIC POINT OF VIEW

Introduction. — The present age is preëminently a metallic one. The advanced state of material civilization is largely due to the availability of enormous stores of metals, chiefly iron, without which such potent agents of progress as the railroad, the great ocean steamships, bridges, submarine tunnels, and machinery in general would be impossibilities. It is a most noteworthy fact that the use of metals on a large scale as a structural material is the accomplishment of less than a century of time in the long history of mankind. The art of metallurgy as practised during the centuries preceding the great scientific awakening of the last one hundred years was more in the nature of a craft, the rules of which had been handed down from father to son for countless generations. New discoveries and new processes were few and far between and then were based most frequently on accident rather than on premeditated improvements. The advent, however, during the eighteenth century of the new era in the physical sciences gave an impetus to the metallurgy of the economic metals, which, while slight at first, for the art seemed not to see the significance of the bearing of physics and chemistry on metallurgy, rapidly grew, until at the present day metallurgic processes are carried out for the most part on a rigorously scientific basis, resulting in an enormous production, at low cost relatively speaking, and of such composition or such purity as to make the metals available for almost any purpose desired in industry or the arts.

Mining, the sister art of metallurgy, developed simultaneously by the application of high explosives and later by the mechanical rock drill and other machinery, was enabled to respond to the demand for greatly increased quantities of raw materials.

The Metals in Prehistoric Times. — As to how man first came to a knowledge of the common metals is shrouded in the obscurity of the dawn of civilization. Hesiod, the Greek poet (about 700 B.C.), outlining in fable the early history of man, divides it into periods. The first a *golden age*, of the nature of paradise of the Old Testament, is followed by a *silver age*, which, while still ideal, was darkened by some of man's troubles. This was followed by an age of dissension and strife, in which man became savage, strong, and fierce, and was armed with keen *bronze* weapons. This age was followed by one peopled with heroes, strong and warlike, most of whom, however, were exterminated in the Trojan war. This age was followed by the present one — the *iron age*, with its trials, tribulations, and sorrows. The fable seems to have given rise to the common belief, held for a long time, that man became acquainted with metals in this order: gold, silver, bronze (an alloy of copper and tin), and finally with iron.

Archeological research has, however, proved this order of discovery as untrue. It is probable that owing to its brilliant color, and that it occurs so frequently in the metallic state, and is widely distributed, gold was the first metal known to the human race. Primitive man, originating possibly in southeastern Asia,[1] after passing through his early evolution and becoming familiar with weapons which he fashioned first from wood and bone and later from stone, and with other implements for his simple needs, wandering along streams, was probably attracted by the glitter of golden grains in the sand and gravel bars of certain streams. But gold served chiefly as an ornamental material and was not suitable for weapons or utensils. As men multiplied and spread from the region in which they originated, some into lands rich in mineral wealth, others into regions in which it was absent, and there passed through stages of evolution in accordance with their environment, it is evident that the first mentioned would become familiar with certain metals, in the course of time, while the second would not know of their existence except as communication might finally become established between the two peoples. The knowledge of the use of metals of course demands a decidedly advanced stage of primitive culture, and this could be attained only by certain favorable environment, which was not possessed equally by the scattered masses of mankind. It is

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[1] The Pithecantropus erectus was found in Java.

therefore fallacious to assume in the general history of mankind the existence of a stone age, a copper age, a bronze age or an iron age, as coincident in time, over the surface of the earth.

If there be a definite succession of these ages, it must be applied to distinct peoples, and not to humanity in general, for even at the present day isolated races and peoples are still in their stone age, as for example in certain portions of Africa, and in islands of the Pacific, while a few thousand miles away are peoples in the height of civilization and culture with all the products of the arts and the learning of the sciences at their command.

Some archeologists and anthropologists still assume that with any given people their stone age was succeeded by a bronze or copper age, and this by an iron age, but here again it must be considered that the question of whether copper or iron was the first to be used is largely dependent upon the nature of the ore deposits that were available. Looking at the question from the standpoint of economic geology and metallurgy, the facts stand out, that easily reducible iron ores are widely scattered over the earth's surface, and that the production of metallic iron from them is a comparatively simple matter, requiring but a low temperature and very primitive furnaces, to get an iron sponge which can be worked and forged into shape. The reduction of sulphide copper ores, on the other hand, in order to get a workable product, is much more difficult, requiring a number of complex operations and a high temperature and consequently greater metallurgical skill. Native copper in workable quantities occurs but in few places, viz., in Michigan. Where it does occur the probabilities are great that its use preceded that of iron. In certain regions oxidized copper ores of great purity are found to a limited extent, such as occur in Arizona, and probably occurred in the Sinai Peninsula. These can be reduced to metal by a simple smelting process. In this case copper was probably the first useful metal known, as seems to be the case with the ancient Egyptians.

Generally speaking, however, iron was probably earlier known to the majority of mankind than copper. As regards bronze, an alloy of copper and tin, it is to be very greatly questioned whether its use was known to prehistoric peoples. It requires a very considerable metallurgical skill to prepare bronze and cast and work it, and the tin required is found in comparatively few places. The invention of bronze is probably to be placed in Mesopotamia, Ancient Babylonia, with the Semitic race, from whence it spread over other lands through commerce. The fact that in some so-called prehistoric graves, stone and bronze implements are found, with the practical absence of iron, can in no instance be considered valid evidence that a bronze age succeeded the stone age, for where these bronze remains are found they almost invariably show themselves to be of superior character and traceable in design and form to those used by some cultured nation at a distance. An instance of this are the remains found in the Lake Dwellings of Switzerland, where certain excavations yield stone implements only, while others those of stone and bronze, but the bronze implements are of such perfection and of clearly Oriental and Etruscan character, that there is but little doubt they were introduced through commerce. Incidentally there are in the same vicinity remains of most ancient, primitive iron smelting furnaces, near which iron and stone tools are found. It is not surprising that in the finds of ancient remains, bronze or copper should be predominant, when the ready corrodibility of iron is considered. Under certain climatic conditions less than a thousand years are amply sufficient to remove all traces of iron remains.

With these facts in view it seems very probable that when the various peoples possessing primitive culture entered into their historic era, viz., that era of which definite records exist, they were acquainted with certain of the common metals, gold, iron, and copper, and somewhat more rarely with silver, lead, and tin, dependent to a large degree on their environment.

The Metals in Early Historic Times.—The earliest known records of a civilization are found in Babylonia, in the district of Mesopotamia, where a people of Semitic origin settled about 8000 to 10,000 B.C., coming from the upper Tigris-Euphrates River regions. The country they came to occupy was inhabited by descendants of primitive Aryan tribes, of Asia Minor and the Caucasus, who probably possessed a decided culture of their own. The mixture of these races gave rise to a decided Babylonian culture which spread into western Asia, northern Africa, and even into Europe. Records of the ancient Babylonians date back to about 5000 B.C.

Both of the races mentioned came originally from mountainous countries rich in gold, iron, copper, and lead ores, and unquestionably brought a knowledge of these metals with them. Copper is found alongside of gold ornaments and stone tools in the most ancient Babylonian (Chaldean) ruins. Most of the finds of ancient metals are from tombs and graves, and the fact that ancient peoples buried with their dead usually precious possessions of intrinsic value, possibly accounts in part for the absence of iron in these remains.

Turning from this very ancient Babylonian civilization to a contemporaneous but probably later one, namely the predynastic Egyptian, I quote from Breasted:[1] "On the now bare and windswept desert plateau through which the Nile has hollowed its channel there once dwelt a race of men. Plenteous rains, now no longer known there, rendered it a fertile and productive region. The geological changes which have since made the country almost rainless, denuded it of vegetation and soil and made it for the most part uninhabitable, took place many thousands of years before the beginning of Egyptian civilization . . . ; but the prehistoric race who before these changes peopled the plateau left behind them, as the sole memorial of their existence, vast numbers of *rude flint implements*, now lying scattered about upon the surface of the present desert exposed by the denudation. These men of the paleolithic age were the first inhabitants of whom we have any knowledge in Egypt. They cannot be connected in any way with the historic or prehistoric civilization of the Egyptians."

"The forefathers of the *pre-dynastic peoples* of whom we have historic records were related to the Lybians or North Africans on the one hand, and on the other to the peoples of Eastern Africa now known as the Galla, Somali, and Bega tribes. An invasion of the Nile Valley by *Semitic nomads* of Asia stamped its essential character unmistakably upon the language of the African people there. The earliest strata of the Egyptian language accessible to us betray clearly this composite origin. This Semitic immigration from Asia occurred in an epoch that lies far below our remotest historical horizon. . . . . The most cunningly wrought flints that have ever been found among any people belong to this age. . . . . The war mace with pear-

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[1] James H. Breasted, "A History of Egypt," 1905.

shaped heads, as found also in *Babylonia,* is characteristic of the period. Side by side with such weapons and implements they also produced and used weapons and implements of *copper.* It is indeed the age of slow transition from stone to copper. Gold, silver, and lead, while rare, were in use. The time of this period is from 4500 to 4000 B.C."

It is noteworthy that in this instance there is again a fusion of a Semitic people with those of another race, and it is held by some scholars that Egyptian civilization is derived from the Babylonian. The metals known to these two ancient civilizations are copper, gold, silver, and lead. Iron has not been found. It is to be considered that the amount of metal found is small compared to that of the stone remains, and the metals were on hand probably in small quantities and it is hardly to be expected that small amounts of iron would survive through sixty-five centuries to the present day. Bronze is not found, though it is more resistant to corrosion than copper, proving conclusively that it was unknown. Even much later than this, during the Old Kingdom in the third to sixth dynasties, 2980 to 2475 B.C., Breasted states that bronze was not yet in use. "The smiths furnished tools of copper and iron, bolts, nails, hinges, and mountings of all sorts for artisans of all classes. They also wrought fine copper vessels for the tables of the rich, beside splendid copper weapons. . . . Silver came from abroad, probably from Silicia in Asia Minor . . . ; it was therefore even more rare and valuable than gold. The Egyptian term for silver was white-gold. In the ruins of Ur and Erech in Ancient Babylonia are found remains of copper vessels dating from 4500 to 2300 B.C. It is probable that in the latter part of this period bronze first came into use, originating in Babylonia. It was introduced into Egypt in the twelfth or eighteenth dynasty, most likely about 2000 B.C."

With the development of the Babylonian and Egyptian civilization, the use of metals increased and they soon entirely replaced stone implements for the purpose of tools and weapons. It is noteworthy that Hill, in 1837, breaking away a massive limestone block from the great pyramid of Cheops, dating about 3000 B.C., found in a masonry joint the broken portion of an iron tool. At the time of Rameses II, 1292–1225 B.C., iron plowshares were in common use. Egypt procured much of its iron from Ethiopia, and monuments at Karnak show the method of ore reduction. Shallow excavations were made in rock or earth and the iron ore was smelted in these with fuel, blast being produced by means of skin bags and led to the furnace by bamboo pipes. The product of the first operation (an iron sponge mixed with slag) was resmelted and then hammered to expel the slag, finally going into use as forgeable iron.

Lead was not widely used by ancient peoples, but was known to them, for it has been recovered in Assyrian cities, *viz.*, Nineveh, and in the tribute lists of the Egyptian king, Thutmose III, 1500 B.C., it is mentioned as having been furnished by Phœnician peoples.

FIG. 1. — Above, at the left, weighing of precious metals and malachite; in the middle, the furnace with men at blow-pipes; at the right, casting and hammering; below, putting together necklaces and costly ornaments.

Tin was known in ancient Babylonia and was probably derived from the Caucasus, or from the southern flanks of the Hindu Kush mountains in Afghanistan, where recently ancient tin workings have been found. This metal was little used previous to the invention of bronze. The mining of tin in the British Isles is much later in history.

An interesting account of a very ancient method of mining and milling gold quartz ore in the Egyptian gold mines in Nubia, which were already worked in the fourth dynasty, 2900–2750 B.C., is given in Diodorus, a Greek historian (Sicily, about 20 B.C.), who quotes from Agatharchides of Knidos:

" The gold is mined from veins of a white marble (quartz) which is found in a black rock. The kings send to the gold

Fig. 2. — Egyptian method of melting gold.

mines the criminals, the prisoners of war, and also those who have been falsely accused and imprisoned in anger, sometimes alone, but sometimes with their families and relations, in order to punish the condemned, but also for the purpose of deriving great income from their labor. Those sent there, whose number is very large, are kept in chains and are forced to work day and night without rest, all opportunity for escape being carefully cut off, for guards of *foreign* soldiery stand close by so that no one by conversation or friendly intercourse can bribe a guard. The hardest of the gold-bearing rock they burn with a big fire (fire-setting). The softened and split rock which can now without further preparation be broken with stone chisels is sorted over by many thousands of miserable human beings. The strongest of these most unhappy condemned break up the marble-like rock, with pointed iron hammers, solely by brute strength, without the employment of any mechanical art."

" They drive the drifts, not in a direct line, but follow the direction of the glinting marble veins. These people carry lights fastened to their foreheads, as the workings are dark, due to the windings of the drifts. They must frequently change the positions of their bodies in working on account of the twistings (dip) in the rock. The loosened pieces of rock are thrown on the floor. This work they carry on uninterruptedly under the abuse and blows of the overseers. The boys under seventeen years of age pass through the drifts into the excavations and laboriously gather the small pieces of broken rock and deposit them at the entrance under the open sky."

" Those persons who are under thirty years old take a certain portion of these broken pieces and crush them in stone mortars, with iron pestles, until they are of the size of peas. The rock of this size is passed to the women and old men who throw it into mills of which there are many in a row, and at each mill two or three persons, working with a foot-power device, grind their portion of the rock into flour. And since none of these people can afford themselves any care, nor have garments to cover their nakedness, no one can see them without feeling pity for their miserable condition. Neither the ill, nor the crippled, nor the weak woman, are given the slightest relief or easement, but all are forced by blows to work unceasingly until they fall exhausted in their misfortune and miserably die. These mines are very ancient and their establishment dates back to the reign of the old kings."

The further treatment of the pulverized ore consisted in washing it on inclined wooden tables in a stream of water and picking from the table the enriched gold sand by means of small sponges, to which even the finest particles of gold adhere. This enriched sand is then melted with lead in crucibles. The resultant bullion, mixed with more lead, salt, and straw, was placed in another crucible and exposed for five days to a red heat, when, on the sixth day, pure gold alone remained, the lead and silver chloride being volatilized and in part absorbed by the crucible. Sculptures from the graves at Thebes, dating from the reign of Thutmose IV (1420 B.C.), show that the enriched sands, gained by washing as above described, were smelted in low furnaces, in shallow crucibles, with the use of blast and the molten gold cast into cup-shaped molds.

The most ancient known mines are Egyptian copper mines in the Valley Wadi Meghara, in the Sinai peninsula. Their beginning is probably pre-dynastic, before 5000 B.C., and they seem to have become exhausted about 1300 B.C. Portions of furnaces, crucibles and some slag is still found there. Copper mines were also worked on the flanks of Mt. Sinai, about 1600–1400 B.C. Extensive slag dumps are still to be found here. These ores were for the most part oxidized, and were easily reduced. They also furnished fine malachite for ornamental purposes.

Neither the ancient Babylonians and the Assyrians, nor the Egyptians, were a commercial people, and the civilization developed by them was not appreciably spread until the rise of a Semitic people in Syria on the coast of the Mediterranean, the Phœnicians. These, originating probably in the Tigris-Euphrates region, and closely related to the Jews, founded the great cities of Sidon and Tyre, the latter probably about 2700 B.C. The Phœnicians were never a nation in the strict sense of the word, even in their earliest history, as the cities were independent. After 1800 B.C., they were successively under Egyptian, Assyrian, Greek, Persian, and Roman rule. In spite of this they were the greatest commercial people of the ancient world. Very early in their history they were a seafaring people and carried the rudiments of the Babylonian and Egyptian civilizations to the lands adjoining the Mediterranean.

They were the most skilful metallurgists of the ancient world and the Phœnicians of Sidon founded a colony on the island of Cyprus, about 1300 B.C., where they extensively mined and smelted copper ores. They founded colonies at many places on the shores of the Mediterranean. They developed into skilful metal workers, and their works of art, weapons, and implements were widely scattered by trade. The Phœnicians accumulated vast stores of metals obtained from the distant peoples they traded with, and at their most western colony, Gades (Cadiz in Spain), they had large stores of silver, lead, and tin, probably procured from Spain. They also obtained tin from England, not directly, but by trade from the Veneti, who brought it to the Phœnician colony Tartessus, the present Tortosa, on the Ebro River, in the northeastern part of Spain. The Veneti dwelt on the north coast of Spain and had intercourse with the west coast of England.

The Phœnicians practically controlled the tin trade between 1000 and 300 B.C., in so far as it was extremely important to them for the bronze industry, which they brought to a high state of perfection. The oldest route of trade between the Mediterranean countries and the English Isles was across the Channel, then up the Seine to the Saone and then down the Rhone to Massilia (Marseilles), a Greek colony founded in 600 B.C. The Phœnicians probably traded in tin at this point. Somewhat later they found the sea route to England and kept it a secret until the Carthaginians (Phœnicians settled in Carthage) discovered it, as also did, later (333 B.C.), the Greek Phyteas of Massilia. This destroyed the tin monopoly of the Phœnicians.

The Phœnicians were masters of the art of making and casting bronze. Most of their bronzes have a composition of approximately 90 per cent. copper and 10 per cent. tin, one of the toughest and strongest of this series of alloys. Coin bronze also usually contained lead. They traded bronze implements and weapons to many peoples, thus probably accounting for the occurrence of bronze in certain localities, with rather crude stone implements.

The Phœnicians were familiar with iron and also with steel in their earliest history. They mined iron in the Lebanon mountains in Syria in the time of Solomon, 990 B.C. Still older are the Phœnician iron mines on Mount Ida in Phrygia, Asia

Minor. Their city of Tyre was a famous market for iron and steel armor and implements.

The Greeks, who early came into contact with the Phœnicians, and through them with Babylonian and Egyptian culture, soon developed a civilization typical of themselves, without a peer in the ancient world. They were familiar with the common metals even in their prehistoric period, as may be seen from the legends of the Iliad and the Odyssey of Homer, about 900 B.C. At that time they had iron as well as steel, and copper; the latter was probably more commonly in use, while bronze was either unknown or very rare. It was introduced to the Greeks by the Phœnicians at a somewhat later period. Iron ore was mined and iron manufactured in Crete and Cyprus and many other of the Greek islands. Chalcis, in Eubœa, thirty-four miles north of Athens, was famous as a source of iron weapons.

The iron industry was very old in Laconia, the chief city of which was Sparta, where iron was used for ornamental and monetary purposes. The ancient Laconians were familiar with the welding properties of iron. Copper ore was mined in Eubœa and in Cyprus. Bronze became common about 600 B.C., and the Greeks developed the art of metal working to a remarkable degree, making bronze castings which are even to this day remarkable for their beauty and technical skill of workmanship. The Greeks mined lead and silver at Laurium, in Attica, probably earlier than 550 B.C., and when Athens was at the height of its power, as many as 60,000 slaves were employed in the mines. It is stated that during the 300 years that these mines were worked by the Greeks, 2,100,000 tons of lead and 4,800,000 kgs. of silver were secured. Rich slags from these mines were later reworked by the Romans, and at present modern plants[1] are treating ore, slag, etc., from these mines in furnaces made in the United States. Lead and silver were mined by the Greeks in Rhodes and Cyprus. They were also probably familiar with zinc, though in the form of an alloy with copper, viz., brass, at an early date, as zinc and copper minerals occur intimately mixed, in Cyprus and islands on the coast of Asia Minor.

The inhabitants of India were familiar with the production

[1] H. F. Collins, Eng. and Min. Jour., Vol. LXXIX, p. 363; Vol. LXXXVII, p. 881.

and the use of metals early in their history, for the Rigveda, dating 1500 B.C., states that iron was fashioned into swords and axes. Steel makes its appearance at a comparatively early period, and Indian steel as an article of commerce was highly prized, particularly the kind known as Wootz steel. Aden on the Red Sea was a great market for Indian weapons and steel. In Delhi stands the Kutub column, a great mass of iron, partly buried, and approximately 59 ft. long and varying in diameter from 16 in. where it emerges from the ground to 12 in. at the top. It weighs approximately 19 tons and dates from about 1000 B.C. The mass is nearly pure iron and seems to be made of small pieces welded together. In the temple of *Kanaruk*, wrought-iron beams were found 20.6 ft. long and 3 in. in cross-section, dating from about 1250 B.C.

At the time of the Romans, and of the Roman dominion of the civilized world, the use of metals had become wide-spread for many purposes, such as for armor, tools, implements, money, and some structural purposes, and mining was prosecuted on a large scale in those portions of their realm rich in mineral wealth. The chief mineral province was Spain. In Huelva, Spain, great copper mines were worked by the Phœnicians, as slag dumps to the extent of 2,000,000 tons show to this day. They were succeeded by the Romans who worked the mines for 400 years, to about 412 A.D., and their slag dumps amounted to about 18,000,000 tons. The greatest operations were carried on at Rio Tinto and Tharsis. It is estimated that the average annual production of copper by the Romans, from these fields, amounted to 2400 tons. Iron came from the island of Elba, from Spain, Gaul, Illyria, and Britain, while tin, for bronze, came chiefly from Spain and Cornwall.

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ANCIENT METHODS OF EXTRACTION OF METALS FROM THEIR ORES

Iron. — There are no records of the methods of extracting iron from ores used by the most ancient peoples, though Egyptian monuments furnish some data. It probably was practically the same as that now employed by semi-civilized tribes in Africa and in India. In Kordofan in the Soudan the method is in use which is depicted on Egyptian monuments. Easily reducible iron ore was mixed with charcoal and smelted in shallow pits in the ground, blast being furnished by means of skin bags through bamboo blast pipes. The product was a mixture of iron sponge slag, and undecomposed ore, which was again smelted with charcoal, producing a hot, waxy mass of iron intermixed with slag or a " bloom," that was hammered into certain shapes, and formed the iron of commerce. A common form of commercial iron, from 1000 to 800 B.C., were clumps, roughly in the shape of a double cone placed base to base, with a hole through one end, weighing from 9 to 45 lbs.

On the west coast of India, an ancient method is still employed at the present day. The ore is fed in alternate layers with charcoal, into round, open furnaces built of clay, 2 to 4 ft. high, 0.8 ft. in diameter at the bottom and 0.5 ft. at the top. A furnace has two openings near the bottom, one for drawing out the slag and iron " bloom," the other for the insertion of the bamboo blast pipe. The bellows producing the blast are made of goat skin. After several hours of blowing, a porous bloom of iron is obtained which is hammered to expel the slag. Wootz steel was produced from iron made in this way, but first repeatedly resmelted, and then cut into small pieces and mixed with pieces of wood of a certain tree to furnish the carbon, and fused in clay crucibles in a shallow pit fired by charcoal. The process was a delicate one, rigorously carried out according to certain precautions.

In various parts of Germany and in Belgium, very ancient furnaces of this Indian type have been found. The iron produced by this method was of course not homogeneous and its value varied widely, dependent on the purity of the ores employed. It was probably, in many instances, steel-like in its character, due to retained carbon. The Greeks and Romans, for instance, distinguish at an early date between soft and hard iron, and Pliny states in his natural history that the Romans greatly prized Indian iron, viz., the Wootz steel. These simple methods furnished the iron supply of the world, and remained practically unchanged until the beginning of the fifteenth century. While artisans developed great skill in working metals, the production of iron was by the same means as were used by the forefathers in the gray dawn of civilization. The first improvements in the manufacture of iron were introduced in Germany and resulted in the making of cast iron. This discovery led to the art of making iron castings. The making of cast iron was accidental. Somewhat larger furnaces had been built, and water power was introduced to operate the hammers and to actuate the blast apparatus. This last, furnishing greater volumes of air at higher pressure, increased the temperature in the furnaces, with the consequent production of a fluid iron — cast iron. The first production of cast iron is probably to be placed in the Rhine region, about 1450.

From this time onward, the making of cast iron spread quite rapidly although the old methods persisted side by side for many centuries, where conditions for them were favorable. Even until very recently, in some countries, as in northern Spain and in this country in New York State, the ancient *direct process* of iron making in bloomery and Catalan forges, though in modern improved forms, was in use. In the sixteenth century furnaces producing cast iron were rectangular in cross-section, and about 14 ft. high. They were tapped about every two hours, yielding 200 to 220 lbs. of iron at each tapping. Somewhat later the furnaces were made circular in cross-section, about 18 ft. high, and were provided with an opening near the bottom (open breast), the iron and slag flowing out into a sort of exterior crucible, the open breast serving for the introduction of tools to clean away obstruction. These furnaces were usually built of sandstone.

This type of iron furnace, the precursor of the present day blast furnace, was introduced into England and France about the middle of the sixteenth century, and at the end of the century into Sweden. The first tuyeres or openings for the introduction of blast into the furnace were of stone; copper tuyeres were invented in Germany at the beginning of the sixteenth century, and iron tuyeres in 1697. After the introduction of the blast furnace in England, progress there was comparatively rapid. Furnaces were made 30 ft. high and circular in cross-section. An effort to replace charcoal as a fuel, by hard coal, was made in Belgium in 1627, while in England Dud Dudley smelted iron ores with coal in 1623, but the method declined again. Then, in 1713, Abraham Darby began smelting with coked coal or coke, but the method was not really successful until, in 1742, Richard Ford solved the problem of coke smelting in the iron works at Coalbrookdale. Darby and Ford at these works also applied the Newcomen steam engine to the wooden blast bellows, and Coalbrookdale became the largest iron works in the world. In 1754 seven furnaces produced each three tons of iron per day, the greatest furnace record then known. In 1768 Smeaton invented the cylinder blast engine, actuated by steam, thereby greatly increasing the capacity of furnaces. In 1829, Neilson, at the iron works at Clyde, introduced heated blast, which greatly increased furnace capacity. From that time to the present day progress in perfection of detail was rapid.

Wrought iron was produced by resmelting cast iron on shallow hearths, many modifications of the process being in use. The invention of the "puddling process," or the smelting of cast iron to wrought iron in reverberatory furnaces by means of coal fuel, is ascribed to Henry Cort in 1784. This was a great step in advance and cheapened the production of iron greatly.

Steel, as already stated, has been known from very early times, but its production was due more to accident than to design. At the beginning of the sixteenth century it was made by smelting cast with wrought iron on shallow hearths, thus reducing the carbon of the cast iron, and then forging the product, but most of the steel was made by the direct process described. Steel making by the cementation process, viz., heating wrought iron for a long time in contact with charcoal, was practised in the sixteenth century in England and France. In 1740 Benjamin Huntsman invented the crucible steel process, making cast steel of a hitherto unknown uniformity and quality. The day of steel begins in 1856 when Henry Bessemer invented his process. For further information reference must be made to the extensive works on the metallurgy of iron and steel.

Copper. — The earliest method of extracting copper from its ores is practically unknown to us. At the ancient Egyptian mines on the flanks of Mount Sinai, and in the valley of Wadi Meghara in the Sinai peninsula, are still found slag heaps, parts of furnaces and crucibles. The ores were seemingly self-fluxing and a simple smelting of some of the old ore without fluxes yielded 18 per cent. of the contained copper. The ores worked were probably almost entirely oxidized, which fact, with their easy reducibility, explains the very early date of their working and the extraction of copper from them. A simple smelting in pits with charcoal would yield copper from these ores.

In the Austrian Alps are found remains of a prehistoric copper metallurgy dating back to probably 1300–1000 B.C. On the Metterberg Mountain were found about twenty roasting and smelting places and one furnace. The furnace was made of broken stone, built together with clay. The interior cross-section was about five square feet. Masses of slag weighing about forty pounds are found, which evidently were pulled out of the furnace in a viscid condition by means of a pole. The coarse, black copper obtained from the smelting of the *roasted* ore was evidently refined by resmelting, as refining slags containing copper shot are found. The copper shot found contained but very little sulphur. The Lake Dwellers at Hallstatt, in Austria, had copper utensils, the metal for which was probably derived from such operations as those described.

About the only record of the metallurgy of copper, and that a confused one, is found in the Natural History of the Roman, Pliny, and in the works of Dioscorides and Galen (A.D. 100–200). Pliny mentions the smelting of sulphide ores, and according to his writings, all the ores were first roasted in piles and heaps until they took on a red color. These were then taken apart, and the roasted ore smelted either in small shaft furnaces, being fed alternately with layers of charcoal while air was blown in near the bottom, by bellows worked by hand. The products of the smelting were a black copper, some matte, slag, and furnace accretions. Much of the copper of the ancients was impure, brittle, black copper fit only for casting, and they distinguished sharply between this and copper that could be beaten and formed.

Pliny states that poor copper can be made good by repeated resmelting. This refining of the black copper was done on small hearths, air being blown on the surface of the molten copper, the fuel being charcoal. The best copper of the ancients was probably derived from oxidized ores. Brass was made by smelting metallic copper with powdered calamine mineral, or zinc furnace accretions. Bronze was widely made by smelting copper with tin. In the interval from the third century to the beginning of the sixteenth century, practically nothing new was added to the metallurgy of copper. The precipitation of copper from certain mine waters was practised in the thirteenth century in Austria, though the Romans were probably familiar with the reactions involved. In Graslitz, in Bohemia, in 1272, sulphide iron copper ores were smelted to matte, which was roasted in heaps, with the object of converting the copper to sulphate, which was then leached out with water and the copper precipitated on iron.

Georges Agricola in his work (Vom Bergwerk), 1556, discusses quite fully the metallurgy of copper prevalent at the beginning of the sixteenth century. The method comprised seven operations: (1) The roasting of the ore in heaps. (2) The smelting of the roasted ores in blast furnaces with open breast and an exterior hearth, with the production of matte and slag. (3) Roasting the first matte, in heaps. (4) Smelting this matte in blast furnaces into one of a higher grade. (5) Roasting this matte to expel practically all sulphur. (6) Smelting this roasted matte in blast furnaces to "black copper." (7) Refining the black copper on hearths or in simple reverbatory furnaces, resembling ancient cupeling furnaces. If the copper ores contained appreciable amounts of silver, this was extracted by smelting either the black copper, or the rich matte with lead, which absorbed the silver, imperfectly however. The lead was then cupeled for its silver. The main principles of the metallurgy of copper were fully realized.

In the succeeding centuries the processes were developed into the typical German blast-furnace method of copper smelting. In England an entirely different method of smelting was developed by Wright in 1698, viz., the smelting of copper ores in reverberatory furnaces using coal as a fuel. The successive operations of roasting and smelting were carried out in reverberatory furnaces in ten operations. The method had advantages over the German method, particularly as regards capacity and economy. The strides made in the metallurgy of copper, particularly in the last twenty-five years, are enormous, and the reader is referred to the works on that subject for further information.

CHAPTER II

PHYSICAL MIXTURES AND THERMAL ANALYSIS

Definition. — In the study of metals and alloys to reveal their properties and constitution, a method of research is employed which is termed "*Thermal Analysis.*"

The methods of thermal analysis are based on the fact that any physical or chemical change within a substance is almost invariably accompanied by either an evolution or an absorption of heat. Some transformations occur (critical points) at which there is no absorption or evolution of heat, or thermal change, but a "volume change." This, of course, is not detectable by thermal methods but involves the use of a "dilatometer apparatus."[1] These physical changes which take place in an alloy or metal are called "critical points," and are frequently accompanied by decided changes of physical properties such as hardness, ductility, tenacity, specific heat, magnetism, coefficient of expansion, electric conductivity, microscopic structure, etc. It is to reveal these "critical points" that thermal analysis is applied. Thermal analysis is carried out chiefly by the taking of "cooling curves," which in their simplest form represent the cooling of a substance during a certain time interval, the temperature being plotted as ordinates and the time intervals as abscissæ. In the event of a chemical or physical change in the substance under analysis, entailing the absorption or evolution of heat, it will show itself either as a retardation or acceleration of the rate of cooling and be indicated in the curve by an inflection or jog.

Before proceeding in detail with thermal analysis, it is essential to define and explain certain terms which will be frequently used.

1. **Polymorphism.** — This is that property of a solid substance causing it to assume different crystal structures and con-

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[1] G. K. Burgess, Elect. and Met. Ind., Vol. VI, p. 366.

sequently different crystalline forms under different physical conditions, such as changes in temperature and pressure. A synonymous term for polymorphism is "dimorphism," although this is usually employed in a more restricted sense to substances capable of possessing but two forms. Another synonymous term is "physical isomerism." These terms all refer to the physical state, *i.e.*, crystal structure, viz., *molecular arrangement.* If the difference in state still exists after the body has been made non-crystalline by fusion, solution, or vaporization, it must be due to a change within the molecule itself, *i.e.*, a rearrangement of atoms, and the case is one of "chemical isomerism." Certain elements as phosphorus and oxygen, etc., may exist in several modifications, each of which possesses both distinct physical and *chemical* properties. This phenomenon is known as *allotropy.* Many cases of polymorphism are known; *e.g.*, iron, sulphur, mercuric iodide, carbon, etc.

These dimorphic changes are frequently accompanied by decided changes of physical properties, *e.g.*, in iron the loss of magnetism in passing from the α to the β condition, etc. As already mentioned, the changes are accompanied by either an evolution or absorption of heat, depending upon the direction in which the change proceeds.

2. **Isomorphism.** — This is the relationship existing between substances similar in their chemical composition, having similar crystalline forms and which are capable of forming homogeneous "mixed crystals." Common examples of isomorphism are found in minerals. For instance, the minerals of the calcite group — calcite, magnesite, siderite, rhodochrosite, etc., form an isomorphous group. Thus, magnesium carbonate, etc., can replace calcium carbonate indefinitely in the crystal without material change of crystalline form. Many cases of isomorphism are known. Just as to what constitutes isomorphism is not definitely settled. Cases of perfect isomorphism are rare, but cases of partial isomorphism, in which one substance can replace another to a limited extent, thus forming two series separated by a break, are frequent.

3. **Morphotropism.** — This is the relationship that each *chemical* constituent (or radical) of a substance (compound) exerts in modifying the crystal structure of that substance or compound. For instance, in mineralogy we have the case of

the pyroxene group forming a morphotropic series. Pyroxene has the general formula of $RSiO_3$, in which R is chiefly Ca, Mg, and Fe and Mn. The magnesium and iron bisilicates (Enstatite and Hypersthene) crystallize in the Orthorhombic system, the lime bisilicate Wollastonite in the Monoclinic system, and the manganese bisilicate Rhodonite in the Triclinic system. Considering the case of the magnesium silicate Enstatite, and adding some CaO radical to it, it undergoes a certain deformation of crystal form but still remains in the Orthorhombic system, and hence is still Enstatite. When, however, the amount of CaO becomes larger, the substance is thrown into the Monoclinic system and becomes a different mineral, *i.e.* Diopside.

4. **Crystals.** — A crystal is a portion of inorganic matter which has a definite molecular structure and an outward form bounded by plane surfaces called crystal faces. A substance which possesses the regular molecular structure of crystals without the development of crystal faces is said to be crystalline. A crystal is by no means necessarily a chemical compound.

An amorphous substance is one that possesses no definite molecular structure, hence is not crystallized. In general, it may be stated that in passing from the liquid state to the solid state if heat be evolved the resulting solid will be crystalline and the heat given off is the heat of *solidification* or of *crystallization.* A truly amorphous substance produced by solidification from the liquid state is unaccompanied by an evolution of heat.[1].

5. **Solid Solutions.** — The term solid solution was first used by van't Hoff,[2] for certain solids that possessed some of the properties of liquid solutions, and were homogeneous substances, the composition of which could vary continuously within certain limits. According to van't Hoff, solid solutions may be both crystalline and amorphous. In this work, however, a solid solution will be considered as an amorphous or non-crystalline substance, such as the glasses, etc., and one from which no heat is evolved (heat of solution) in passing from the liquid to the solid state. In other words, a true solid solution is one which possesses all the properties of a solution,

[1] Vogt, Schmelzpunkt-Erniedrigung der Silikatschmelzlösungen, p. 35.

[2] Zeitschrift Phys. Chemie, 1890, Vol. V, p. 323.

the heat of solution not being evolved when passing from the liquid to the solid state. The glasses (certain silicates) approximate very closely to true solid solutions.

6. Mixed Crystals. — This is a term first used by German scientists and refers to crystalline substances occurring as members of both isomorphous and morphotropic series. For instance, a crystal of dolomite may be considered a mixed crystal composed of calcium and magnesium carbonate belonging to an isomorphous series. The same is true of an alloy, which forms a member of an isomorphous series. Also, a crystal of pyroxene may be a mixed crystal of the several individual silicates, say magnesium, iron, and lime silicates, but forms a member of a morphotropic series. It must be clearly understood that a mixed crystal is not of definite composition, but will vary within certain limits of composition just as a solution may. It will follow from the definitions which have preceded that the substances entering into an isomorphous series may form a continuous series of mixed crystals of the same kind, while those entering into a morphotropic or partial isomorphous series will form two discontinuous series of mixed crystals of different kinds. The main distinction between a mixed crystal and a solid solution is that the first is crystalline while the latter is amorphous. A mixed crystal on forming from a molten or a liquid mass will evolve its heat of solution or crystallization.

Cooling Curves. — A cooling curve is the graphic record of the cooling of a substance, the ordinates and abscissæ of the plotting representing such values as will bring out most clearly the occurrence of "critical points." Cooling curves are commonly plotted with temperature as the ordinate and time as the abscissæ. The cooling curve of a substance that has no critical points is based on the following data: Consider a body

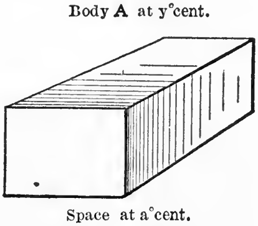

FIG. 3. — A body radiating into space.

A at a temperature *y*°, surrounded by space at the temperature *a*°.

There will be radiation of heat from the body *A* to the space, until the temperature of the body is that of the space surrounding it. It is assumed that there is no change in the temperature of the space. From Newton's law of radiation it follows that,

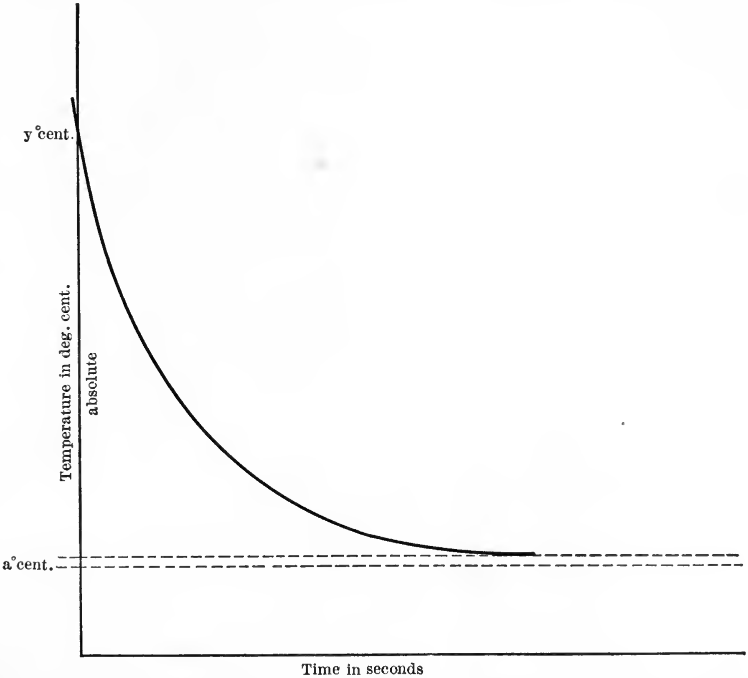

FIG. 4. — Theoretic cooling curve of a simple substance possessing no critical points and passing through no change of state. The body cools in space.

$$y - a = e^{(-\text{c}\text{T} + \text{k})}.$$

y = the absolute temperature of the radiating body *A*.
a = the absolute temperature of the space.
c = a constant = conductivity of the body, *i.e.*, specific heat, emissivity, etc.
k = constant of integration.
e = base of Naperian system of logarithms.
T = time in seconds.

Plotting this curve for different values of *y* and *T* there is obtained the type of logarithmic curve shown in Fig. 4, which is the ordinary cooling curve.

As already stated, when there is an evolution or absorption of heat, due to an internal change, this will show itself as a jog or inflection in the curve, thus marking the temperature at which the "critical point" occurs and also measuring roughly the amount of heat liberated or absorbed. The cooling curve of pure electrolytic iron is shown in Fig. 5 and of cast iron in Fig. 6.

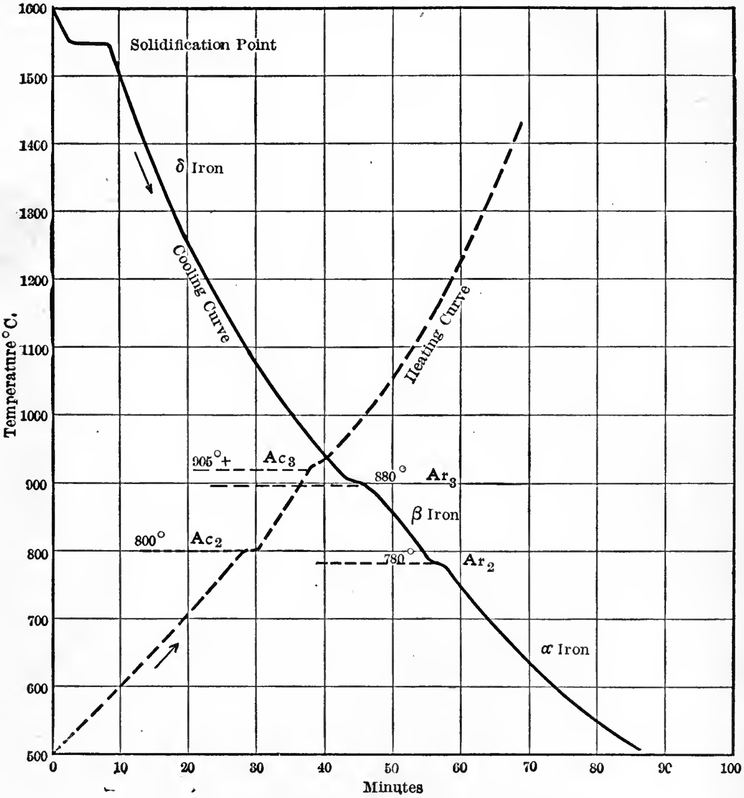

FIG. 5. — Cooling curve of pure iron, Goerens.

In Fig. 5, Ar_3 marks the change of Gamma iron to Beta iron, a dimorphic point; Ar_2, the beginning of the change of Beta to Alpha iron, a dimorphic point. This last marks a decided change in a physical property of the iron, viz., that of the regaining of the property of magnetism. A curve may also be taken during the heating of a substance and is known as the "heating curve."

This is shown as a dotted line in Fig. 5 and the "critical points" are now designated as Ac_3 and Ac_2, and it will be noted that these do not occur at the same temperatures as Ar_2 and Ar_3. The interval between Ac_2 and Ar_2 and Ac_3 and Ar_3 is known as the *hysteresis* and measures the so-called molecular inertia. The upper jog in the curve marks the passage of the molten liquid metal to the crystalline solid state of the metal and of course the consequent evolution of the heat of solidification. It serves distinctly to mark the freezing or the melting point of the substance, and it may be said that in general this method serves excellently for the determination of the freezing or melting point of substances.

Electrolytic iron is an elementary substance possessing certain dimorphic points. The cooling of a simple substance with no dimorphic points will give a curve as in Fig. 4, with only those jogs present incidental to the freezing, or, if carried through sufficient range of temperature, that of vaporization. It will be noted that the jog marking the freezing is represented as a nearly horizontal line. Theoretically, this would imply that the radiation of heat from the substance is exactly counterbalanced by the internal evolution of heat. This is by no means necessarily so and frequently in cooling curves the direction of this jog will be either downward or upward. Usually, however, it is downward. The shape of the curve for normal cooling is concave, as will be seen by referring to Fig. 4. Under certain conditions the curve becomes either a straight line or convex. In so far as any section of the curve really shows the rate of cooling, it is seen that if we compare the time interval corresponding to a unit drop of temperature the concave curve gives the shortest time, hence the most rapid cooling, and the convex curve the longest time interval, hence the slowest cooling. As the concave curve is the normal curve, any convexity of the curve indicates an internal evolution of heat, and further, any change of direction from a concave to a convex curve marks a critical point, and vice versa.

Fig. 6 represents the cooling of a certain alloy, a member of the series iron and carbon. This alloy is no longer a simple substance, but a mixture of two substances, and its cooling curve therefore presents very marked features. The curve is concave from the point *A* to the point *B*, where the first inflection occurs at 1176° C. From here on to the point *C*, the curve is convex and marks an internal evolution of heat caused by the freezing out from the mixture of a substance called austenite, a solution of carbon in iron. We have, therefore, during the freezing period between the points *B* and *C*, present both frozen material, austenite, and mother metal, carbon dissolved in iron. This type of freezing, whereby the freezing out of a certain substance from the mixture lowers the freezing-point of the mother metal and thus keeps it molten, is termed *selective freezing.* When the point *C* is reached the mother metal freezes or congeals, in this case into a conglomerate, called the *eutectic,* which term will be fully explained farther on. It will be noted that in the portion of the curve marking the freezing of the

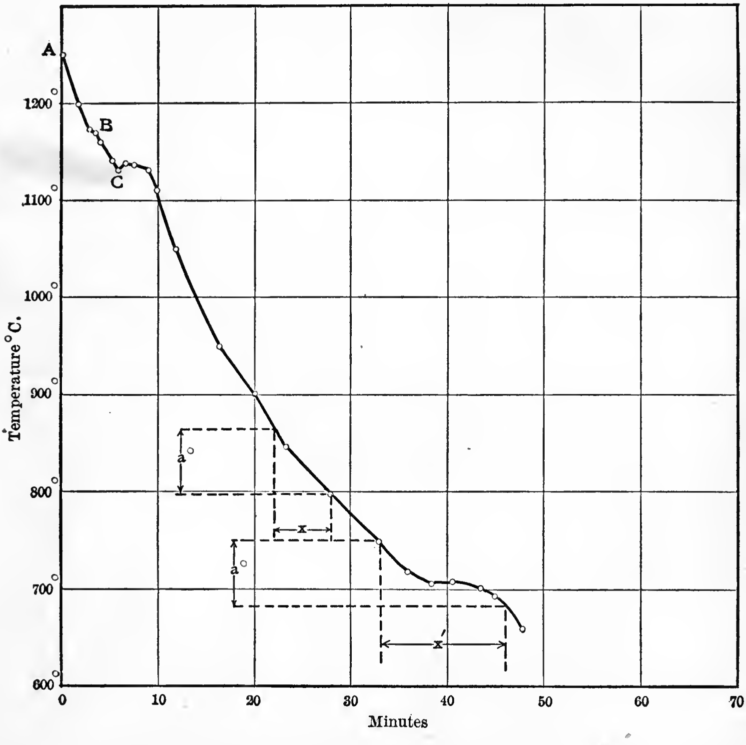

Fig. 6. — Cooling curve of cast iron. C = 3.91; Si = 0.12; Mn = 0.18; S = 0.008; P = 0.02%. Goerens und Gutowski, Metallurgie, V, 145.

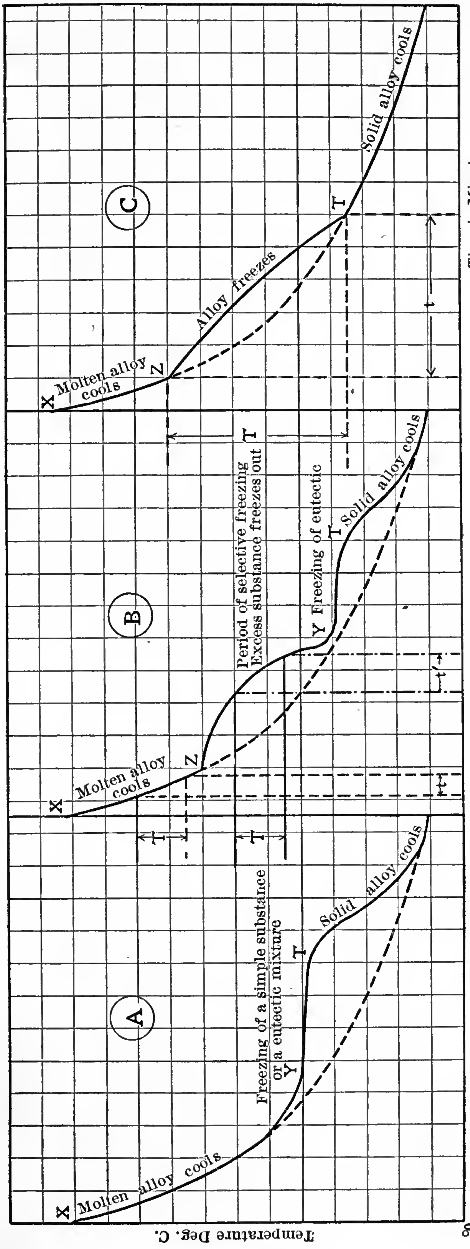

FIG. 7. — Theoretic cooling curves. No changes are supposed to take place in the solid state.

eutectic there is a depression in the curve, and then, as the eutectic freezes, a rise. This depression marks the *under cooling* of the liquid mass below its true freezing-point, which is termed "surfusion," *i.e.*, the state of a substance in a liquid condition below its true freezing-point. This is another instance of what may be termed molecular inertia, as referred to under hysteresis. When a liquid in surfusion begins to freeze, the temperature of the mass will rise toward the true freezing-point, but may not reach it. As to how near it will rise to the freezing-point depends largely on the degree of surfusion. Pure gold, silver, and copper present cases of surfusion; tin may exist in the liquid state 20° C. below its freezing-point.[1]

The Cooling Curves of Various Substances Based on Temperature and Time. — In Fig. 7 are shown: *A* — theoretic cooling curves of a pure metal or a chemical compound or a eutectic; *B* — of an alloy of two metals which are completely insoluble in each other in the solid state, showing the maximum amount of selective freezing and the freezing of the eutectic; *C* — of an alloy forming a member of a series of mixed crystals, in this case isomorphous mixtures, as, for example, gold and silver.

It will be seen that in *A* there is no selective freezing. This type of curve also shows the freezing of an alloy forming a eutectic and of eutectic composition, *i.e.*, of such composition as to form solely eutectic. Curve *B* in the convex portion shows the selective freezing of the *excess substance*, and in the horizontal portion the freezing of the eutectic. Curve *C*, which illustrates the freezing of an alloy, a member of a series forming no eutectic, shows an upper freezing-point and a lower freezing-point. In most cases, curve *C* will have two inflections, the upper and the lower one, the upper one marking the freezing-point, the convex portion the change in the constitution of the mixed crystals, and the lower inflection the cessation of this change and the beginning of cooling of the solid alloy. Fig. 8 shows the cooling curve of a true solid solution. There is no inflection point as there is no evolution of heat in passing from the liquid to the solid state. This case is not met with in alloys, but occurs in some instances in siliceous slags which congeal to a true glass.

Other Types of Cooling Curves. — In the cooling curves

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[1] Roberts-Austen, Cantor Lecture, Jour. Soc. of Arts, Oct. 22, 1897.

discussed, the parameters are time and temperature. This is the common and in most instances the best method of depicting cooling curves. When it is desired to depict as clearly as possible any changes, such as dimorphic points, etc., the data for this curve may be plotted in a different manner, according to Osmond.[1] The method is known as the inverse rate method.

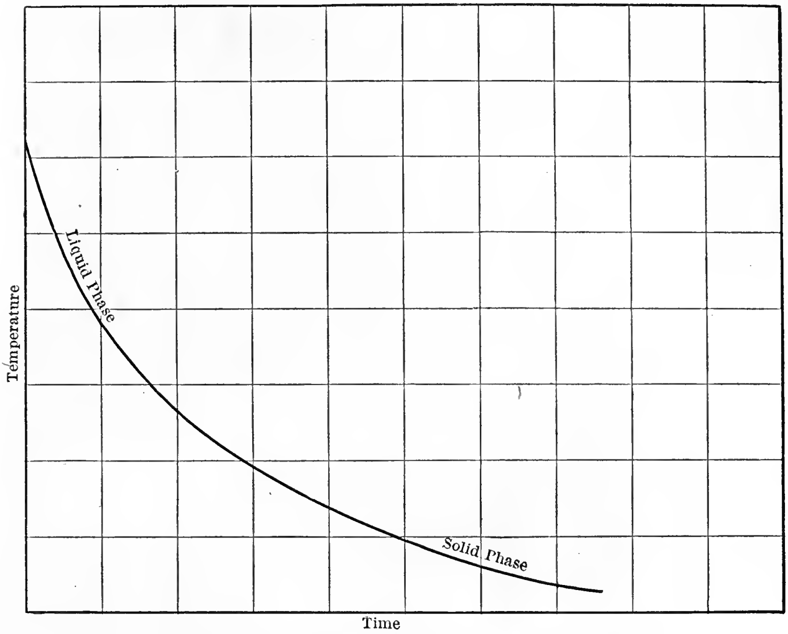

FIG. 8. — Cooling curve of a true solid solution.

The mode of plotting is as follows: By reference to Fig. 6, it will be seen that in one portion of the curve it takes x minutes to cool through $a°$, while in another it takes x' minutes to cool through the same number of degrees. If now we determine the value of x for every 10° drop throughout the curve and plot, these values of x as ordinates, to corresponding temperatures as abscissæ, a curve will result as shown in Fig. 9, which is the cooling curve of the same cast iron as shown in Fig. 6, reproduced in this manner. It is evident that this method brings

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[1] F. Osmond, Comptes Rendus, Vol. CIII, p. 743, 1122, and Vol. CIV, p. 985, 1887; Annales des Mines, Vol. XIV, p. 1.

out the critical points very sharply, but it does not define the temperature at which they occur as definitely as might be desired, as the ordinates are temperature intervals and not definite temperatures. A modification of the method is known as the temperature rate curve. The plotting in this case is simple and is shown in Fig. 10. The curve as before shows the rate of cooling and when there is an isothermal transformation for any time interval, that is, when the radiation from the body is counterbalanced by the internal evolution of heat, the rate of

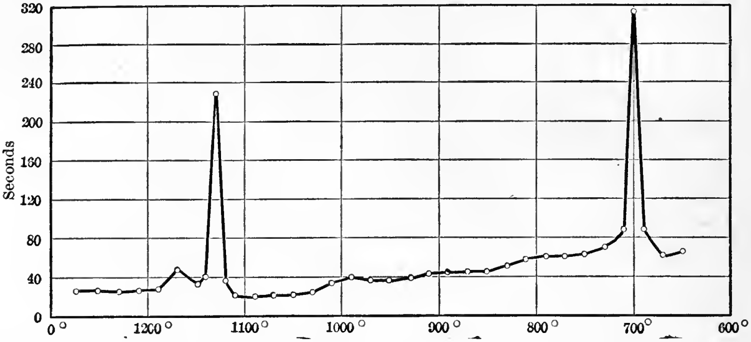

FIG. 9. — Cooling curve of cast iron, inverse rate method. Same as shown in Fig. 6.

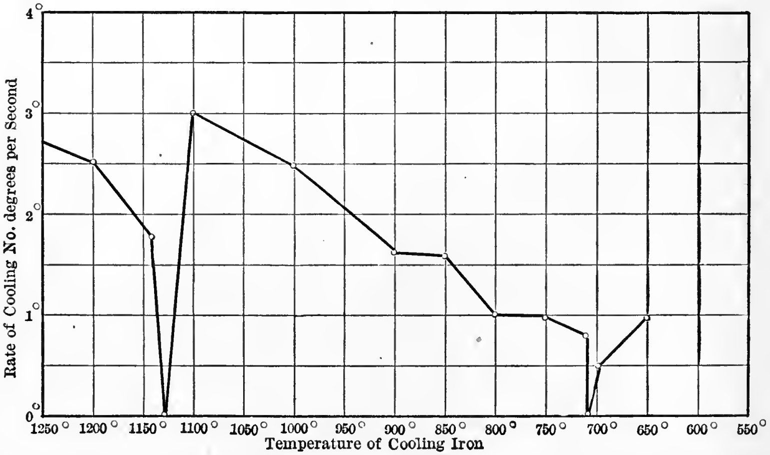

FIG. 10. — Cooling curve of cast iron. Temperature rate method. Same iron as shown in Fig. 6.

cooling is of course zero and the curve touches the basal line. This serves to identify the location of the transformation point better than the first-mentioned curve.

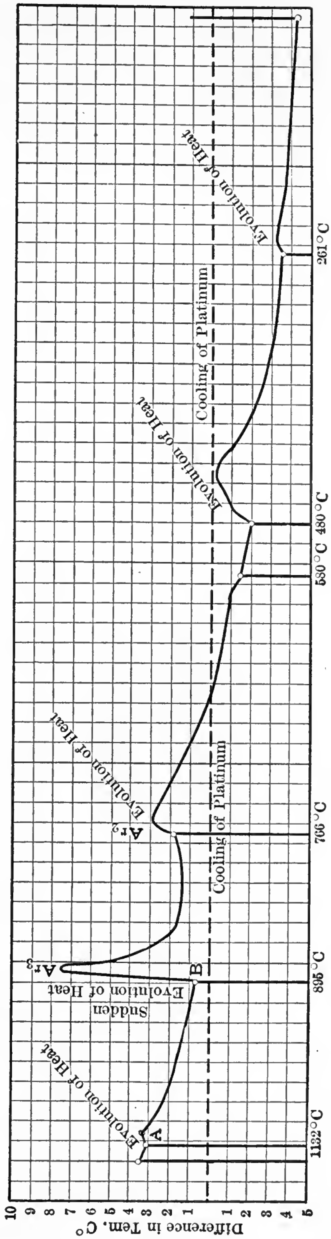

FIG. 11. — Differential cooling curve of electrolytic iron, taken against platinum. Roberts-Austen.

Differential Cooling Curves. — The ordinary time-temperature cooling curves are subject to deformations due to outside disturbing influences such as drafts, irregular cooling of furnace, etc. Under these circumstances, it is sometimes difficult to determine whether a deformation in the cooling curve is due to internal changes of the body or to outside influences. In order to obviate this difficulty, it is the practice to cool with the substance whose cooling curve is being taken a certain neutral body like porcelain or platinum placed in the furnace with it, side by side, and compare their cooling curves. As the cooling curve of any substance depends upon certain physical constants of that body, such as specific heat, emissivity, etc., the cooling curves are not necessarily parallel. However, the record of the two cooling bodies, one of which is neutral, *i.e.*, possessing no dimorphic points, and the other the substance whose cooling curve is being taken, when placed side by side, shows clearly whether any deflection or jog in the curve is due to internal change or to outside influences; for if it were due to outside influences, the cooling curve of the neutral body would also show the same.

Fig. 11 shows the cooling curve of electrolytic iron taken against platinum. It is usually so arranged in taking these cooling curves that one galvanometer reads the temperatures of the substance under investigation, and the other records directly the difference in temperature between the substance and the neutral body. For methods of taking cooling curves see p. 162.

The Relation between Cooling Curves and Freezing-Point Curves. — The freezing-point curve is the locus of the freezing-points of all the members of a given series. The parameters are temperature as ordinates, and composition, or, as it will be hereafter called, *concentration* as abscissæ. Freezing-point curves are constructed from the cooling curves of various members of the series. For instance, considering alloys made up of the metals A and B, ranging in composition or concentration from 100 per cent. A to 100 per cent. B, we may take ten alloys of the following compositions: 90 per cent. A, 10 per cent. B; 80 per cent. A, 20 per cent. B, etc., until 100 per cent. B is reached. The cooling curve of each of these alloys is taken and from the freezing-points indicated thereon the freezing-point curve of the whole series is constructed. Fig. 12 shows the relationship between the two types of curves.

Theoretic Considerations on Freezing-Point Curve. — Raoult and van't Hoff have formulated definite laws of the depression of the freezing-point of a solvent due to the addition of a solute.

Taking van't Hoff's formula or equation, viz.,

$$E = \frac{R}{100} - \frac{T^2}{W} \quad \text{or} \quad E = 0.02\,\frac{T^2}{W}$$

in which E = molecular depression of the freezing-point.
R = the gas constant = 2.
T = the freezing-point of the solvent in degrees C., absolute.
W = heat of fusion of one gram of the pure solvent in calories.

The molecular depression of the freezing-point is that depres-

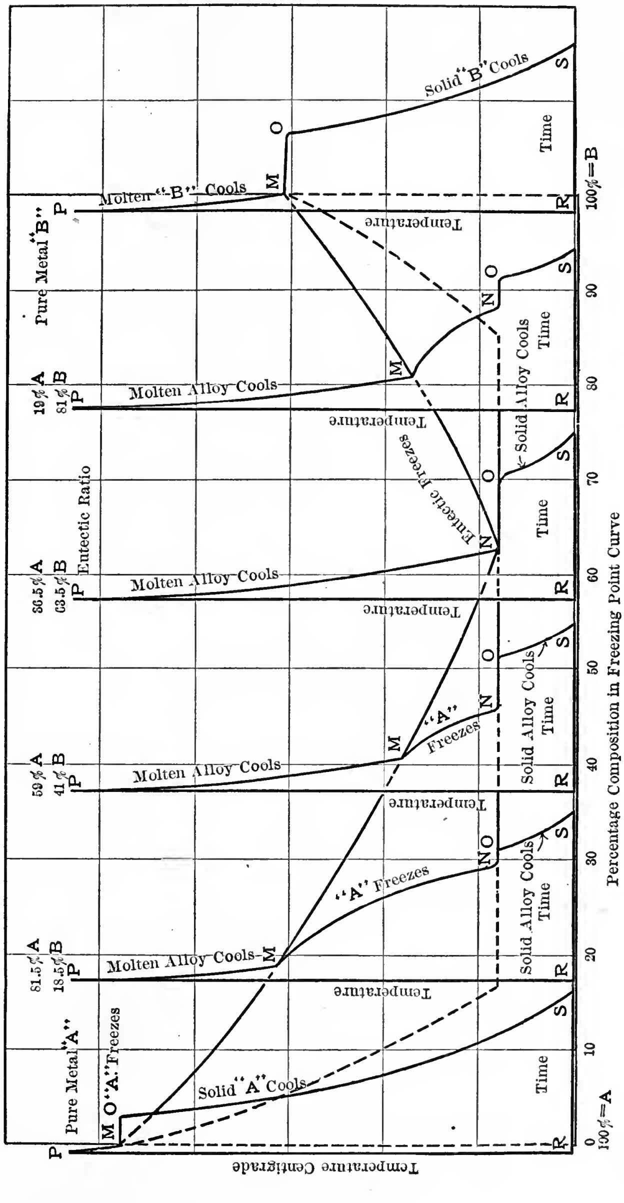

FIG. 12. — Showing the relation between cooling and freezing point curves. Consider the cooling curves as being set out at right angles to the freezing-point curve, which is projected on the plane of the page.

sion caused by the solution of a gram molecule (*i.e.*, the molecular weight in grams) of the solute in 100 grams of the solvent.

Further, let t = depression of the freezing-point of the solvent due to the solution of 1 gram of the solute in 100 grams solvent.

A' = the molecular weight of the solute.

Then $t = \frac{E}{A'}$,

The law states that the depression of the freezing-point of a given solvent, due to the solution in it of a *molecule* of any solute, is a constant. The law applies only in those cases where the solute separates completely from the solvent upon the freezing of the solution, *i.e.*, where there is no solubility in the solid state, and also only for dilute solutions.

For concentrated solutions, such as occur in alloys, the law holds in the modified form, viz.:

$$E = 0.02\,\frac{(T - t)^2}{W}$$[1]

For further calculation let us assume that

n = number of atoms to the molecule in the solute;

E_a = atomic depression of the freezing-point, defined similarly as molecular depression;

and that $n = \frac{E}{E_a}$.

Therefore, when $E = E_a$, $n = 1$.

Further,

$$E_a = \frac{A}{M}$$

in which A = the atomic weight of the solute.

M = the number of grams of solute dissolved in 100 grams of solvent.

From this it follows that the curve for the depression of the freezing-point may be depicted graphically with ordinates as absolute temperatures, and abscissæ as composition or concentration, as in Fig. 13.

Or, combining the two curves on one diagram as is adopted in depicting freezing-point curves, we have Fig. 14.

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[1] H. F. von Jüptner, Sideralogie, 1900, p. 31; Heycock and Neville, Trans. Chem. Soc., Vol. LVII, pp. 376–393.

This gives what is commonly known as the **V** curve, typical of certain binary systems of alloys.

The point *I* is known as the *eutectic* point and marks that composition or concentration of the two substances entering into the series that has the lowest possible freezing-point. From the discussion it follows that *I* is a fixed point, and further:

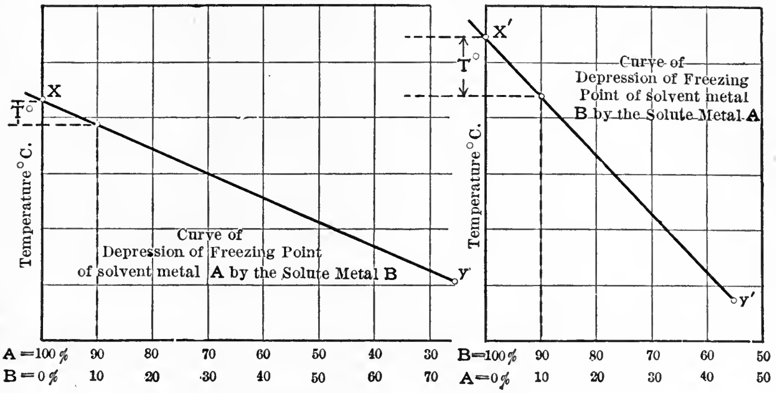

FIG. 13. — "Depression of freezing-point" curves.

1. The eutectic is a *conglomerate* composed of *A* and *B* (as the law of the depression of the freezing-point in the form as expressed by van't Hoff holds only for reciprocal insolubility in the solid state).

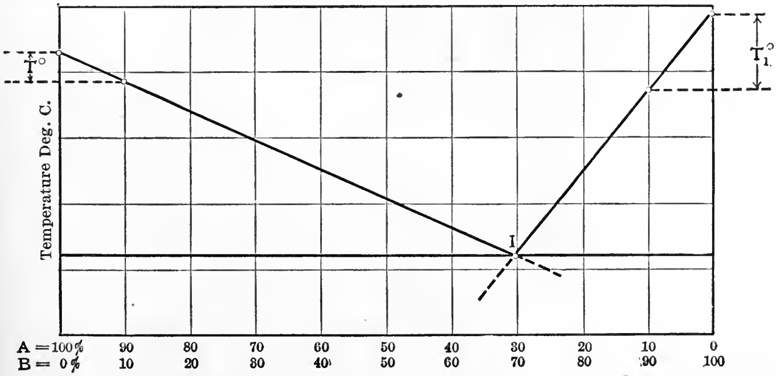

FIG. 14.—V curve constructed from the "depression of the freezing-point" curves, shown in Fig. 13.

2. That the composition of the eutectic is constant.

3. That the eutectic always freezes at the same temperature.
4. That this temperature is the lowest which can be obtained in the series and the alloy still remain liquid.

It also follows that if any alloy in the series be taken which is not of eutectic composition, that substance which is present, over and above the *eutectic ratio,* and which is called the *"excess substance,"* will begin to freeze out when the temperature of the molten alloy sinks to the freezing-point curve, since by its freezing the freezing-point may be further depressed. This freezing out of the "excess substance" follows the freezing-point curve until the eutectic concentration and the eutectic temperature are reached simultaneously, when the "eutectic" also freezes. This type of freezing is known as "selective freezing," already briefly defined.

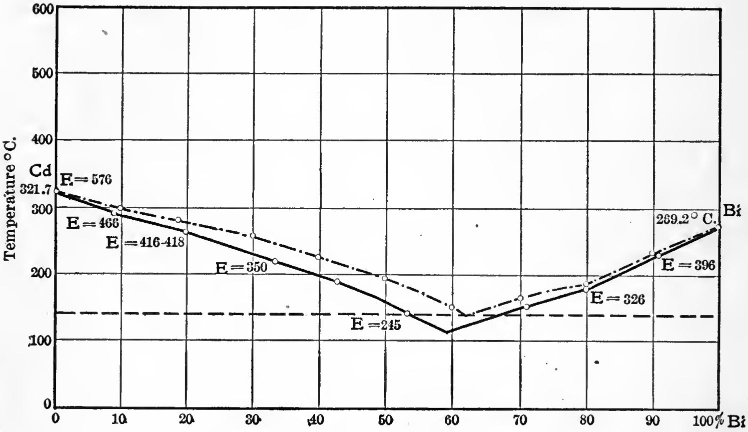

FIG. 15. — Actual and calculated freezing-point curve. Cd–Bi series. Dotted line is the experimental curve, solid line the calculated curve.

In order to demonstrate the agreement between the theoretical **V** curve above outlined and experimental data, both the theoretic freezing-point curve and the actual freezing-point curve of cadmium-bismuth are shown in Fig. 15. Cadmium-bismuth was chosen as forming a simple example in that both metals have molecules that are monatomic, and are practically reciprocally insoluble in the solid state, *i.e.*, do not form "mixed crystals" or "solid solutions."

Since van't Hoff's law is based originally on thermodynamic principles, it applies generally to all solutions, although when there is partial solubility in the solid state, viz., the solvent in part crystallizes (freezes) out with the solute, its constants change, still it is generally applicable[1]; so that the deductions as regards eutectic, etc., arrived at in preceding paragraphs, hold true for freezing-point curves of the substances which form mixed crystals belonging to partial isomorphous, morphotropic or discontinuous series.

When two substances are isomorphous, which in freezing form mixed crystals of a continuous series, the law has no application and it logically follows that it cannot have, since there is no freezing out of solute from solvent. This is also true of a continuous series of solid solutions. In fact, under these circumstances there may even be and often is a rise in the freezing-point of the substance, due to the addition of another substance.[2] With this discussion of the nature of freezing-point curves as an introduction, the following will be more readily understood.

Types of Freezing–Point Curves.[3] Binary Systems

The freezing-point curves are divided into two general classes with subdivisions.

I. *The two substances entering into the series do not form chemical compounds.*

A. The two substances are reciprocally soluble in all proportions, both in the liquid and the solid states, and form a *continuous series of mixed crystals* of varying composition. In this case the mixed crystals are members of an isomorphous series — hence, isomorphous mixtures.

a. The freezing-points of all the mixtures lie between the freezing-points of the pure components. Examples: Au–Ag, Au–Pt.

b. The freezing-point curve passes through a maximum; this case is rare.

c. The freezing-point curve passes through a minimum. Example: Ag_2S–Cu_2S.

B. The two substances are reciprocally soluble in all pro-

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[1] Zeitschrift, Phys. Chem., 1890, Vol. V, p. 322.

[2] Nernst, Theoretische Chemie, 1909, pp. 109, 168.

[3] This classification is partly based on B. Roozeboom's "Erstarrungspunkte der Mischkrystalle Zweier Stoffe"; Zeitschrift für Phys. Chem., Vol. XXX, p. 385.

portions in the liquid state, but are completely insoluble in each other in the solid state.

This is the typical **V** curve already theoretically discussed. No rigid example of this type is known in the alloys, but the systems Pb–Sn, Pb–Ag, Pb–Sb come very near to it.

C. The two substances are reciprocally soluble in all proportions in the liquid state, but only partially so in the solid state. The two components may thus form mixed crystals belonging to two distinct series which may belong to either the partial isomorphous type or the morphotropic type.

a. The freezing-point curve exhibits a transition point. Example: Hg–Cd.

b. The freezing-point curve has a eutectic point. Examples: Al–Zn, Au–Ni.

D. The two substances are only partially reciprocally soluble in the liquid state, the solubility varying with the temperature, and are:

a. Completely reciprocally insoluble in the solid state. No definite cases are as yet known.

b. Partially reciprocally soluble in the solid state. Examples: Cu_2S–Cu, FeS–Fe, Pb–Zn. In these two cases there may be a eutectic or there may not be. These two curves are to be considered modified forms of **ICa** and **ICb**.

II. *The two substances form one or more chemical compounds.* These chemical compounds may form mixed crystals with each other or with the pure components of the series. The solubility in the liquid and solid states may also be variable, as has been described for Case I. Very complex curves may occur in this class, a discussion of which does not fall within the scope of this book.

A. The compounds in the series show as definite maxima in the freezing-point curve. Examples are Cu–Sb, Al–Au.

B. The compounds in the series show only as hidden maxima, viz., the compound is dissociated before it melts, or forms after the alloy has solidified. Example: Pb–Au.

Discussion I. *The two substances entering into the series do not form chemical compounds.*

Case IAa. In Fig. 16 TAT' represents the freezing-point curve of the series, and TBT' represents the melting-point curve or, as it may also be termed, the "temperature composition curve." It should be stated that in the curves of class **IA,** which represent two substances that are completely reciprocally soluble both in the liquid and the solid states, this solubility cannot be quite equal and must be more complete in the liquid state, hence during freezing there will always tend to dissolve out from the mixed crystal formed that component whose entrance into the *mother metal* will cause a lowering of the freezing-point. The eventual result of this "*tendency to selective freezing*" is to form continuously varying mixed crystals of the same type; those first frozen being richer in the more difficultly fusible metal than those last frozen. A process of diffusion will, however, tend to again restore the mixed crystals to a uniform composition. For instance, in the freezing of an alloy of *aa′* concentration, the first frozen mixed crystal "*a*" will finally solidify as a mixed crystal of "*c*" composition. As the process of freezing continues, the composition of the frozen mixed crystals will travel along the curve "*cb*," while the composition of the mother metal will travel along the curve "*ad*." So that if no diffusion were active the final mixed crystal frozen would have the composition "*d*," so that the series of mixed crystals will range in composition from *c* to *d*. The alloy will solidify during the temperature interval "*ab*."

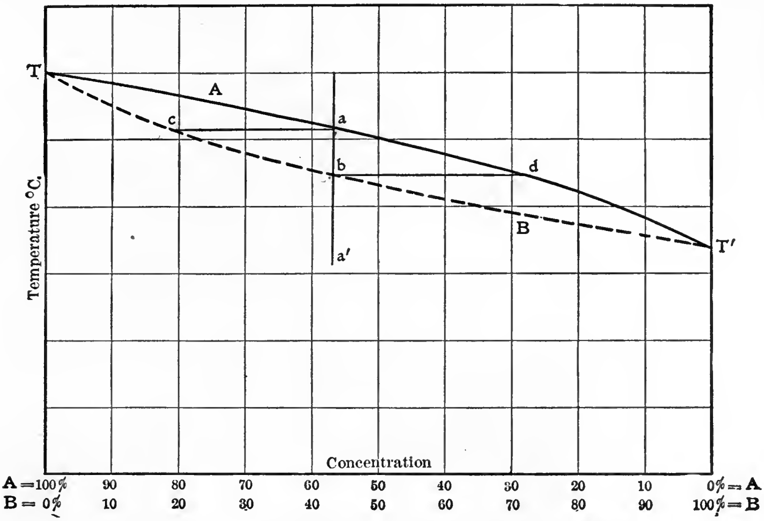

FIG. 16. — Freezing-point curve of the type **IAa.**

On melting an alloy of the composition *aa'* the above order of things will be reversed.

The area enclosed between the curves *TAT'* and *TBT'* marks the zone in which both solid and liquid phases of the alloy exist simultaneously. This zone is present in practically all freezing-point diagrams, no matter of what type, and will be again referred to.

Examples: Gold-silver; gold-platinum; iron-manganese; antimony-bismuth.

Case IAb. This case is unknown for alloys and will not be discussed here.[1]

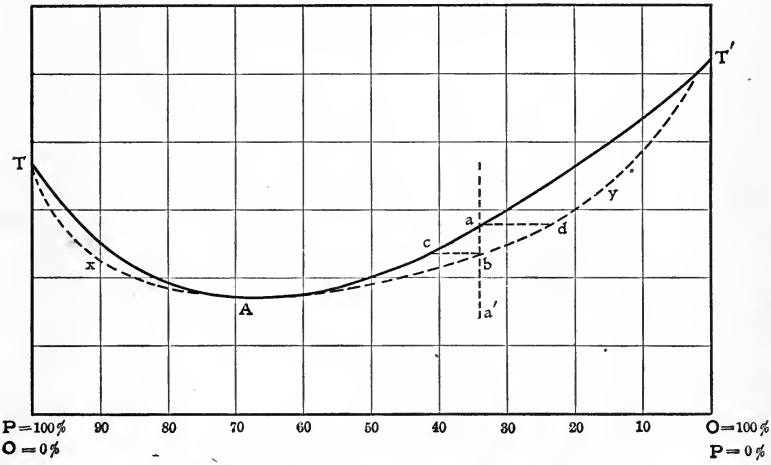

FIG. 17. — Freezing-point curve of type **IAc.**

Case IAc. In Fig. 17, *TAT'* represents the freezing-point curve and *TxAyT'* the melting-point curve. They have a common point *A*, so that here freezing occurs at a definite temperature, and not during a temperature interval as in other portions of the curve. Also the mixed crystals deposited at the minimum point are of the same composition as the mother metal. The method of freezing is similar to that described for case **IAa.**

Examples: Ag_2S–Cu_2S, Au–Cu.

Case IB. The foundation for this curve has been discussed under the theoretical matter on freezing-point curves. It consists of the two "depression of the freezing-point" curves *TA*

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[1] For a discussion see Findlay, the "Phase Rule," 1904, p. 184.

and $T'A$ intersecting at the eutectic point A. (Fig. 18.) The line BC is the "eutectiferous range" and marks the occurrence of eutectic in reference to concentration. Under the theoretic assumption of complete reciprocal insolubility of the two substances in the solid state it extends from ordinate to ordinate. The areas TAB and $T'AC$ mark the zones in which the liquid and the solid phases can be coexistent. For example, in the

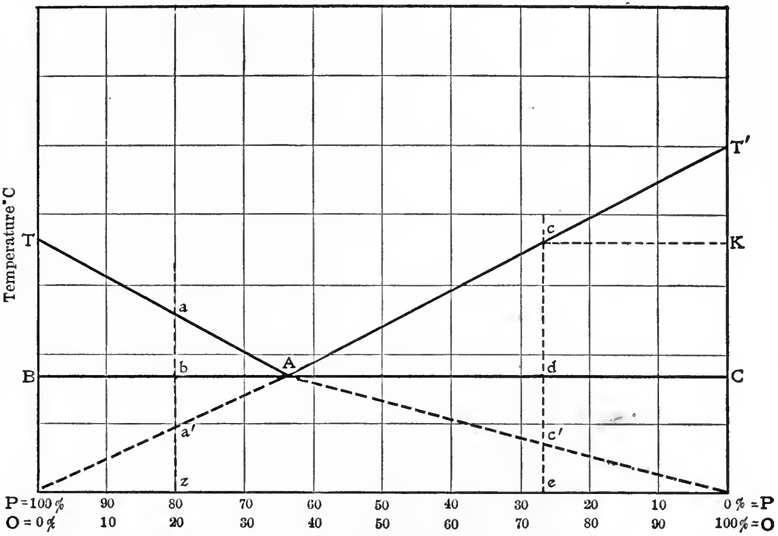

FIG. 18. — Freezing-point curve of the type **IB**.

alloy "*ce*," during the temperature interval "*cd*," both solid "excess substance" and liquid mother metal exist; the excess substance is the metal O and the liquid mother metal varies in composition along the line "cA," until A is reached, when it freezes as the eutectic, a conglomerate of the pure metals O and P. On the left of the point A, the excess substance is metal P and the mother metal varies in composition along "aA." The relative amounts of eutectic and excess substance are graphically represented by the lines bz or de = 100 per cent. of alloy, and the distances ba' and dc' representing the amount of excess substance, and $a'z$ and $c'e$ the amount of eutectic for the alloys a and c respectively.

Case ICa. In this case represented by Fig. 19, the two substances do not form a continuous series of mixed crystals as in case **IAa**, but two distinct series of mixed crystals. While in case **IAa** the mixed crystals were of the same type and members of an isomorphous series; in the present instance the mixed crystals are of two distinct types and members of a morphotropic or possibly of a partial isomorphous series. The change in the mixed crystal type occurs at the transition point *A*.[1]

For an elucidation of the curve the freezing of several alloys is described in detail.

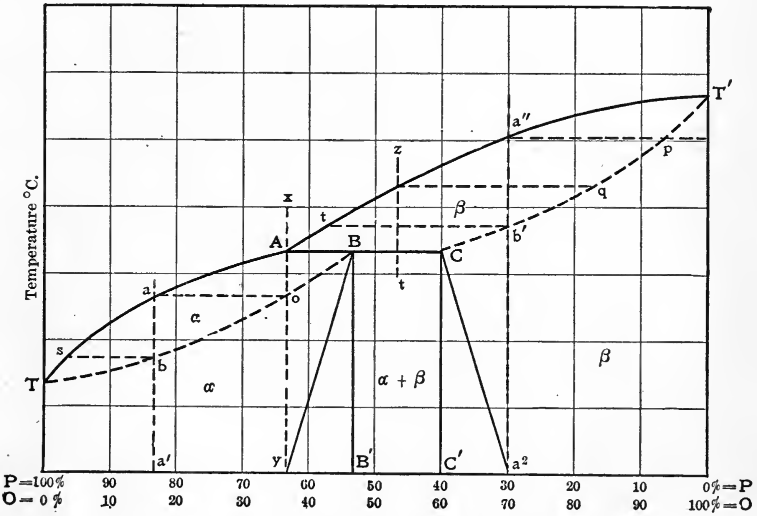

FIG. 19. — The freezing-point curve of type **ICa**.

1. *Alloy a–a′.* This cools until it reaches its freezing-point at *a*, when mixed crystals **α** begin to separate out of the composition from *o* to *s*, while the mother metal varies in composition along the curve *as*. With no diffusion active, the mixed crystals in this series range in composition from *s* to *o*. The alloy freezes during the temperature interval *ab*.

2. *Alloy a″–a²*. This cools until it reaches its freezing-point at *a″*, when mixed crystals **β** separate out of the composition from *t* to *p*, while the mother metal travels along the curve *a″ t*. With no diffusion active, the mixed crystals in this series range in composition from *t* to *p*.

3. *Alloy x–y*. This cools until it reaches the temperature

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[1] For a theoretical discussion see Findlay, "The Phase Rule," pp. 109, 188.

indicated by A, when freezing starts, α crystals separating out which vary in composition from B to a, while the mother metal varies in composition along the curve Aa, finally solidifying at a. The temperature interval of freezing is Ao.

4. *Alloy z–t.* This cools until the temperature reaches the freezing-point curve, when mixed crystals β will separate out of q composition. The composition of the mixed crystals will vary along the line qC. The mother metal varies in composition along the curve zA, and solidifies finally into mixed crystal α of B composition. The frozen mass is a conglomerate of α and β crystals. This method of freezing applies to any alloy of a composition between B and C. It is, however, true that in this instance a reaction can go on between the mother metal rich in P and the frozen crystal β comparatively rich in O to form mixed crystal α, as follows:

Mother metal + mixed crystal β = mixed crystal α. This reaction will, of course, go on only when the mother metal has reached a composition to the left of the point B. It also follows that the mixed crystals α and β separating out between the compositions B and C will be saturated crystals. If the capacity of metal P to form mixed crystals with O, and vice versa, changes in the solid state with a decrease of temperature as indicated by the lines By and Ca^2, further reactions take place in the zone Bya^2C whereby mixed crystal α loses metal O and mixed crystal β gains it, or vice versa.

Case ICb. If the gap BC in the continuity of the crystals in case **ICa** be markedly widened by the decreased capacity of two metals to crystallize with each other as mixed crystals, the shape of the curve will materially change, since the throwing out of a comparatively large amount of the solute from the solvent during freezing will cause a material lowering of the freezing-point in the case of both substances.

Fig. 20 represents the typical freezing-point curve for this case. Metal P can crystallize with PX per cent. of O at zero degrees C. and $T''X'$ per cent. at T'' degrees C., the curve XX' being the solubility curve of O in P with temperature. The metal O can crystallize with OY per cent. of P at zero degrees C., and $Y'T°$ per cent. at $T°$ C. YY' is the solubility curve of P in O. Any alloy in this series varying in composition from P to X and O to Y will consist of mixed crystals of either the α or β type respectively. Any alloy between the points X and Y in composition will consist of the mixed crystals, α and β. The eutectic A will be a conglomerate of the mixed crystals α and β in such proportion as indicated by the percentage composition. The line KL is the "eutectiferous range" and marks the limits of occurrence of eutectic in the series.

For illustration, the freezing of several different alloys is described in detail.

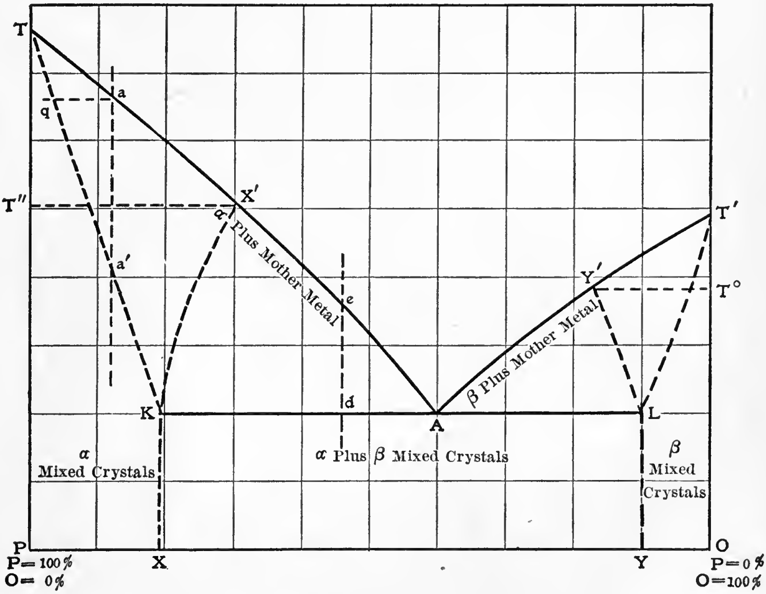

FIG. 20. — Freezing-point curve of the type **ICb.**

1. *Alloy a–a'*. The molten alloy cools, and on beginning to freeze when the point a is reached there separate out mixed crystals α of q concentration, the mother metal following the curve aX' in composition. The alloy finally freezes at say the temperature T''. The case of alloys between T and X' and T' and Y' in composition is similar to that described for the freezing of alloys of type **IAa.**

2. *Alloy e–d*. This alloy begins to freeze when the temperature e is reached, saturated α mixed crystals separating out as "excess substance," while the mother metal follows in compo-

sition the curve from e to A. When the temperature reaches A, the eutectic point, the mother metal freezes as eutectic, a conglomerate of α and β mixed crystals. To the right of A, as far as the point Y', the same method of freezing takes place, except that the excess substance is β mixed crystal.

Case IDa. This case may be considered a modified instance of the following one, so that the discussion of case **IDb** applies.

Case IDb.[1] In Fig. 21, $TAFGT'$ represents the freezing-point curve of the type under discussion. The curve EI represents the solubility curve of O in P in the solid state; HD of P in O in the solid state; and $AFJG$, the reciprocal solubility of the two metals in the liquid state. Since the solubilities of substances are usually radically different in the liquid and solid conditions, it is evident that the solubility curves for these two conditions are discontinuous, and thus cannot form a continuous curve. As regards the solubility curve for the liquid state in the case under discussion, it will be seen from the figure that at T'' degrees temperature PI' per cent. of O is soluble in P, and that at T''', PJ' per cent. of O is soluble in P, and that above the temperature T''' the reciprocal solubility is complete. Thus within the region FJG there exist two distinct liquids varying in composition from that indicated by the point J' to that of K and L respectively.

To further elucidate the curve, the freezing of several alloys of different compositions is discussed.

1. *Alloy a–a'.* This alloy cools to a, when saturated mixed crystals β–DO per cent. of P in O separate out as "excess substance" during the period when the mother metal travels in composition along the freezing-point curve from a to G. When G is reached the mother metal separates into two liquids of G and F (K and L) composition respectively. Freezing then commences at *stationary* temperature T_4, saturated mixed crystals β separating out, the mother metal meanwhile concentrating toward F (K) composition. When the mother metal has reached F composition, selective freezing commences along the curve FA, the excess substance separating out being again saturated mixed crystals β. When the mother metal reaches

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[1] Howe, "The freezing-point curve of binary alloys of limited reciprocal solubility when molten," the Metallographist, Vol. V, p. 166.

A composition it freezes as the eutectic, a conglomerate of β and δ mixed crystals in the ratio indicated by the concentration of the point *A*. The frozen alloy therefore consists of eutectic of δ and β mixed crystals and excess substance of β crystals.

2. *Alloy b–b′*. This alloy cools to *b* when it splits up into two liquids of respectively *b* and *x* composition, solution "*b*" being present in greater quantity than solution "*x*." As cooling proceeds, these two liquids follow in composition the curves *bF* and *xG* respectively, and when the temperature T_4 is reached the liquids are of the composition *K* (*F*) and *L* (*G*) respectively. Further freezing, and the final constitution of the alloy, are similar to that described for *a–a′*, except that the quantities involved vary. This method of freezing represents the solidification of alloys between *K* and *L* compositions.

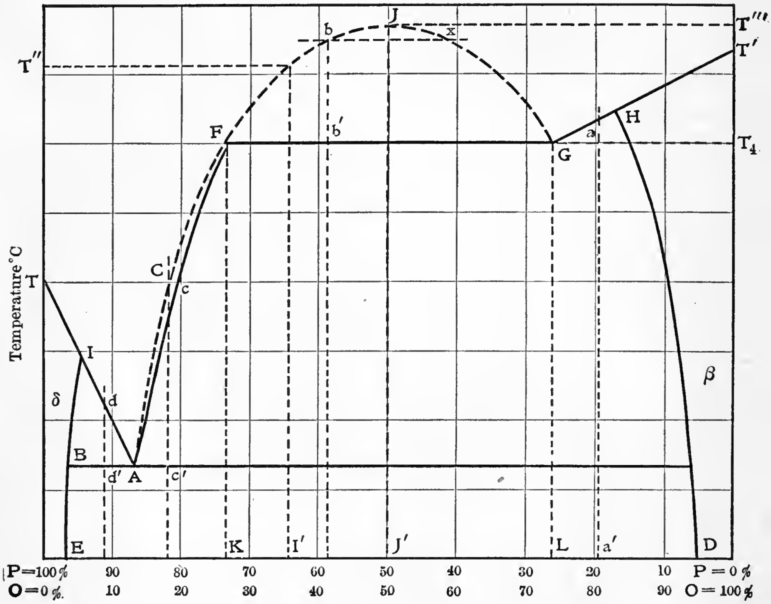

FIG. 21. — Freezing-point curve of the type **IDb**.

3. *Alloys c–c′*. This alloy cools to the temperature *T* when excess substance, mixed crystals β, freezes out, while the mother metal follows the curve *cA* in composition. When it reaches *A*, it freezes as the eutectic *A*. The frozen alloy then has the

same composition, qualitatively, as the alloys *a–a′* and *b–b′*. Quantitatively it consists almost entirely of eutectic.

4. *Alloy d–d′*. This alloy cools to the temperature *d* on the freezing-point curve when "excess substance" freezes out as *mixed crystals* δ. The mother metal concentrates to the point *A*, when it freezes as eutectic.

For alloys between composition *I–T* and *H–T′*, the freezing is identical with the alloy *a–a′*, in case **Icb**.

Discussion. II. *The two substances entering into the series form one or more chemical compounds.*

Case IIA. As already stated, under case **II** complex cases may arise and in this discussion only the fundamental ones are outlined. For instance, the number of compounds (intermetallic) that may form is not restricted by the law of valency ordinarily applicable, in so far as intermetallic compounds do not seem to follow the general law of valency of the elements. The compounds that form may be capable of forming mixed crystals with the pure components of the series, or amongst themselves, in a similar manner as has been discussed in the examples cited under case **I**.

In order that an alloy of certain composition in a series may be looked upon as a chemical compound it must fulfil three main conditions:

1. During its freezing the temperature must remain constant, *i.e.*, it must not freeze selectively, but have a definite freezing and melting point, except its dissociation temperature lies below the freezing-point curve.
2. Its constituents must be present in stochiometric proportions.
3. If it undergoes no change in cooling from its freezing-point to that of room temperature (which change can be detected, since "critical points" would be involved), it must show as a homogeneous substance under the microscope in the metallographic examination.

The dissociation temperature of the compound is of importance. If it lies wholly above the freezing-point curve, the presence of the compound will show itself as a "maximum" point in the curve (Fig. 22, the point *C*). If it lie below one of the branches of the curve, but not below the eutectic point, it will manifest its presence, though not its composition, as an inflection in the freezing-point curve, where its temperature of transformation occurs (Fig. 23, the point *D*).

If it lie wholly below the freezing-point curve, including the eutectic point, its presence will be, of course, not manifest itself in the freezing-point curve, and its detection will involve the thermal analysis of the material in the solid state. In general it may be stated that great changes in structure may take place in alloys in the temperature range, between the freezing-point curve and room temperature. The iron-carbon series (steel) and copper-tin series (bronze) are examples of this type.

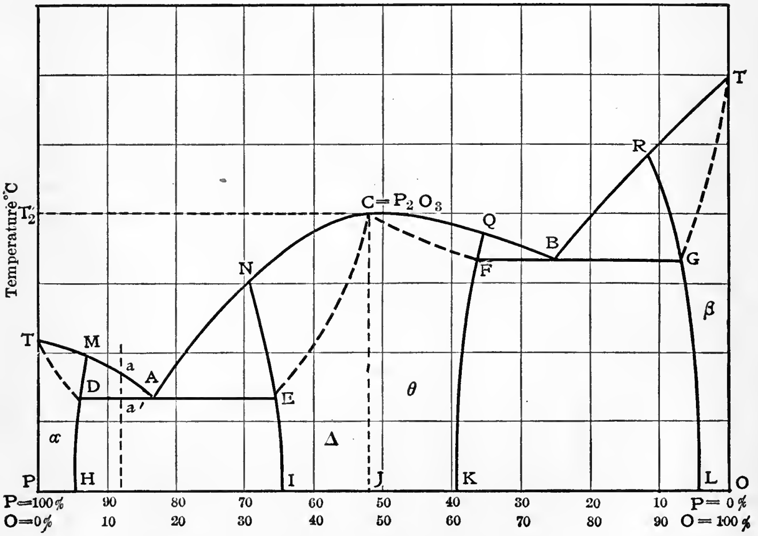

FIG. 22. — Freezing-point curve of the type **IIA.**

Fig. 22 represents a typical freezing-point curve of a series in which a chemical compound occurs. This compound indicated by the point *C* or P_2O_3 freezes at T_2° C. Such a portion of it is soluble in the solid state in the metal *P*, that *OH* per cent. of *P* will contain *PH* per cent. of *O*, and this will be called *α* mixed crystal. Such a portion of it is soluble in the metal *O* that a saturated solution will contain *OL* per cent. of *P* in *PL* per cent. of *O*. This will be called mixed crystal *β*. Further, the compound P_2O_3 is capable of dissolving in the solid state the metal *P* and *O* as expressed by the concentration *I–J* and *J–K*, forming the mixed crystals Δ and θ respectively. The eutectic *A*, therefore, consists of a conglomerate of α and Δ crystals and the eutectic *B* of a conglomerate of θ and β crystals. It is evident that two eutectics may be presents in the series. Some series of alloys may show even more than two eutectics. The case in which the formation of mixed crystals occurs is chosen for discussion, since the simpler case in which there is no reciprocal solubility in the solid state readily follows from the discussion. The freezing of alloys between *T* and *M*, *N* and *C*, *C* and *Q*, and *R* and *T′*, need not be discussed, since they freeze as the mixed crystals α, Δ, θ and β respectively, and their mode of freezing is outlined in case **ICb**.

Alloys between *M* and *N* in composition freeze in a precisely similar manner as does alloy *e–d* in Case **ICb**. The alloy of *C* composition freezes as the compound P_2O_3. Alloys between *Q* and *R* in composition freeze in a similar manner as those between *M* and *N*.

The case may arise where the pure metals are not soluble in the compound, *i.e.*, in the above case the mixed crystals Δ and θ will be absent. Then in the freezing of the alloys between *N* and *Q* there will separate out, as the excess substance, the compound P_2O_5, and eutectic *A* will consist of mixed crystal α and compound P_2O_3, while eutectic B will consist of mixed crystal β and compound P_2O_3 and the eutectiferous ranges will extend to the line *CJ*.

Case IIB. As already stated, the compound may have a dissociation point which lies below one of the arms of the freezing-point curve, but not below the eutectic point. In this case it will not show its presence as a maximum in the freezing-point curve, but it will manifest itself by an inflection in the curve, though this inflection by no means necessarily indicates by its position the composition of the compound. The compound in this instance has no melting-point. The process of freezing of alloys in this series is somewhat complex (Fig. 23). Some are discussed.

1. *Alloy b–b′.* This alloy begins to freeze when the point *b* is reached, pure metal *O* separating out, the mother metal meanwhile concentrating along *bD*, until *D* is reached, when the liquid mother metal in part reacts with all the solid crystals of *O* to form the compound PO_4. Then freezing continues along

the line DA, PO_4 separating out as excess substance, until A is reached, when the mother metal freezes as eutectic A, which is a conglomerate of pure metal P and compound PO_4.

2. *Alloy a–a′.* This begins freezing when the point a is reached, pure metal O separating out, the mother metal meanwhile following aD in composition, until at D, as before, a reaction takes place to form the compound PO_4, only in this instance the final result is all PO_4, and the freezing ceases at the temperature of the point D.

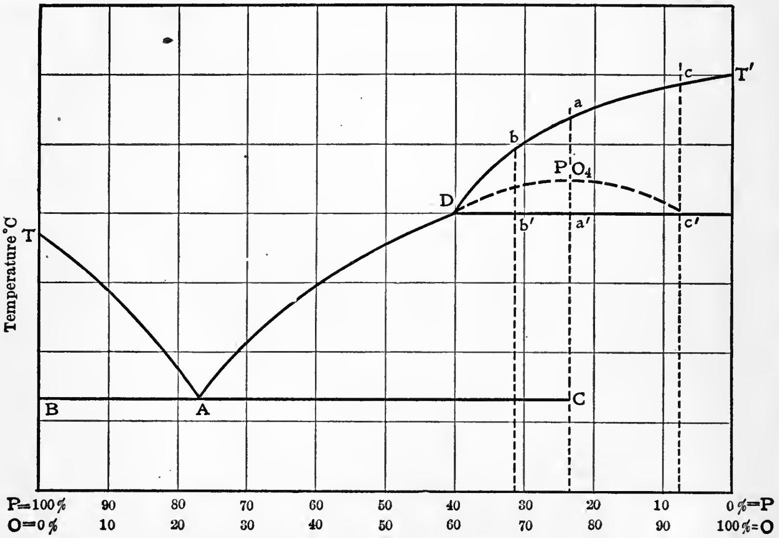

FIG. 23. — Freezing-point curve of the type IIB.

3. *Alloy c–c′.* This begins freezing when the point c is reached, pure metal O separating out, the mother metal meanwhile concentrating along cD as before. When D is reached, the metal O already frozen out reacts in part with all of the liquid mother metal, forming compound PO_4. The final frozen alloy consists of compound PO_4 and metal O.

Alloys in composition between A and D freeze out as the excess substance the compound PO_4, and form eutectic A.

Alloys in composition between A and T freeze out the metal P as the excess substance and form eutectic A.

The position of the point PO_4, as regards concentration and hence the composition of the compound, can be determined by a close examination of the cooling curves of the series of alloys. As already stated, at temperature *D* the transformation into the compound PO_4 occurs. That alloy, during the freezing of which the temperature *D* remains constant for the maximum period of time, marks the compound PO_4. It is further to be noted that the disappearance of the jog in the cooling curves marking the freezing of the eutectic *A* will coincide with this occurrence of the maximum time of freezing of the compound. The point PO_4 is known as a " hidden maxima."

Other possible curves under case **II** are combinations of the types discussed under cases **I** and **II**. The examples outlined cover practically all known cases of alloys, or other physical mixtures.

FREEZING-POINT CURVES OF TERNARY SYSTEMS

The curves which have been discussed are those of systems of two components, viz., binary systems. It matters not whether the components are simple substances or compounds, *i.e.* whether we have, for instance, Fe–Mn; or Cu_2S–FeS; or Fe–FeS. Since in the case of Cu_2S–FeS, S is in combination with both Fe and Cu, we have a binary system, and not a ternary system of Fe–Cu–S, as it is the Cu_2S and the FeS which are the components, and not the Cu, Fe, and S. There are many systems, however, into which three or more components may enter, and it follows, in view of the complicated equilibrium curves (freezing-point curves) of some of the binary systems, viz., those forming several chemical compounds, that ternary and higher systems may be very complex. This fact has retarded the investigation of such systems and comparatively few have been formulated.

As an example of complexity we may consider a ternary system of Cu–Sn–Sb. There are three binary systems involved in this series:

1. Cu–Sn. This is the bronze series and contains in all probability two chemical compounds, which can form mixed crystals with each other and with the pure components.
2. Cu–Sb. This series contains two chemical compounds.
3. Sb–Sn. This series contains two and probably three chemical compounds.

It is, therefore, possible that aside from the three pure metals and the seven chemical compounds in the three binary systems which enter into this ternary system, compounds involving the three metals may form and the system become very complex.

In what follows only the simplest case of a ternary system is presented. The method of graphically depicting the freezing-point curve as a projection on a plane surface is no longer adequate, as three components are now involved, and the equilateral prism method will be used.

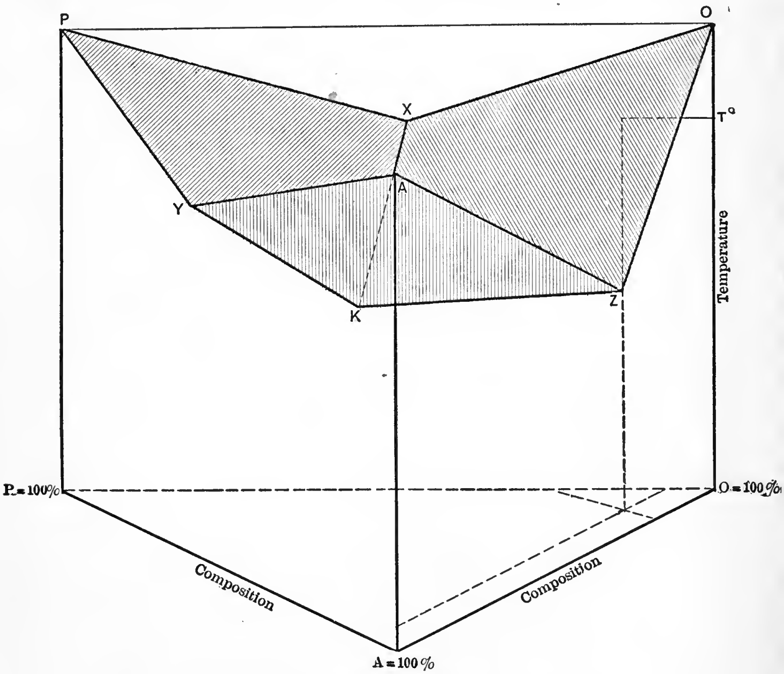

Fig. 24. — Equilateral prism diagram.

In the right prism construction in Fig. 24 the sides of the basic equilateral triangle represent the concentrations of the different components. If we employ an equilateral triangle the length of whose side is equal to 100 units, the sum of the percentage amounts of the three components A, O, and P are represented by a side of the triangle. It follows that any point in the system on a side of the triangle has but two components, but any point in the area enclosed by the triangle has three components. In the last case the composition of any ternary mixture is determined as follows:

In Fig. 25 the point X represents the mixture whose composition is to be determined. There are drawn through it three lines parallel respectively to the side of the triangle.

Then o = 50 per cent. represents the amount of O present; p = 20 per cent. represents the amount of P present; and a = 30 per cent. represents the amount of A present. Conversely, if it is desired to locate a point corresponding to a given composition, we would lay off on OP, from left to right, the percentage of the composition in O, and through it draw a line parallel to PA, then lay off on OP from right to left the percentage of P, and through this draw a line parallel to OA. The intersection of these two lines marks the position of the sought-for point.[1]

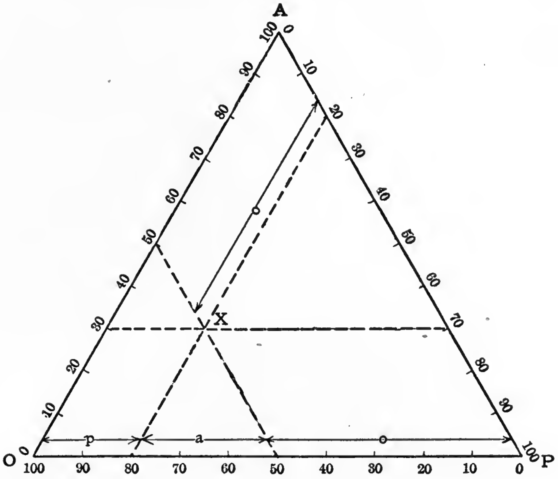

FIG. 25. — Equilateral triangle for representing the composition of ternary systems.

Taking a system composed of the three components A, O, and P, which, for the sake of simplicity, are considered as com-

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[1] This method is due to Roozeboom. Zeitschrift Phys. Chem., 1894, Vol. XV, p. 147.

pletely reciprocally soluble in the liquid state, but totally insoluble in the solid state, we will have the three binary systems A–O, O–P, and A–P, whose freezing-point curves may be depicted one on each face of the equilateral prism, since the ordinates can be made to indicate temperature. The freezing-point curve for A–O is AZO; for O–P is OXP; and for A–P is AYP; the eutectic points being Z, X, and Y respectively. Considering now the systems P–O and P–A, and for the moment P as the solvent metal, it follows, from discussion on page 34, that the curves PX and PY represent the depression of the freezing-point curves of P due to the addition of O and A respectively; therefore the altitude of any point in a plane passed through the curves PX and PY represents the upper freezing-point of that particular mixture, or that subtracted from the temperature of freezing of P, the lowering of the freezing-point ($t°$), due to the admixture of A and O to P in the concentration, indicated by the position of the point within the basic triangle. This is true for all the systems entering into the series. If now a plane is passed through the " depression of the freezing-point " curves of O, viz., OX and OZ, and one through those of A, viz., AY and AZ, these three planes will be common in only one point, K, which logically is the eutectic point of the ternary system.

Now this point "K" may lie either *above* or *below* the lowest eutectic point of any of the binary systems entering into the ternary system, in this case Z. Whether it lies above or below is dependent upon the relative position of the three binary eutectics. If one of the binary systems possess a eutectic point much below the freezing-point of either constituent and near the middle of the concentration, and the other two have eutectic points not much below the freezing-points of the pure constituents, and located as regards concentration much nearer one component than the other, the ternary eutectic point will fall above the lowest binary eutectic point.

When the point "K" lies below the lowest binary eutectic, the ternary system possesses a true ternary eutectic, which will show as a conglomerate of three components. Example: Bi–Pb–Sn.

When the point "K" lies above the lowest binary eutectic the ternary system has what may be termed a " hidden ternary eutectic " toward which the mother metal concentrates during part of the freezing. When the point "*K*" is reached the mother metal readjusts itself by freezing out an excess substance, and from then on concentrates toward the lowest binary eutectic, which is one of the eutectics found in the solid alloy. In these cases no ternary eutectic is found, but the frozen alloy may contain two binary eutectics aside from the "excess substance."

CHAPTER III

PHYSICAL PROPERTIES OF METALS

1. The Crystalline Structure of Metals.[1] — When polished sections of pure metals and alloys are examined under the microscope they are seen to be made up of crystalline grains, which in turn are composed of smaller grains visible under higher magnification. The grains are often of irregular outline, but sometimes present roughly the outline of a cross-section of the common crystal form in which the metal crystallizes. Thus iron crystallizes in the isometric system, a common form being the octohedron. This gives rise to a polygonal cross-section of grain. These crystal grains are known as "allotriomorphic" crystals, *i.e.* crystals that have taken their shape from their surroundings, in distinction to "idiomorphic crystals," *i.e.* those which have their external form freely developed.

The latter will form when a substance is free to crystallize from a liquid or molten medium, as for instance in certain alloys of tin and antimony, the compound $\mathrm{Sn{-}Sb}$ will crystallize out from the molten mother metal, in the form of small cubes. When, however, a pure material, or certain alloys, freeze at a definite temperature or during a small temperature interval, the crystals do not have the opportunity to develop external form, and their shape is determined by that of their neighbors, crystallizing at the same time.

Material of this kind is said to be "holocrystalline," *i.e.* composed wholly of crystalline matter, with no interstitial fillings between grains, or no ground mass present. When metals or alloys are permitted to cool in molds, the surface of the ingot and the bottom or sides will frequently show the presence of "dendrites" or skeleton crystallites, very finely developed.

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[1] Wm. Campbell, Über das Gefüge der Metalle, etc., Metallurgie, Vol. IV, pp. 801, 825; The Structure of Metals and Alloys, Metallographist, Vol. V, p. 286; Mineral Industry, Vol. XI, p. 659. John A. Matthews, Mineral Industry, Vol. X, p. 723.

These dendrites represent the incipient crystals which were free to develop on the surface of the mass during the freezing. They are also sometimes found in the cavities of ingots, where they are at times developed into nearly perfect crystals.

When sections of pure metals, or alloys consisting of isomorphous mixtures, are polished, and then etched with dilute acids or other reagents, in preparation for examination by the microscope, they seem to consist of a number of different kinds of grains, some of which appear light, while others are dark. It would seem at first sight as if several different substances or entities are present. If the angle of illumination of the specimen be changed, or it be revolved through an angle, it will be noted that light grains will become dark, and dark grains, light. This fact is due to the different orientation of the several grains, the difference in orientation being brought out strongly by etching. The etching reagent will dissolve metal from the polished surface, leaving small cavities of definite form or shape, their position having a certain relation to the crystallographic axes of the crystal. If now a crystal be in a certain position or orientation with reference to the reflected light under which it is examined, the cavities in this crystal will be in such position as to reflect nearly all the light thrown on it to the eye, and it will appear bright, while a neighboring crystal whose crystallographic axes are not in relatively the same position or orientation as those of the first crystal will have its cavities in such position as to reflect the light away from the eye, and will hence appear dark. As far as known, all metals are crystalline.

The crystalline or grain structure of metals and alloys has an important bearing on such properties as tensile strength, elastic limit, ductility, etc. When metals like lead, tin, cadmium, bismuth, gold, platinum, and many others are severely strained by compression, tension, or bending, the original crystals of the metal are broken up and replaced by a much finer crystallization, the new crystals being much smaller than the old ones. When a metal is strained under its elastic limit, no change appears in the crystal structure, but if the elastic limit be exceeded it is noticed that fine lines develop in the crystal grains, which are called "slip bands." These slip bands always have a definite orientation in a given crystal. Several systems of them at angles to each other frequently develop as the strain

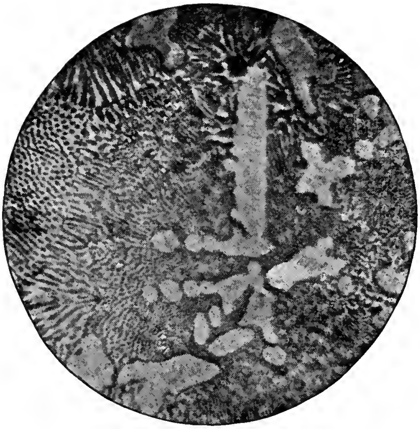

FIG. 26. — Silver-copper alloy. Showing "eutectic" and silver dendrites.

FIG. 26a. — Microstructure of tin. Showing crystal outlines.

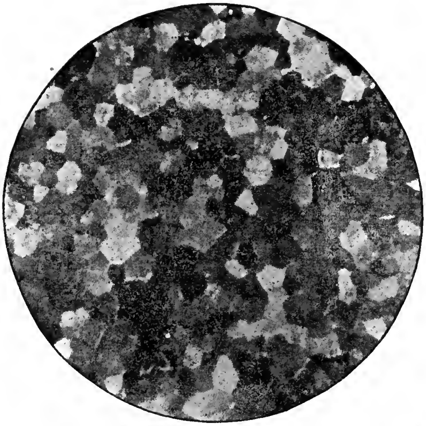

FIG. 26b. — Microstructure of cadmium. Showing crystal outline.

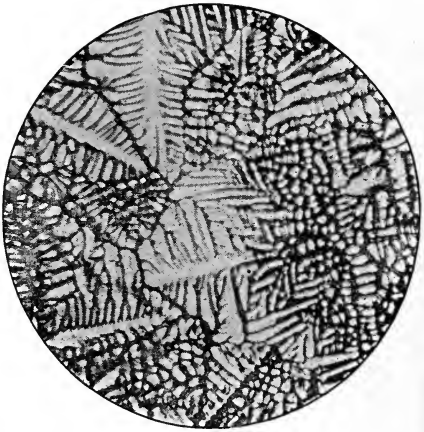

FIG. 26c. — Aluminium cast on stone. Showing crystal structure.

is increased. These slip bands are intimately connected with the formation of the new small crystals.[1] The slip bands may be compared to the cleavage planes and cleavages developed in certain minerals.

When a severely strained piece of metal which has developed a finely crystalline structure is reheated, or "annealed" at a comparatively low temperature (70-100° C.) for soft metals like lead, the small crystalline grains grow quite rapidly, sometimes to large size ($\frac{1}{2}$ to 1 in.), giving an entirely new and coarsely crystalline structure to the metal. In many instances, *e.g.* tin, zinc, cadmium, the rolled metal, of fine crystalline structure, is comparatively tough and strong, while the annealed material with the coarse crystalline structure is weak and brittle. It seems that if a metal be cast and then allowed to cool, a certain size of crystal will be developed, the size depending on the rate of cooling in the immediate vicinity of the freezing-point. If the cooling be rapid the grain will be small, while if the cooling be slow the grain will be comparatively large. The rate of cooling after the metal has once solidified seems to have little influence on the grain size. The annealing of a cast metal, if it has passed through no strain, produces no change in the size of the crystal grains. In order to produce a growth of crystal grains by annealing the metal must first be strained. If a perfectly pure metal[2] having certain definite sized crystal grains be strained and then annealed, the annealing does not produce a growth of crystal but simply a change in the orientation of the crystal, but if the metal be not pure, containing even only minute quantities of impurities which will be present as a film of "eutectic" forming interstitial spaces between the crystal grains, certain of the grains will grow at the expense of others, thus producing eventually a much coarser crystalline structure than the original non-strained metal possessed.[3] The reason for this, as stated by Ewing and Rosenhain, is as follows:

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[1] Structure of Platinum and Effect of Stress on Platinum, Thomas Andrews and C. R. Andrews, Metallographist, Vol. V, pp. 233, 237.

[2] J. C. Humphrey, Phil. Trans. Royal Society, Series A, Vol. CC; Metallographist, Vol. VI, p. 250.

[3] J. A. Ewing and Walter Rosenhain, The Crystalline Structure of Metals, Phil. Trans. Royal Society, vol. CXCV, p. 279; Metallographist, Vol. V, p. 81; also Phil. Trans., Series A, Vol. CXCIII, p. 353 (1900), and Metallographist, Vol. III, p. 94.

The individual crystals are separated from each other by thin interstitial films of a "eutectic" composed of the metal of the crystal and the impurity, this eutectic having a lower melting-point than the metal of the crystal. In strained metal this film is squeezed out from certain portions between crystals so that two crystals may touch at a certain point. These two crystals being differently oriented, two different crystal faces are in contact, which probably have a different electrical potential so that one crystal becomes a positive electrode and the other the negative electrode, the circuit being completed through the film of "eutectic" still left between portions of the faces. One of the crystals, the most electro-positive, therefore dissolves, passing into the eutectic which acts as the electrolyte and is deposited on the other or more electro-negative crystal, this last thus growing at the expense of the first. This diffusion may take place in solid metal, as has been shown by Roberts-Austen.[1] If now the specimen be heated so that the thin film of eutectic between crystal grains be liquid, the rapidity of action will be greatly increased. In cast metal which has not been strained, the eutectic film surrounding crystal grains is continuous, preventing contact of different crystals, so that the above electrolytic action does not take place, and hence no growth of crystal grains occurs.

The growth of crystal grains in metallic alloys, such as steel, may be more complex, and be associated with certain critical temperatures involving molecular changes. The crystalline and grain structure of steel has been very fully studied,[2] and reference should be made to original papers.

In the working of metals the crystalline and grain structure of metals and alloys has an important bearing in connection with heat treatment, on the tensile strength, ductility, and malleability of the metals. As already stated, the mechanical working of various metals by stamping, rolling, or hammering tends to produce a fine-grained crystalline structure and sets

[1] Diffusion of Metals, Phil. Trans., Series A, Vol. CLXXXVII, p. 383 (1896).

[2] Dudley, The Rolling and Structure of Steel Rails, Metallographist, Vol. VI, p. 111; Corson, Heat Treatment of Steel, T. A. I. M. E., Vol. XXXVII, p. 389; Howe, Iron, Steel and Other Alloys, 1900, p. 245; Stead, Jour. Iron and Steel Institute, 1898, I, p. 145, and 1898, II, p. 137.

up internal stresses. This mechanical work very frequently makes the metal tough and often elastic; copper, for instance, when rolled out into sheets is tough and possesses considerable "spring." Under the microscope it is shown to consist of uniform small elongated grains which show no orientation. If the copper be "annealed," viz., reheated to a yellow heat and cooled, this structure is replaced by a large grain structure showing orientation. The metal also loses its elasticity and becomes more ductile. Zinc which has passed through mechanical treatment by rolling shows a finely granular structure and is quite tough. In reheating to a temperature well below its melting-point (462° C.), it develops a large crystalline structure, but becomes very brittle, unlike copper in this respect.

This phenomenon of becoming brittle on annealing is shared by other metals, notably cadmium, tin, and wrought iron. This last tends to develop very coarse structure and great brittleness on prolonged heating to about 750° C. (Stead.)

In the mechanical working of metals, it is frequently necessary to reheat and cool or "anneal" between workings to prevent fracture from the slip bands which develop. These slip bands or incipient fractures are obliterated by the recrystallization induced by "annealing." Annealing accomplishes the release of strain in the crystals which has been induced by the mechanical working of the metal or by rapid cooling from high temperatures. The degree of reheating necessary to relieve strain varies with different metals, but frequently a temperature of 100 to 200° C. will effect considerable annealing. The rate of cooling after reheating is immaterial with many metals like copper, silver, gold, etc., but in certain alloys like the bronzes containing 20 per cent. tin, and iron-manganese alloys, containing more than 7 per cent. manganese, a sudden quenching after reheating produces a very tough malleable metal, while cooling slowly has the opposite effect. The appearance of the fracture produced by breaking bars of metal is evidently closely related to the crystalline structure and in many instances furnishes valuable data as to the condition of the metal. It has been and still is largely used to commercially determine the quality of metals, particularly pig iron, steel, copper, and brasses, but the mode of breaking and other factors sometimes decidedly influence the nature of the fracture. The shape of the mold from which the test piece is taken, the temperature at which the break occurs, the rate of cooling of the test piece through the temperature range of freezing, all vitally affect the nature of the fracture. Metals and alloys have a definite fracture which is indicative of their best physical condition. Experience alone will enable one to judge of fracture. Grading metals by fracture is largely replaced by the much more accurate microscopical examinations of metallography. Wrought iron by proper manipulation may be made to break with either a granular or a fibrous fracture. The method is therefore not always a reliable indication of the structure of the metal.

2. **The Density of Metals.** — The density of a substance is the mass of the substance in a unit volume, provided the unit volume is completely and uniformly filled by the substance, at a standard pressure and temperature. Usually water at 760 mm. and 4° C. is taken as a standard = 1. Density is an absolute term, and is independent of the force of gravity.

Specific gravity is the ratio between the weights of equal volumes of any substance and some other at a given temperature and pressure, taken as a standard. While density and specific gravity are not synonymous terms, they are frequently used interchangeably. As above stated, the true density is only attained when a unit volume is completely and uniformly filled by the substance and no cavities and pores are present. In metals which are cast, this condition can never be fully realized and therefore the density of a given metal or alloy will vary with the crystalline structure as influenced by the rate of cooling, the temperature of casting, the mechanical treatment through which it has passed, and the purity of the metal. Metals can be made denser by compression when confined on all sides, which, however, is not a true increase in density but results from the closing of minute cavities and pores. This increased density may again be lost when the pressure is removed. Pressure, however, may induce atomic rearrangement, or allotropic change, in which case a true change in density may occur. There is a difference in the density of metals in the liquid and the solid states. As far as investigated, all metals except bismuth are denser in the solid than in the liquid state, *i.e.* they contract in solidifying. Bismuth, however, is denser in the liquid state than in the solid, and hence expands on solidifying. It attains, like water, its greatest density just before becoming solid.[1] The increase in volume is about 3 per cent. Certain alloys may possess this property of expanding on solidifying; it is claimed for an alloy of zinc-aluminium, known as Sibley metal. Gray cast iron passes through a pasty stage just before solidifying, in which condition its density is less than that in either the fluid or solid state. Its density in the solid state is said to be less than that in the liquid state.[2] The density of the metals in the fluid and solid states are given in Table VII of this chapter.

3. **Malleability and Ductility.** — Malleability is that property which permits a substance to be permanently extended in all directions without rupture either by impact, as hammering, or steadily applied pressure. There is no fixed standard of malleability. The following data expresses the malleability of the more important metals in the order of their malleability. (1) Gold; (2) silver; (3) copper; (4) aluminium; (5) tin; (6) platinum; (7) lead; (8) zinc; (9) iron; (10) nickel. Pure gold can be beaten into leaves not exceeding 0.0000033 inches in thickness, and is by far the most malleable metal known. It is malleable at nearly all temperatures below its melting-point.

Silver approaches gold in its malleability. It may be beaten into leaves as thin as 0.0001 inch. Copper is also very malleable, even at ordinary temperatures, and may be beaten into very thin plates. This mechanical working hardens copper very perceptibly, which hardness may be removed by annealing (to about 230–250° C.). Copper just below its melting-point, 1084° C., becomes very brittle and may even be pulverized at that temperature. Tin when pure may be readily beaten into thin sheets and foil and as such is a commercial article. Its malleability varies with the temperature. At 200° C. it becomes brittle and may be readily crushed with the hammer. Sheets as thin as 0.0254 inch may be obtained by beating. Tin ceases to be malleable at about 14° below zero degrees C. At low temperatures ordinary tin may pass to an allotropic modification, or gray tin, which is extremely brittle. Platinum is readily rolled and hammered into thin sheets and spun into forms for laboratory use. Lead possesses the same property in a somewhat lesser degree, but may be rolled into very thin sheets, when pure. Zinc at ordinary

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[1] Lüdeking, Annalen, Physik und Chemie, Vol. XXXIV, p. 21 (1888).

[2] H. M. Howe, T. A. I. M. E., Vol. XXXVIII, p. 9.

room temperatures is rather brittle, but when heated to between 100 and 150° C. is readily rolled into sheets. Above 150° its malleability again rapidly decreases. Iron is malleable at ordinary temperatures, but very much more so at higher temperatures, and between 1000 and 1200° C. possesses the property to a remarkable degree. It may be rolled into sheets 0.001 in. thick. Nickel may readily be spun into forms and rolled into sheets, in many respects resembling iron. Nickel plates may be obtained not more than 0.01 in. in thickness. Aluminium is very malleable and may be beaten into sheets 0.000025 in. in thickness. It is easily rolled into sheets 0.001 in. in thickness.

It will be noted that temperature influences the malleability of metals, some being malleable at all temperatures, others only at ordinary temperatures, and others again only at high temperatures. When a metal is malleable at ordinary temperatures, but not at high ones, it is known as being "red short"; when the reverse is true it is known as " cold short."

Ductility is that property of a substance which permits it to be drawn into wires. It is related to malleability in so far as malleable metals are usually ductile, but the order of ductility is not the same as that of malleability. The following is the order of ductility: (1) Gold; (2) silver; (3) platinum; (4) iron; (5) nickel; (6) copper; (7) aluminium; (8) zinc; (9) tin; (10) lead. Ductility, like malleability, is affected by the temperature, and usually increases with it although not invariably so. Gold may be drawn so that one grain makes over 500 ft. of wire, and silver may be drawn into wire so that one grain makes 400 ft. Tin may be drawn into wire, its maximum ductility occurring at about 100° C. Iron is very ductile, particularly at high temperatures, and may be drawn into very fine wire. Aluminium may readily be drawn into wire 0.004 in. in diameter. Nickel may be drawn into wire as small as 0.01 in. in diameter. The property of ductility is associated more or less closely with that of tenacity and toughness, particularly the latter property.

4. **Toughness, Brittleness, and Hardness.** — Toughness is that property of a substance which enables it to resist fracture or a separation of its molecules, after the " limit of elasticity " has been passed. Tough metals may be much bent or twisted before fracture takes place. Most of the malleable metals are tough.

Brittleness is the property of breaking or rupturing suddenly when subjected to sudden application of stress such as hammer blows; or those due to sudden changes of temperature. Brittleness is that property which is the direct antithesis of toughness. The cause of brittleness is but little understood. Small amounts of impurity may make otherwise malleable and tough metals very brittle. This may be due to a filling in of the interstitial space between grain crystals with a brittle eutectic, which, even when present in very small amount, is sufficient cause for rupture to take place along these interstitial planes. When the impurity gives rise to a non-brittle eutectic, no brittleness of the metal ensues. Brittleness in metals is tested for by drop tests, viz., metals are permitted to fall from certain elevations on to a hard, rigid body, or by falling weight tests, in which a given weight falls through a measured height on the metal to be tested.

Hardness is fully discussed under that heading in Chapter V, the Physical Properties of Alloys. Table I gives the hardness of the metals based on Bottone's scale in which the diamond = 3010.

TABLE I. HARDNESS OF METALS

Metal	Hardness	Metal	Hardness	Metal	Hardness	Metal	Hardness
Mn	1456	Cu	1360	Ag	990	Cd	760
Co	1450	Pd	1200	Ir	984	Mg	726
Ni	1410	Pt	1107	Au	979	Sn	651
Fe	1375	Zn	1077	Al	821	Pb	570

5. **Tenacity.** — This is the property of a substance enabling it to resist rupture on the application of tensile or compressive stress. It is possessed by the different metals in a widely varying degree. It varies also with the physical condition of the metal, viz., its crystalline grain structure, whether this be fine or coarse, or whether it has passed through mechanical working or not. Usually the finer the grain structure the greater stress will the metal be able to withstand. This, however, is not invariably true. The temperature also has an important bearing on the tenacity of metals. Generally speaking an increase in tempera-

ture decreases the tenacity, although in nearly pure iron[1] the maximum tenacity occurs at 300° C., at which temperature, however, it seems also to be most susceptible to sudden shock. At temperatures much below zero the tenacity of iron is much increased. Thus Prof. John Dewar[2] found a steel having an ultimate tensile strength of 68,000 lbs. per square inch at ordinary temperatures to have its strength nearly doubled at minus 180° C. This fact is also true of other metals and alloys. The influence of foreign elements on the tenacity of a metal is very pronounced, either increasing or decreasing it. Prominent examples of this are the influences of carbon, silicon, manganese, phosphorus, tungsten, nickel, etc., on iron, which cannot be discussed here in detail.[3] Some further reference is made to this topic in the chapters on alloys and the physical properties of alloys.

When a metal or other substance is subjected to a pulling stress, it is under what in engineering nomenclature is known as a *tensile stress.* When it is subjected to pushing or compression it is under a *compressive stress.* It is the tenacity of the metal that enables it to withstand these stresses, though its resistance to tension may differ from its resistance to compression. Elasticity is the property a body possesses of resuming its original form after the removal of an external force which has produced a change in that form. The amount of change or deformation is known as a "strain." When a metal is subjected to a tensile stress a deformation, or stretch, takes place which is proportional to the tensile stress, until a certain limit is reached, when the proportionality ceases and the stretch increases relatively faster than the stress. The limit of stress above is known as the "limit of proportionality." Within the "elastic limit" the material is elastic, *i.e.* resumes its original dimensions upon the removal of the stress; when the "elastic limit" is exceeded the stretch or strain becomes permanent, and is known as the "permanent set." The limit of proportionality is usually considerably below the "elastic limit," but in many instances no distinction is made between the two points, and the elastic limit is taken to be the point where stress and strain

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[1] André LeChatelier, Comptes Rendus, Vol. CIX, p. 58 (1889).

[2] Lecture before the Royal Institution, London, Jan. 19, 1904.

[3] Roberts-Austen. An Introduction to the Study of Metallurgy, p. 30, etc. (1903).

cease to be proportional. The "modulus of elasticity" is that force which theoretically will stretch a bar one inch in cross-section to twice its length, or compress its length to zero, on the assumption that the stress is proportional to the strain even after a certain limit is exceeded. If force be called stress $= s$, per unit area, and the stretch or compression $=$ strain $= a$ per unit length, then from the above:

$$a : 1 = s : E; \text{ or } E = \text{modulus elasticity} = \frac{s}{a}$$

E is also called Young's modulus.

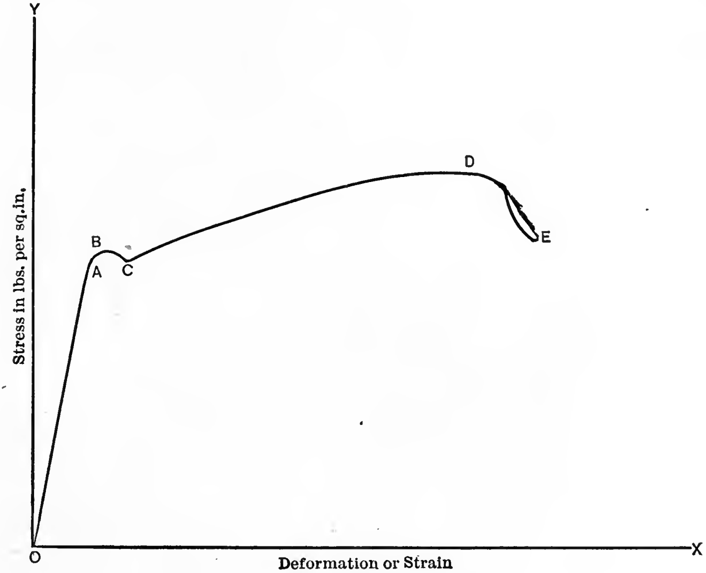

Fig. 27. — Strain diagram.

Fig. 27 represents[1] a strain diagram showing the graphic relation between stress and strain in testing a rather ductile material under tension. Distances parallel to ox measure strain in suitable units, while those parallel to oy measure stress in pounds per square inch. A is the yield point where the stress and strain cease to be proportional, viz., practically the elastic limit. In ductile material the sudden increase of strain from A to C is often accompanied by a decrease in stress, caused

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[1] Experimental Engineering, Carpenter, p. 70 (1906).

by the testing machine adjusting itself to the sudden yield of the material. The curve then continues to rise, reaching its maximum position at *D*, which indicates the "ultimate tensile" strength. The material then begins to " neck," *i.e.* to stretch locally, decreasing the area, and finally breaks at *E*. In testing under tension, the "elongation " of the test piece is measured; this is the total relative stretch or strain and is usually expressed in percentage of the full length and is calculated for the point of rupture. In connection with the elongation the " reduction of area " from that of the original cross-section of the piece at the point of rupture is taken into consideration. The greater the reduction in area of cross-section before rupture and the greater the per cent. of elongation the more ductile is the material tested. Wrought iron will show a high per cent. of reduction of area and elongation, with a comparative low limit of elasticity, while a high carbon steel (1.5 per cent.) will show but very little elongation and reduction of area, and a high limit of elasticity. The latter usually breaks very suddenly and sharply, while the first draws out and breaks rather gradually. These two materials are more or less typical of the way metals and alloys behave under tensile stress to the point of rupture. The strength of metals is influenced also by the manner in which the stress is applied. A metal will stand greater stress if this be gradually applied than if the application be sudden. The resistance of metals to frequently repeated alternations of stress is considerably less than that to continued stress in one direction only. Thus the axle of a railway car in motion is subject to rapidly alternating stress of tension and compression. It has been shown that this repeated reversal of stress for many million times will produce rupture even if the stress applied be below the " elastic limit" of the material. Ewing and Rosenhain[1] in this connection made extensive experiments on Swedish iron, which had an elastic limit of 26,000 lbs., and an ultimate strength of 47,200 lbs. per square inch. On applying alternating stresses to this material ranging from 18,000 to 28,000 lbs. per square inch, slip bands appeared in the crystals, which finally widened, developing eventually into cracks, causing rupture of the piece. It was found that stresses of 10,000 lbs. per

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[1] The Fracture of Metals under Repeated Alternations of Stress, Phil. Trans. Royal Society, Nov. 20, 1902.

square inch, even though repeated many times, produced no slip bands; stresses of 14,000 lbs. per square inch, after repeated reversals, showed fatigue in the metal, slip bands forming, while stresses of 18,000 lbs. per square inch after frequent repetition gave rise to many slip bands and ultimate fracture. It is to be noted that this stress of 18,000 lbs. is much below the elastic limit, 26,000 lbs., and that in using material for purposes in which it is subjected to frequently repeated alternating stresses, low-working values must be used.

6. Vapor Tension, Boiling-Points, Fusing-Points of Metals. — If a vessel be partially filled with a liquid, closed, and the air exhausted from it, vapor will arise from the liquid, due to its vapor tension, viz., its tendency to assume the gaseous state, and fill the unoccupied space. The vapor tension of a liquid is dependent upon its temperature, and for any given temperature the liquid will continue to vaporize until the pressure of its vapor above the liquid is equivalent to the vapor tension. Then a condition of equilibrium will exist. If now the temperature be lowered, vapor will condense to liquid; if it be raised, more liquid will be vaporized until equilibrium again be established. If instead of a vacuum existing above the liquid at the start, the space be filled with any inert gas at any pressure, the liquid will still vaporize just as before, until equilibrium is attained, its vapor tension for a given temperature being unchanged. The vaporization due to the vapor tension may be very much retarded, viz., the rate of vaporization may be much decreased, due to a high pressure of gas resting on the substance; but if time be given equilibrium will establish itself, by the full amount of the substance vaporizing for the given temperature. This explains why metals may be more easily vaporized in a vacuum than under atmospheric pressure.

The pressure above the liquid will be that of the gas filling the space, plus that due to the vapor tension of the liquid for the existing temperature. If now the liquid be heated to such a temperature that its vapor tension for that temperature equals or exceeds that of the pressure resting upon it, the liquid boils[1] and passes completely to the state of vapor. Solids, just as

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[1] Young defines the boiling-point as the highest temperature attainable by a liquid under a given pressure of its own vapor when evaporating with a perfectly free surface and when the heat reaches the surface from without.

liquids, have a definite vapor tension, but while that for liquids at ordinary temperatures is considerable and easily measurable, that for solids is very small for ordinary temperatures. Certain metals have a very appreciable vapor tension in the liquid state, which is made use of metallurgically, viz., zinc. The vaporization of a solid is termed "*sublimation.*" Certain substances may pass rapidly from the solid condition to the vapor condition without an intermediate liquid state. This is the case when the vapor tension of the solid equals or exceeds the pressure above it, viz., under ordinary conditions the atmospheric pressure, at the melting-point of the solid. Usually the vapor tension of a solid at its melting-point is much less than the atmospheric pressure. The curve of the vapor tension of a substance in the solid state is different from that of the vapor tension in the liquid state, and the two curves intersect each other as shown in Fig. 28. This intersection marks the melting- or fusing-point or freezing-point of the substance, since this is the only point in which the liquid and solid states are in equilibrium and at which they have a common vapor tension.

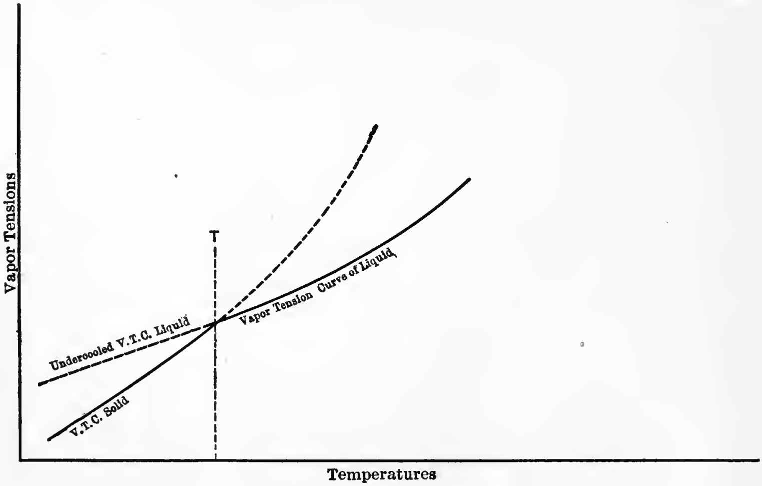

Fig. 28. — Triple-point; vapor tension curves.

If a substance be undercooled, viz., cooled below its freezing-point, and still remain liquid, it has a vapor tension corresponding to a continuation of the liquid vapor tension curve. A number of metals are subject to undercooling, viz., tin, and silver produced by cupellation. The vapor tension of metals both in the liquid and in the solid state is of importance since the vaporization of certain metals and losses incurred thereby is of interest metallurgically. If such metals as copper, lead, zinc, etc., or gold and silver, particularly the latter, are in a heated solid condition or in the molten condition, in a furnace overlain by furnace gases, the overlying space becomes "saturated" with metallic vapor for the temperature existing. The amount of metallic vapor may be very small, and comparatively insignificant, if the overlying gases remain in place. But if the gases over the metal are constantly removed by draft, etc., which conditions exist in furnace work, there is evidently a removal of metallic vapor and a constant condition of "non-saturation" for the space above the metal. Therefore a constant vaporization or evaporation of the metal takes place, which may lead to serious loss with such high-valued metals as gold and silver, unless proper precautions are taken.

Table II gives the vapor tensions of certain metals. The pressures are expressed in millimeters of mercury. (See table, page 72.)

Notes to the Table. Atmospheric pressure, 14.5 lbs. per square inch, corresponds to 760 mm. of mercury column. If mercury be taken at 350° C., its vapor tension is 658.515 mm. of mercury. At atmospheric pressure it will continue to vaporize until the pressure of its vapor above it is equal to 658.515 mm., when equilibrium is established. Supposing the mercury were in a vessel, the space above the mercury being filled with air at atmospheric pressure, 760 mm., and the vessel provided with a small orifice at the top, so that as mercury vaporized the pressure could not rise above 760 mm. If the mercury now be at the temperature mentioned, viz., 350° C., and equilibrium establishes itself, there will be a total pressure above the mercury liquid of 760 mm. made up of the "partial pressure" 658.575 mm., due to mercury vapor, and 101.42 mm. "partial pressure" of the air.

If now the temperature be raised to 357.25° C. the mercury boils, for at this temperature its vapor tension is 760 mm., equal to the pressure above it. In condensing metallic vapors the following is to be noted. Suppose in the above case of mercury

TABLE II. VAPOR TENSION OF METALS

Mercury[1]		Cadmium[2]		Zinc[2]		Gold[3]		Silver[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.
50	0.015	552	25	582	10	942	0.0002	729	0.0002
100	0.270	574	32	675	26	987	0.0005	766	.0005
150	2.684	606	63	684	28	1031	.0013	802	.0013
200	17.015	622	84	699	35	1075	.0029	839	.0029
250	74.592	639	105	710	41	1120	.0063	876	.0063
300	246.704	667	157	732	65	1165	.013	913	.013
350	658.515	681	189	757	96	1209	.026	949	.026
360	785.11	686	226	772	101	1254	.05	986	.050
400	1495.6	704	274	785	156	1298	.093	1023	.093
450	2996.1	722	342	792	158	1343	.165	1059	.165
500	5434.99	752	510	802	166	1387	.285	1096	.285
520	6736.60	760	563	838	264	1432	.478	1133	.478
—	—	770	636	863	368	1476	.779	1169	.779
—	—	786	755	884	477	1520	1.240	1206	1.240
Bismuth[2]		—	—	900	557	1565	1.93	1243	1.93
		—	—	914	653	1611	2.93	1280	2.93
1119	32	—	—	933	764	1654	4.38	1316	4.38
1207	34	—	—	—	—	1699	6.41	1353	6.41
1217	40	—	—	—	—	1743	9.23	1390	9.23

at 350° C., a cubic meter of saturated air and vapor be removed from above the liquid mercury and cooled. The mercury vapor would condense as the temperature sank, in accordance with the vapor tension — temperature curve. If, however, the cubic meter of air and vapor were not saturated with mercury for the temperature 350° C., and the mercury vapor had only a partial pressure of 246.7 mm., it would then have to be cooled to 300° C. before condensation would begin. These facts apply in a general way to all metallic vapors.

Referring more particularly to the vaporization of gold and silver, it will be seen that the vapor tension of gold is very low at the temperatures employed in its metallurgy, and hence

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[1] Ramsay and Young, Jour. Chem. Society, Vol. XLIX, p. 37 (1886); Landolt und Börnstein, Physikalisch-Chemische Tabellen.

[2] Carl Barus, taken from "Physikalische Chemie der Metalle," R. Schenk, 1909.

[3] Calculated by J. W. Richards, Metallurgical Calculations, Pt. III, p. 589 (1908).

danger of loss is slight, except in the case of uncovered crucibles where the air above the metal is constantly changed. It is to be noted, however, that the vapor tension of solutions, viz., in this case, of alloys, is very different from that of the pure metals. Thus we may distinctly have the case where the vapor tension of one metal may be raised by the addition of another, or lowered by the addition of another.[1] In case it is raised, the alloy may suffer much greater vaporization than the pure metal at the same temperature. This is probably the case of gold-copper, and of lead-silver, and would tend to explain the greater losses by volatilization of gold and silver in the presence of certain other metals or impurities. There is very little actual data available on this subject.

7. The Fusion-Point or Melting-Point of Metals. — The physical state of a metal, viz., whether solid, liquid, or gaseous, is like that of all other substances a function of the temperature and the pressure, though, as has been pointed out, metals may pass from the solid to the vapor condition without going through the intermediate liquid form. In fact the three states of matter are by no means divided from each other by such sharp lines as was formerly thought. The temperature at which a metal passes from the solid to the liquid form is known as its fusion or melting-point, and in passing from the liquid to the solid state the point is known as the freezing-point.

While in the case of vapor and liquid, both the pressure and temperature have much influence on the transformation of one to the other, in the case of the liquid and solid states the pressure, while undoubtedly a factor, plays a subordinate role. It takes great changes in pressure to influence very appreciably the melting-point of the metals.[2] As already pointed out the melting-point of a solid may be defined as that temperature indicated by the intersection of the vapor tension curve of the solid state with that of the curve for the liquid state. The addition of even very small quantities of impurities to a metal will appreciably alter its vapor tension, either raising or lowering it, and in the same way affect its melting-point. This subject is somewhat more fully dealt with in Chapter II, page 32. Under certain conditions of "molecular inertia," a liquid metal

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[1] Nernst, Theoretische Chemie, 1909, p. 109.

[2] Nernst, Theoretische Chemie, 1909, p. 71.

may be cooled below its freezing-point for the existing physical conditions, and remain liquid. This phenomenon is termed "undercooling." The most recent determinations on the melting-points of metals are given in Table VI of this chapter. There are a number of old determinations of the melting-points of metals which are not reliable, due to the imperfect methods used in the determination. Most of the recent data has been obtained by highly perfected methods.

8. The Boiling-Point of Metals.—The position of the boiling-point as regards pressure has already been referred to. Moissan[1] has succeeded in attaining the boiling-point of most metals by means of the electric arc, but definite temperature measurements of the boiling-points are comparatively few, due to the fact that the boiling temperatures in most cases are very high and the determinations present great experimental difficulties. Determinations have been made both in vacuum in quartz vessels and under atmospheric pressure. The latest definite figures are given in Table VI. The molecules of metals in the vapor condition as far as determined are monatomic. The probable boiling-points of the metals at atmospheric pressure are given as follows:

TABLE III. BOILING-POINT OF METALS

Metal	Boiling-Point	Metal	Boiling-Point
Zinc	918° C.	Antimony	1440° C.[2]
Cadmium	1025[2]	Gold	2200
Lead	1525[3]	Platinum	2650[1]
Silver	1955[3]	Titanium	2700[1]
Copper	2310[3]	Rhodium	2750[1]
Tin	2270[3]	Ruthenium	2780[1]
Aluminium	1800[3]	Palladium	2820[1]
Manganese	1900[3]	Iridium	2850[1]
Nickel	2450	Osmium	2950[1]
Chromium	2200[3]	Uranium	3100[1]
Iron	2450[3]	Molybdenum	3350[1]
Bismuth	1420[3]	Wolfram	3700[1]

[1] O. P. Watts, Elec. Chem. and Met. Ind., V, 450 (1907).

[2] O. P. Watts, Elec. Chem. and Met. Ind., V, 450 (1907).

[3] H. C. Greenwood, Chem. News, c. 39, 49.

In a vacuum such as is suitable for the production of green cathode light the metals begin to vaporize at the following temperatures:[1]

Zn – 430°
Pb – 320°
Sb – 670°
Bi – 540°
Ag – 1200°
Cu – 1315°
Au – 1375°

Lead boils at 1160° in vacuum. Iron begins to show vaporization in a vacuum at 900° C.[2]

9. **The Welding of Metals.**[3] — Welding as usually defined is that property possessed by those metals which on cooling from the molten state pass through a plastic stage before becoming perfectly solid and rigid, of being joined together by the cohesion of the molecules that is induced by the application of an outside force such as hammering. This property is possessed in the most marked degree by iron and platinum at a white heat. In fact iron or steel and platinum may be welded together. In welding it is essential that the faces of the metals to be welded should be clean, so that molecular contact may be obtained. This cleanliness is achieved by using certain chemicals as ammonium chloride, mixed with sand and borax, during the weld. The ammonium chloride volatilizes certain impurities present as chlorides, and the sand and borax unites with the iron oxide forming a fusible slag which is readily expelled from between the surfaces by hammering.

Electric welding is carried on by means of a powerful electric current of great amperage and very low voltage as the heating agent, with pressure applied slowly as the means of consolidation. A sand blast is used to clean the surfaces previous to the application of the current. So-called welding is also carried out by the Goldschmidt Thermit process, in which powdered aluminium is mixed with ferric oxide and an igniting material to start the reaction. The surfaces to be welded are surrounded in a suitable manner by the welding mixture and the great heat developed produces a high temperature which causes the surfaces to unite by fusion. The procedure, therefore, is

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[1] Krafft, Kuch und Haagn, Berichte der Deutschen Chem. Gesellschaft, Vol. XXXVI.

[2] Boudouard, Metallurgie V, p. 280.

[3] Roberts-Austen, An Introduction to the Study of Metallurgy, p. 47.

not true welding. It produces, however, a stronger joint than a simple weld. A weld of no very great strength may also be produced when two clean surfaces of certain metals are brought together under great pressure at ordinary temperatures. Thus discs of gold and lead pressed together at ordinary temperatures for three months, welded firmly the two metals alloying at the junction. Lead may be welded to lead by simple pressure. In this connection the experiments of Walthere Spring[1] are of interest. He subjected particles of metallic powder to great pressures and was enabled to produce solid homogeneous masses of metal by these means. The following data gives the pressures required:

Table IV.

Metal	Pressure tons per sq. in.	Metal	Pressure tons per sq. in.	Metal	Pressure tons per sq. in.
Lead.......	13	Antimony ...	38	Copper.....	33
Tin........	19	Aluminium ..	38		
Zinc	38	Bismuth	38		

He also claimed to have produced certain alloys by pressure, thus 15 parts bismuth, 8 parts lead, 4 parts tin, and 3 parts cadmium form an alloy which melts at 98° C. The component metals were mixed in a finely powdered state and strongly compressed, then again powdered and pressed, producing what seemed a perfect alloy and not the mechanical mixtures of the metals. That it is impossible to produce true alloys by pressure only, has recently been shown by G. Masing.[2]

10. The Occlusion of Gases by Metals. — Many metals, both in the molten and solid states, have the property of occluding or absorbing gases. Thus if palladium be used as the cathode or negative element in decomposing water by the electric current, or if palladium foil be cooled from a red heat in an atmosphere of hydrogen, it will absorb approximately 900 times its own volume of the gas. This is expelled on reheating to a red heat. Silver in the molten condition absorbs about 22 times its volume of oxygen, most of which is expelled when the metal solidifies.

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[1] Bull. de l'Académie Royale de Belgique, Vol. XLV, No. 6; Vol. XLIX, No. 5, etc.; Berichte der Deutschen Chemischen Gesellschaft, Vol. XV, p. 595.

[2] Zeitschrift Anorgan. Chemie., LXII, 265 (1909).

The expulsion takes place only when the metal is pure. Solidified silver can occlude 0.7 of its volume of hydrogen. Gold in the solid state can occlude 0.48 of its volume in hydrogen and 0.2 of its volume in nitrogen.[1] In what form this absorbed gas may be is not always definitely known. In some cases, like that of oxygen and copper, it unites chemically with the metal to form a compound. In the instance of palladium and hydrogen, it is supposed that the hydrogen assumes a metallic form and alloys with the palladium. In certain other cases the gases are probably in simple solution in the metal both in the solid and liquid forms. Iron occludes in some instances much hydrogen in the solid state which can in part be expelled by heating the iron in a vacuum. It is thought that some of the lower critical points of pure iron (see Fig. 11) are closely associated with the evolution of hydrogen from the iron. The absorption of gases by metals is of much importance metallurgically. Thus the absorption of oxygen by copper depreciates its value for certain purposes very much and must be guarded against. The absorption of large volumes of gases by molten steel, and their partial release at the time of solidification, causes at times serious imperfections in steel ingots, which can be prevented by the adoption of proper means. Molten copper absorbs oxygen[2] which unites with the copper to form Cu_2O. This Cu_2O alloys with the copper, and a eutectic mixture exists of 3.5 per cent. Cu_2O and 96.5 per cent. copper that melts at 1066° or 18° C. below the melting-point of copper. The Cu_2O is scattered throughout the mass of the copper, in the manner of a mechanical impurity. Its presence very decidedly reduces electric conductivity.

Copper produced by the converter, in which air is blown through molten matte, contains usually 2 per cent. and over of Cu_2O. After electrolytic refining the contents in the oxide are reduced to usually less than 0.1 per cent., but subsequent melting and casting again increase it from 0.50 per cent. to 0.75 per cent. in the best instances. If solid copper be heated to somewhat below its melting-point it will absorb oxygen and form

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[1] Roberts-Austen, An Introduction to the Study of Metallurgy (1902), p. 58.

[2] E. Heyn, Short Reports from Metallurgical Laboratory of the Royal Inst. Charlottenburg, Metallographist, Vol. VI, p. 50.

Cu_2O, which is absorbed throughout the mass of copper; and if the process is continued long enough so-called "burnt" copper results. This sometimes happens in the heating of copper preparatory to its rolling or working and gives a product unable to stand the strain of subsequent stamping and cutting.[1] If copper be heated in an atmosphere of hydrogen at a temperature of 600° C. and above, the surface layers become very brittle and show shell-like fractures of a yellowish red color. With prolonged heating the whole of the copper is converted into this condition.[2]

Molten iron and steel absorb great quantities of gas relatively speaking, the largest part of which escapes as the metal cools towards its freezing-point. Steel in the molten condition sometimes "boils," due to the expulsion of gas. Some of this gas is retained by the iron or steel after solidification, and frequently a part of that escaping at the moment of solidification is imprissoned, causing the formation of "blow holes." The addition of small quantities of silicon and aluminium, or manganese, acts as a deoxidizer for any iron oxide present and also seems to increase the power of iron to dissolve gases.[3] The nature and quantity of gases obtained from wire containing 0.047 per cent. carbon by three prolonged reheatings to 1100° C. in a vacuum,[4] is shown in Table V.

TABLE V. GASES IN IRON

MASS OF IRON GRAMS	VOLUME OF GAS OBTAINED c. c. 760 mm.					WEIGHT IN GRAMS				
Grams	Total	CO_2	H_2	CO	N_2	N_2	CO_2	H_2	CO	Total
34	33.70	6.22	11.89	12.70	2.89	0.0030	0.012	0.0011	0.016	0.0321
50	36.43	7.01	7.83	20.23	1.36	0.0017	0.014	0.0005	0.025	0.0412
82.5	78.75	5.08	17.40	53.46	2.81	0.0035	0.010	0.0017	0.067	0.0822
46.0	106.00	5.16	29.17	66.45	5.22	0.0065	0.010	0.0026	0.083	0.1021

The expulsion of the gases on heating iron and steel is rather

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[1] W. Stahl, Verbrennung des Kupfers, etc., Metallurgie, Vol. V, p. 289.

[2] Heyn, *ibid.*

[3] Howe, Iron, Steel and other Alloys, p. 368.

[4] O. Boudouard, Gases in Metals, Revue Metallurgie, 1908, p. 69; Metallurgie, V, p. 277.

closely associated with the critical points of iron.[1] In heating toward Ac_2, the beginning of change of alpha, or magnetic iron, to beta iron, but little gas is set free, but at Ac_2 a large evolution of gas takes place, which then decreases until Ac_3 is reached, the point of change of beta to gamma iron, when another increased evolution takes place. The first gas to be expelled beginning at about 150° C. is CO_2, which is practically completely eliminated at 550° C. At this temperature nitrogen begins to be expelled and its expulsion continues throughout the heating. Above 400° C. the composition of the gas is chiefly hydrogen and carbon monoxide.

The influence of the occluded gases on the properties of iron and steel is probably considerable. Heyn[2] has shown that heating mild steel in an atmosphere of hydrogen at from 730° to 1000° C., and quenching it, causes considerable more brittleness than that produced by quenching from reheating in air.

It is very possible that the ultimate strength of iron and steel and such properties as the electric conductivity are affected by the presence of certain gases.

11. Polymorphism[3] of the Metals. — Polymorphism is that property of a solid substance by virtue of which it is able to exist in two or more different forms, due to a different molecular arrangement, the various forms possessing distinct physical properties. The several forms may belong to different crystal systems, or one may be amorphous, or they may be different crystal forms belonging to the same system. The term *allotropism* is practically synonymous, but is employed in reference to elements only, while polymorphism applies to both elements and compounds. The term "allotropism" is falling into disuse.[4]

Among the metals a number of cases of polymorphism are known. Thus, antimony exists in two forms, a hexagonal and amorphous form. The amorphous form is known as explosive antimony and is produced by electrodeposition on copper from chloride solutions. Its specific gravity is 5.78 as against 6.52,

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[1] Belloc, Bulletin de la Societé d'Encouragement, Vol. CX, No. 4, p. 492, (1908); Metallurgie, Vol. V, p. 386.

[2] Heyn, *ibid.*

[3] Ostwald, Grundriss der Allgemeinen Chemie, 1909, p. 117.

[4] Allotropy refers also to the liquid and gaseous state, while polymorphism has reference to the solid state only. Refer to polymorphism in Chapter II.

that of the ordinary form. It is usually dark gray to black in color and when touched with a sharp, heated point changes into the gray or hexagonal antimony with explosive violence. Iron furnishes a prominent example of polymorphism. In the range from very low temperatures to 780° C., there exists what is known as alpha iron, crystallizing in cubes in the isometric system. It is strongly magnetic. When this iron is heated past 780° C. its volume increases, and heat is absorbed as it gradually changes to beta iron, which also crystallizes in the cubic form in the isometric system, but is non-magnetic. This iron, on passing the temperature of 880° C., changes to still another condition, gamma iron, the crystal form now being the octahedron. Gamma and alpha iron both have a greater specific gravity than beta iron. There are probably other critical points in pure iron, as may be inferred from an inspection of the differential cooling curve of iron shown in Fig. 11.

The metal iridium exists in both the isometric and hexagonal forms. Palladium is similar to iridium. Silver crystallizes in the isometric system, but an amorphous form is also known. Thallium changes its form at 225° C. Tin exists in what is termed the white form, crystallizing in the tetragonal system with a specific gravity of 7.3, which is the normal condition for temperatures above 20° C., to the melting-point, and also in the gray form, which has a specific gravity of 5.85. The transition from white tin to gray tin on lowering the temperature is very gradual until great cold is obtained, when it is rapid.

12. Electric Conductivity and Heat Conductivity. — Electric conductivity is discussed in Chapter V on the "Physical Properties of Alloys." In Table VII the electric conductivities of the various pure metals are given. It is to be noted that the addition of very minute quantities of impurities very greatly reduces the electric conductivity of metals, as is discussed in Chapter V. There is a close relationship between electric conductivity and heat conductivity. If the ratio of the absolute heat conductivity to the electric conductivity at one temperature be divided by the ratio for another temperature, a constant will result which is the same for nearly all the metals for the temperatures involved.[1] The absolute heat conductivity of a metal

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[1] Jäger und Diesselhorst, in Schenk, Physikalische Chemie der Metalle (1909), p. 20.

is designated by the symbol K and is expressed as follows: If a piece of metal be considered whose thickness is 1 cm. and whose surfaces are plane and parallel and differ 1° C. in temperature, then K expresses the number of small calories that pass per second per square centimeter of the metal; *i.e.* is the absolute conductivity.

This conductivity has a temperature coefficient in the same way that electric conductivity has, viz., the heat conductivity may increase or decrease with a rise in temperature. Data on this subject is given in Table VI. Heat conductivity is also expressed relatively, with silver usually as the standard. If silver is taken as 100, the following are the relative heat conductivities of certain metals:

Lead	8.5	Gold	53.2
Steel	11.6	Platinum	8.4
Copper	73.6	Zinc	28.1
Bismuth	1.8	Tin	15.2
Iron	11.9		

13. **Specific Heat.** — The specific heat of a substance is the number of calories of heat required to raise one gram of a substance one degree in temperature. It usually refers to a rise of temperature from zero unless otherwise specified. The specific heat varies with the temperature. It is closely related to heat conductivity and to the linear and cubical expansion of substances. The subject of specific heat is somewhat more fully treated as regards variations with temperature, etc., in Chapter VIII, on "Slags." While the specific heat increases with temperature for the solid state, the specific heat for the liquid state seems to be practically constant. The question of linear expansion is discussed in Chapter V, on "Physical Properties of Alloys." Data on specific heat and linear expansion of the metals are given in Table VI.

14. **Magnetic Properties of Metals.** — Metals vary very much in their behavior in the magnetic field. They are divided into two classes: First, Paramagnetic; second, Diamagnetic. Paramagnetic bodies have the property that if a strip of the substance be freely suspended from its center and placed in a magnetic field, the induced magnetism causes it to set itself parallel to the direction of the magnetizing force. Diamagnetic

bodies, under similar conditions, tend to take up a direction at right angles to the direction of the magnetic force. Iron, nickel, and cobalt are paramagnetic, copper and bismuth are diamagnetic. Paramagnetic bodies have a magnetic permeability which is greater than air, while diamagnetic bodies have a magnetic permeability less than air. Certain magnetic properties of alloys are more fully discussed in Chapter V.

15. The Diffusion of Metals.—When a solid salt, which is soluble, is placed in contact with a liquid, it will dissolve and become uniformly diffused in time throughout the whole mass of the liquid. The same is true of two soluble liquids. The cause of this diffusion is osmotic pressure, and the rapidity of diffusion is dependent on a number of factors, among which is temperature.[1] This diffusion force is also active in metals; thus when two metals are brought together in the molten condition, and they are soluble, they will diffuse into each other, until no difference in concentration exists in any portion of the mass. This diffusion is entirely independent of any mechanical mixing, although mechanical mixing will greatly aid diffusion. Under certain conditions this diffusion is very rapid, while under others it may be very slow. While at first sight it might seem that diffusion would take place only with molten metals, it actually takes place also with a solid and a molten metal, and in some instances between perfectly solid metals.[2]

Roberts-Austen has made many experiments to determine diffusion of metals and the accompanying table gives some quantitative results. (See table, page 83.)

The term K is the diffusion constant, viz., the number which expresses the quantity of metal in grams diffusing through unit area (1 sq. cm.) in unit time (one day) when unit difference of concentration (in grams per cc.) is maintained between two sides of a layer 1 cm. thick. It is to be noted in the given data, with the exception of the case of lead in tin, that the diffusing metal is solid, viz., below its freezing-point, while the solvent metal is liquid, viz., above its freezing-point.

As a means of comparison it may be stated that the diffusion constant for sodium chloride in water at 18° C. is 1.04.

Diffusion is probably intimately connected with vapor ten-

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[1] Nernst, Theoretische Chemie (1907), 169.

[2] Roberts-Austen, Proc. Royal Soc., Vol. LXVII, p. 101 (1900).

TABLE VIII. DIFFUSION CONSTANTS OF METALS

Diffusing Metal	Solvent	Temperature Degrees C	K in square centimeters per day
Gold	Lead	492	3.00
"	"	492	3.07
Platinum	"	492	1.69
"	"	492	1.69
Gold	"	555	3.19
"	Bismuth	555	4.52
"	Tin	555	4.65
Silver	"	555	4.14
Lead	"	555	3.18
Gold	Lead	550	3.18
Rhodium	"	550	3.03

sion, already discussed, and osmotic pressure, even when the diffusion of solid metals is considered, *e.g.* solid solutions. Solid gold diffuses into solid lead at ordinary temperatures, but of course only to a very slight extent (at 100° C. about $\frac{1}{100000}$ of that of gold in fluid lead at 550°) when the two metals are brought into close contact.[1]

An important example metallurgically of diffusion in the solid state is the "cementation process," whereby solid carbon and solid iron are heated together, the carbon diffusing into and through the iron, forming steel. In a similar manner iron heated in contact with hydrocarbon gases will have carbon penetrate into its interior for certain distances. Carburizing, case-hardening processes, for iron are examples of the cementation process. Many instances are known of the penetration of solid metals by gases (first demonstrated by Graham), viz., not the occlusion of gases but the actual penetration of the gas through the mass of metal. Thus nascent hydrogen will readily penetrate through iron at ordinary temperatures.[2]

[1] Roberts-Austen, Proc. Royal Society, Vol. LXVII, p. 101 (1900).

[2] Belloti und Lussana, abstracted in Zeistchrift Physik. Chemie., Vol. VII, p. 229 (1891).

TABLE VI. PHYSICAL PROPERTIES OF METALS

Metal	Melting-Point, Degrees C.	Boiling-Point at 760 mm. Degrees C.	Heat Conductivity, K at 100°C.	SPECIFIC HEAT		LATENT HEAT CALORIES PER GRAM		Coefficient of Linear Expansion at 20° C.
				Sm. Solid	S. Liquid	Fusion	Vaporization	
Aluminium	657.3	1800	0.4923	(15–435°) 0.2356	0.308	76.8	227.7	0.0_4255
Antimony	630.5	1440	0.0396	(0–100°) 0.0495	0.0605	40.2	359.	$.0_40976$
Barium	850.0	1580	—	—	—	—	—	—
Bismuth	268.0	1435	0.0161	(20–100°) 0.03024	0.0363	12.6	—	$.0_41575$
Cadmium	321.7	778	0.2149	(0–100°) 0.0548	0.0623	13.7	216.0	$.0_42879$
Caesium	26.37	—	—	(0–26°) 0.04817	—	—	—	—
Calcium	780.0	—	—	(0–100°) 0.1804	—	52.6	—	—
Cerium	623.0	—	—	(0–100°) 0.04479	—	—	—	—
Chromium	1489.	2200	—	(0–100°) 0.1208	—	—	—	—
Cobalt	1463.	—	—	(15–100°) 0.1030	—	68.0	—	$.0_41234$
Copper	1084.[1]	2310	0.8771	(20–100°) 0.0936	0.133	41.63	858.0	$.0_41669$
Gold	1063.5	ca. 2200	0.7027	(0–100°) 0.0316	0.0358	16.3	—	$.0_41390$
Indium	155.0	—	—	(0–100°) 0.05695	—	—	—	$50°.0_44594$
Iridium	2292.0	—	—	(0–100°) 0.0323	0.055	24.2	—	$.0_406486$
Iron	1512.0	2450	0.1420	(20–100°) 0.11396	0.22	31.64	—	$.0_41110$
Lead	326.9	1525	0.0815	(18–100°) 0.0310	0.0402	4.78	—	$.0_42756$
Lithium	186.0	—	—	(27–99°) 0.9408	0.975	73.0	—	—
Magnesium	651.0	1120	(0–100°) 0.3760	(20–100°) 0.24922	—	58.0	1315.0	$.0_42541$
Manganese	1207.0	1900	—	(20–100°) 0.12109	—	—	—	—
Mercury	—38.85	357	at 50° 0.0189	(20–50°) 0.03312	—	2.82	67.8	—
Molybdenum	>2100.	—	—	(20–100°) 0.06468	—	—	—	—
Nickel	1435.	—	0.1384	(21–99°) 0.1084	—	62.0	—	$.0_413593$
Osmium	2500. ?	—	—	(19–98°) 0.03113	—	—	—	$50°.0_40679$
				(0–100°)				

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[1] No air present; in presence of air — Cu 1064.9° C; Ag 955° C.

TABLE VI. PHYSICAL PROPERTIES OF METALS (*Continued*)

Metal	Melting Point, Degrees C.	Boiling Point at 760 mm. Degrees C.	Heat Conductivity, K at 100°C.	SPECIFIC HEAT		LATENT HEAT CALORIES PER GRAM		Coefficient of Linear Expansion at 20° C.
				Sm. Solid	S. Liquid	Fusion	Vaporization	
Palladium ..	1546.	—	0.1817	0.0592 (−78 to −23°)	—	36.3	—	$.0_411757$
Potassium ..	62.5	667	—	0.1662 (0–100°)	0.2137	15.7	592.	50°$.0_483$
Platinum....	1753.	—	0.1733	0.0323 (10–97°)	0.053	27.2	—	$.0_409821$
Rhodium....	1907.	—	—	0.05803 (0–100°)	—	—	—	50°$.0_40858$
Silver	961.5[1]	1955	0.9919	0.0559 (−79 to 17°)	0.0748	24.7	397.	$.0_418462$
Sodium	97.	742	—	0.2830 (20–100°)	0.333	31.7	1015.	(0-50°) $.0_472$
Thallium ...	303.7	1280	—	0.0326 (19–99°)	—	5.8	224.5	50°$.0_43135$
Tin........	232.	2270	0.1423	0.05515 (0–100°)	0.0637	13.82	271.	$.0_42138$
Wolfram	3000.?	—	—	0.0336	—	—	—	—
Zinc	419.	918	0.2619	0.0935 (0–100°)	0.1275	29.86	425.	$.0_42835$

TABLE VII. PHYSICAL PROPERTIES OF METALS

Metal	Atomic Weight 0 = 16	Atomic Volume	Density[1]	Crystal System	Tensile Strength. Lbs. per sq. in.	Electric Conductivity. Solid State at 0° C.
Aluminium	27.1	10.4	2.54 2.60	Isometric octahedra	—	35.6 × 10^4
Antimony	120.2	18.1	6.41 6.62	Hexagonal rhombohedra	[2] 1000	2.71 × 10^4
Barium	137.37	36.6	3.75	—	—	—
Bismuth	208.0	21.2	10.039 9.80	Hexagonal rhombohedra	[2] 3000	0.872 × 10^4
Cadmium	11 2.40	13.0	7.97 8.64	Hexagonal	—	14.6 × 10^4
Cæsium	132.81	70.6	1.836 1.88	—	—	molten at 27° 2.54 × 10^4
Calcium........	40.09	25.2	1.59	—	—	at 20° C. 9.5 × 10^4
Cerium	140.25	19.9	7.04	—	—	—
Chromium	52.10	7.5	6.92	—	—	—

[1] The upper figures in the density column refer to the liquid state and the lower to the solid state.

[2] Cast metal.

TABLE VII. PHYSICAL PROPERTIES OF METALS (*Continued*)

Metal	Atomic Weight O = 16	Atomic Volume	Density	Crystal System	Tensile Strength. Lbs. per sq. in.	Electric Conductivity. Solid State at 0° C.
Cobalt	58.97	6.7	8.70	—	—	at 20° C. 10.3×10^4
Copper	63.57	7.1	8.217 8.93	Isometric	[2] 30,000–50,000	60.0×10^4
Gold	197.2	10.2	19.227 19.32	Isometric	[1] 20,000 to 14,000	45.5×10^4
Indium	114.8	16.1	7.12	—	—	11.95×10^4
Iridium	193.1	8.6	22.42	Isometric hexagonal	—	—
Iron	55.85	7.1	6.88 7.86	Isometric cubes and octahedra	[2] 55,000 to [1] 48,000	10.37×10^4
Lead	207.10	18.2	10.37 11.37	Isometric	[1] 2800	5.18×10^4
Lithium	7.0	11.8	0.59	—	—	11.9×10^4
Magnesium	24.32	13.9	1.74	Hexagonal	—	24.47×10^4
Manganese	54.93	7.4	7,39	—	—	—
Mercury	200.0	14.0	13.69 14.19	Isometric	—	fluid at 0° 1.063×10^4
Molybdenum	96.0	10.6	9.01	—	—	—
Nickel	58.68	6.5	8.79 8.90	—	50,000 to 54,000	14.42×10^4
Osmium	190.9	8.4	22.48	—	—	at 20° C. 10.53×10^4
Palladium	106.7	8.9	11.90	Isometric hexagonal	50,000	9.79×10^4
Potassium	39.10	45.9	0.8298 0.851	Tetragonal	—	15.05×10^4
Platinum	195.0	9.06	21.32 21.50	Isometric	30,000 to 50,000	9.12×10^4
Rhodium	102.9	8.5	12.1	—	—	—
Silver	107.88	10.2	9.51 10.50	Isometric	[2] 40,000	68.12×10^4
Sodium	23.00	24.1	0.9287 0.9519	Tetragonal	—	21.10×10^4
Thallium	204.0	17.2	11.85	—	—	5.46×10^4
Tin	119.0	16.3	white 6.988 7.29	Tetragonal rhombic	[1] 4000 to 6000	9.346×10^4
Wolfram	184.0	9.8	18.7	—	—	—
Zinc	65.37	9.2	6.48 7.10	Hexagonal	[1] 4500 to 6500	18.6×10^4

[1] Cast metal.

[2] Rolled metal.

CHAPTER IV

ALLOYS

General. — Alloys are of great importance in the industries and the arts, in fact, more so when quantitatively considered than the pure metals. Their application is increasing rapidly with time. Properly classing ordinary carbon steel and cast iron with the alloys, and naming here but the chief of the others — brasses, bronzes, antifriction metals, solders, type metals, etc., — the immense application, industrially, of the alloys is at once apparent. Very recently the perfection of certain types of electric furnace has added impetus to the importance of certain kinds of alloys; viz., those of iron, with nickel, tungsten, vanadium, molybdenum, silicon, manganese, etc., which are now widely used in the manufacture of alloy steels. There are examples of metals in the state of great purity being used in the arts, such as copper, aluminium, and lead, but greater quantities of these same metals are used in the form of alloys with other metals.

A metallic alloy is a mixture or union of metallic substances which, after melting, does not separate into two separate liquid layers. When such separation occurs, each layer becomes a separate and distinct alloy.[1] A substance is said not to alloy when neither substance is capable of dissolving the other in the liquid state, but form two distinct liquids of the perfectly pure substances. A cooling curve of such a mixture would show two horizontal jogs representing the freezing out of the pure constituents. Two substances may be capable of dissolving each other reciprocally in the molten condition without limit, while again the reciprocal solubility may be limited. In the first case there will be an unbroken series of alloys in the system; in the second case there will be two distinct series of alloys in the system of the two components. The solubilities

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[1] Stead., Metallic Alloys, Cleveland Inst. of Engineers, Dec., 1900.

referred to are those of the liquid or molten state only. The solubility in the solid state or the capacity to crystallize together is not referred to in defining alloys, since from Chapter II it is evident that solid "alloys" are frequently conglomerates.

It is not *essential* that the components of an alloy be metals, for certain non-metallic elements — carbon, sulphur, phosphorus, tellurium, arsenic, etc. — combine with metals to form metallic compounds, which alloy with metals. In this volume, for instance, unions of metallic sulphides, such as copper sulphide with iron sulphide, will be called alloys. The constituents or components of an alloy are defined as separate bodies which have distinct and peculiar entities of their own. These constituents may be simple or elementary substances, or they may be chemical compounds of the substances entering into the series, as is evident from what has preceded in the second chapter; or they may be the so-called mixed crystals, already discussed.

In considering alloys it is desirable to divide them into two classes: First, those in which some of the constituents are present in minute amounts only, *e.g.* a few tenths of one per cent.; and second, those in which both or all constituents are present in considerable amounts. The first class may be considered in the light of very dilute solutions and the second in the nature of concentrated solutions. The first class shows peculiarities in the fact that even minute quantities of one metal may cause profound alteration of the physical properties in another, and is discussed generally in Chapter V, on the "Physical Properties of Alloys." The second class, the alloys proper, is discussed in this chapter. The accompanying table IX, by Tammann,[1] gives in tabular form most of the binary alloys investigated to date.

Classifying the binary metallic alloys under the systems adopted in Chapter II, we find the following grouping:

1. IAa. — The components form no chemical compounds with each other and are reciprocally soluble in all proportions, both in the liquid and the solid states.

Cu–Mn; Cu–Ni; Ag–Au; Bi–Sb; Mn–Fe; Mn–Ni; Mn–Co; Fe–Co; Fe–Ni; Ni–Co; Pt–Cu; Pt–Au; Pd–Cu; Pd–Ag; Pd–Au; Pt–Ag; Cu–Au.[2]

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[1] Über die Fähigkeit der Elemente, Verbindungen zu bilden, Zeit. Anorg. Chemie, Vol. LV, p. 90.

[2] This alloy comes under class IAc.

TABLE 9 — BINARY ALLOYS

Showing the systems forming compounds, and those not forming compounds

Cu	Ag	Au	Mg	Zn	Cd	Hg	Al	Tl	Sn	Pb	Sb	Bi	Mn	Fe	Co	Ni	Pd	Pt	Cr
Cu	○	○	$CuMg_2$ $\underline{Cu_2Mg}$	Cu_3Zn_2 $CuZn_4$	Cu_2Cd_3		$\underline{Cu_3Al}$ $CuAl$ $CuAl_2$	○	Cu_4Sn Cu_3Sn $CuSn$	○	$\underline{Cu_3Sb}$ $CuSb$	○	○	○	○	○	○	○	
Ag		○	$AgMg$ $\underline{AgMg_3}$	Ag_3Zn_2 $AgZn$ Ag_2Zn_3 $AgZn$			Ag_3Al $AgAl$	○	Ag_4Sn	○	Ag_4Sb	○		○	○	○	○	○	
Au				$AuZn$ Au_3Zn_5	Au_4Cd_3 $AuCd_3$		$Au_4Al, AuAl$ $Au_5Al_2, AuAl_2$ $AuAl$	○	Au_4Sn $AuSn_2$ Au_4Sn	Au_2Pb $AuPb_2$	$AuSb_2$	○		○		○	○	○	
Mg				$MgZn_2$	$\underline{MgCd}$		Mg_4Al_3	Mg_3Tl_2 Mg_2Tl Mg_3Tl	$\underline{Mg_2Sn}$	Mg_2Pb	$\underline{Mg_3Sb_2}$	$\underline{Mg_3Bi_2}$				Mg_2Ni $MgNi_2$			
Zn					○	○	○	○	○	○	$\underline{Zn_3Sb_2}$ $\underline{ZnSb}$	○		Zn_7Fe Zn_3Fe		Zn_7Ni			
Cd						○	○	○	○	○	$\underline{Cd_3Sb_2}$ $CdSb$	○				Cd_5Ni			
Hg								Hg_2Tl	No Alloy	○		○							
Al								○	○	○	$\underline{AlSb}$	○		Al_5Fe					
Tl									○	Tl_2Pb?	$\underline{Tl_3Sb}$	Tl_3Bi_5 $\underline{Tl_3Bi}$		○		○			
Sn										○	$SnSb$	○	$SnMn_4$ $\underline{SnMn_2}$? $SnMn$	No Alloy	$SnCo_2$ Sn_4Co_3	Sn_2Ni_3 $SnNi_3$ $SnNi_4$?		$SnPt_3$ $\underline{SnPt}, Sn_8Pt_3$ Sn_3Pt_2	○
Pb											○	○	○	○	○	○	Pb_2Pd $PbPd$ $PbPd_2$	$PbPt$	
Sb												○	$\underline{Sb_2Mn_3}$ $SbMn_2$	Sb_2Fe $\underline{Sb_2Fe_3}$	$SbCo$ Sb_2Co	Sb_5Ni_4 $NiSb, SbNi_4$ Sb_2Ni_4			Sb_2Cr $\underline{SbCr}$
Bi														○	○	Bi_2Ni $BiNi$?			○
Mn														○					
Fe															○	$FeNi_2$			
Co																○			No Alloy
Ni																			
Pd																			
Pt																			
Cr																			

2. ICa *and* b. — The components form no chemical compounds with each other and are reciprocally soluble in all proportions in the liquid state, but only partially so in the solid state.

Cu–Tl; Cu–Co; Ag–Tl; Ag–Ni; Au–Bi; Zn–Hg; Zn–Al; Hg–Pb; Pb–Ni; Mn–Bi; Cu–Zn; Cu–Ag; Pb–Sb; Cd–Zn; Hg–Cd; Au–Tl; Cd–Tl; Sn–Zn; Cd–Sn; Al–Sn; Pb–Ag; Cd–Pb; Sn–Pb; Bi–Cu; Bi–Ag; Cd–Bi; Hg–Bi; Al–Bi; Sn–Bi; Pb–Bi; Fe–Cu; Au–Fe; Co–Pb; Co–Bi; Au–Ni; Tl–Ni; Pb–Ni; Cr–Sn; Cr–Bi.

3. IDa *and* b. — The components form no chemical compounds with each other, are only partially reciprocally soluble in the liquid state, and partially reciprocally soluble in the solid state or reciprocally insoluble in the solid state.

Ag–Fe; Ag–Co; Zn–Pb; Cu–Pb; Zn–Tl; Zn–Bi; Cd–Al; Al–Tl; Al–Bi; Fe–Tl; Fe–Pb; Fe–Bi; Mn–Pb; Mn–Bi; Na–Mg; Na–Al; Na–Zn; Al–Pb.

4. IIA *and* B. — The components form chemical compounds with each other, one or more, which in the solid state may form mixed crystals with each other or with the pure components of the series.

Cu–Mg; Ag–Mg; Ag–Zn; Au–Zn; Mg–Zn; Cu–Cd; Au–Cd; Mg–Cd; Cu–Al; Ag–Al; Au–Al; Mg–Al; Tl–Mg; Tl–Hg; Cu–Sn; Ag–Sn; Mg–Sn; Au–Pb; Mg–Pb; Cu–Sb; Ag–Sb; Au–Sb; Mg–Sb; Zn–Sb; Cd–Sb; Al–Sb; Tl–Sb; Sn–Sb; Mg–Bi; Tl–Bi; Sn–Mn; Sb–Mn; Zn–Fe; Al–Fe; Sb–Fe; Sn–Co; Sb–Co; Mg–Ni; Zn–Ni; Cd–Ni; Sn–Ni; Sb–Ni; Bi–Ni; Pb–Pd; Sn–Pt; Pb–Pt; Sb–Cr; Au–Sn.

The nature of intermetallic compounds is still undetermined, as many of the compounds are combined in stochiometric proportion not corresponding to any known valency of the metals entering into them. In the table of alloys those compounds underlined represent those in which the metals are combined according to their valencies; and those not underlined, in which the compound does not correspond to a known valency of the metal. Foerster[1] suggests that intermetallic compounds not obeying the laws of valency may be held together in the manner of "double salts," may in fact be "molecular" and not atomic

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[1] Naturwissenshaftliche Rundschau, 1895; also, Roberts-Austen, Metallographist, Vol. I, p. 352.

compounds. In this case they may be dissociated when in solution, but, like the alums, exist in the solid form. It is, of course, in the alloys in which the components form chemical compounds that the most profound changes occur from the physical characteristics of the pure components.

Many of the alloys in the four main groups are of scientific interest only, at present, and only some of those of importance in the arts or in metallurgic reactions will be discussed and their equilibrium diagrams and physical properties given.

ALLOYS OF CLASS IA

No. 1. — *Gold-Silver.*[1] The addition of silver to gold to the extent of 50 atoms of gold to 50 atoms of silver, or 64.6 per cent. gold and 35.4 per cent. silver by weight, lowers the freezing-point of gold very little, this alloy solidifying at 1061° C., 3° below that of gold. With a further addition of silver there is a steady lowering of the freezing-point to that of silver at 962°. The series forms a continuous series of mixed crystals or isomorphous mixtures.

The freezing of this type of alloy has been discussed under the theoretical curve *IAa*. The cooling curves of alloys of the gold-silver series show the tendency of "selective freezing," the first mixed crystals frozen out being richer in gold. However, in this instance, diffusion seems to be active and rapid and the solidified mixed crystals are of nearly uniform composition if silver is not over 50 per cent., and the cooling does not take place too fast; the alloys containing more silver tend to liquate and show heterogeneity. Very fast cooling may, however, also tend to produce a uniform alloy by arresting the tendency to selective freezing, though this phenomenon is not frequently observed. The gold-silver alloys consist of large grains, which are built up of smaller cubic crystals so that the ultimate structure is very fine. Prolonged heating of an alloy of 91.66 per cent. gold and 8.34 per cent. silver, for two months at a temperature of 700° C., showed an increase in size of grain, but developed no segregation of the two metals, the alloy remaining perfectly uniform and homogeneous in composition. On account

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[1] Roberts-Austen, Proc. Royal Soc, LXII, 161 (1903); T. K. Rose, Chemical News, 1903, I.

of this homogeneity of composition, the British mint now uses an alloy of gold and silver, 916.6 parts gold and 83.4 parts silver for "trial plates," *i.e.* the alloy used for making up the check pieces in the assay of gold bullion for coining purposes. The alloys of gold and silver are harder than either constituent metal, the hardest alloy being 2 parts of gold to 1 of silver. The color of gold is materially lessened by the addition of silver, and when 50 per cent. of silver is present, the color of the alloy is white.

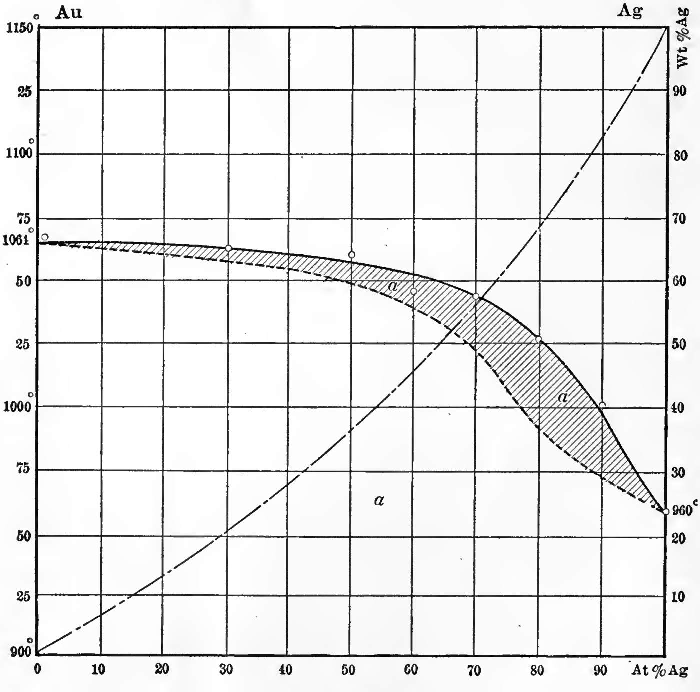

Fig. 29. — Gold-silver series.

Silver-gold alloys are used largely in jewelry manufacture, the most common compositions being gold 75 per cent., silver 25 per cent.; gold 70 per cent., silver 30 per cent.; and gold 60 per cent., silver 40 per cent. "Electrum" are pale yellow alloys containing from 15 to 35 per cent. silver. Jewelers, however, more frequently use ternary alloys of gold, silver, and copper. Alloys of gold and silver are also used to some extent in the manufacture of scientific instruments, and as solders for special purposes.

No. 2. — *Manganese-Iron.* The manganese-iron alloys are of interest, in view of the importance of manganese steel, and other alloy steels. Iron-manganese form an unbroken series of isomorphous mixed crystals. In the rapid cooling ordinarily observed, liquation or segregation is very pronounced and under the microscope alloy sections appear to consist of two distinct types of crystals. The first crystals frozen out are invariably richer in iron than those last frozen out. When the alloys are cooled very slowly they take on a practically homogeneous structure, showing one mixed crystal only.[1]

The magnetic permeability of iron is much decreased by the addition of manganese. The change of magnetic properties occurs as follows:

Per cent. Iron	100	90	80
Magnetism disappears on heating to	950° C.	820° C.	750° C.
" reappears on cooling to	750° C.	715° C.	720° C.

The critical point in the case of manganese-iron alloys is usually a non-reversible one, viz., does not occur at the same temperature on heating as on cooling. Thus according to Hadfield,[2] a 10 per cent. manganese steel loses its magnetic properties on heating to 600° C. and regains them only on cooling to zero degrees C. The rapidity of cooling of the alloys probably plays an important part in affecting the position of the critical points. In general it may be stated that the addition of manganese lowers the temperature at which the critical points occur. (See Chapter V, on magnetic properties of iron-nickel, page 138.)

No. 3. — *Copper-Nickel.* This alloy is of interest, forming one of the binary systems entering into the composition of the German silver alloys — copper-nickel-zinc. An alloy of nickel and copper is also being used quite extensively in sheet metal

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[1] M. Levin und G. Tammann, Zeit. Anorg. Chem., Vol. XLVII, p. 136.

[2] Guillaume, Revue Générale des Sciences, 1903, p. 756.

work of various kinds. The alloys form an unbroken series of mixed crystals (isomorphous mixtures) which are of uniform composition when the alloy is slowly cooled. Fig. 30 shows the freezing-point curve.[1]

In the freezing of an alloy, those crystals solidifying first are richer in nickel than those solidifying later, but diffusion is active and the frozen alloy consists of nearly a homogeneous mass of crystals of the same composition. A rapidly chilled alloy shows a more heterogeneous mass of crystals of somewhat varying composition. Nickel possesses a dimorphic point at 320° C., corresponding to the $Ac_2 - Ar_2$ of iron, above which it loses its magnetism. The transformation is not accompanied by thermal change. The influence of the presence of copper is to depress this critical point so that at 20° C. alloys of 40 per cent. copper and over are non-magnetic.

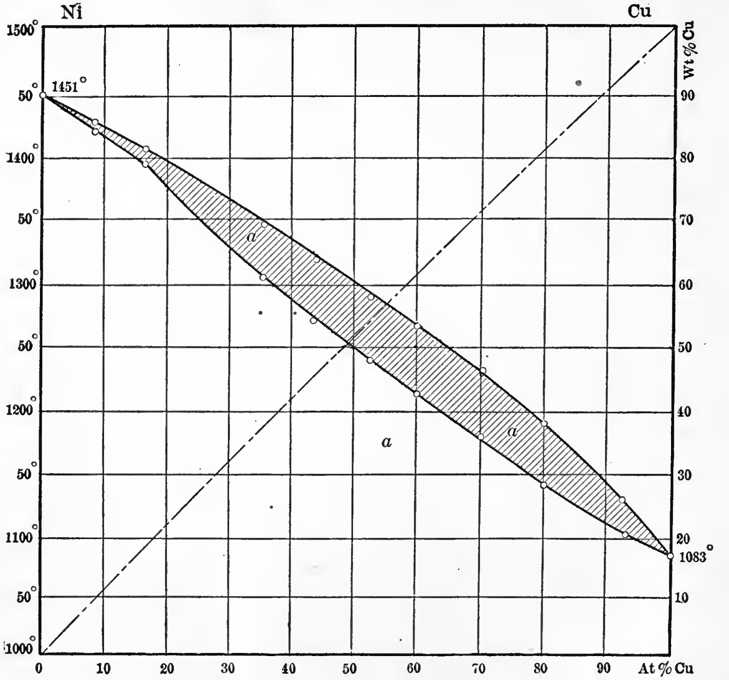

Fig. 30. — Copper-nickel series.

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[1] W. Guertler und G. Tammann, Konstitution der Kupfer-Nickel Legierungen, Zeit. Anorg. Chemie, Vol. LII, p. 25.

"Monel Metal" is an alloy of copper and nickel of the following composition: Nickel, 68 to 72 per cent.; copper, 26.5 to 30.5 per cent.; iron, 1.5 per cent. It is made directly by the refining of nickel copper matte from the Sudbury district, Canada, into an alloy instead of separating the respective metals. It gives an alloy which is ductile, flexible, and easily worked. It can be readily soldered and brazed. Monel metal sheets are used quite widely for roofing purposes in place of copper, having much greater strength and resistance to corrosion than the latter. The following table gives the physical constants of Monel metal:

TABLE X. PHYSICAL PROPERTIES OF MONEL METAL

Property	Castings	Rolled
Tensile strength per sq. in.	70,000 to 85,000 lbs.	100,000 lbs.
Elastic limit	27,000 to 40,000 lbs.	50,000
Reduction in area	25 to 35 per cent.	50 per cent.
Coefficient of expansion	0.00001375	—
Specific gravity	—	8.94
Weight per cu. in.	—	0.323 lbs.

No. 4. — *Copper-Gold.*[1] Copper-gold belongs to group *IAc* in which a minimum is present. Former researches placed it in group *ICb,* with a eutectic present, but more recent work, into the first named group. These alloys are of interest from the fact that they are used so largely in coinage and in the manufacture of jewelry. They also have interest to the metallurgist in the fact that their study sheds some light on the distribution of the valuable metal gold in copper bullion. The alloys of gold and copper are harder, less malleable, but more elastic than the pure metals. The addition of comparatively little copper to gold gives the latter a reddish tint. Alloys with less than 12 per cent. copper are fairly malleable, but with a greater percentage are too hard to work readily. The density of the alloys range between those of gold, 19.32, and copper, 8.93. English standard gold — 916.6 gold and 83.4 copper — has a

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[1] Kurnakow und Zemczuzny, Zeit. Anorg. Chemie, Vol. LIV, p. 159 (1907); also, Roberts-Austen and T. K. Rose, Proc. Royal Soc., Vol. LXVII, p. 105, (1901).

density of 17.48, while the American and French standard — 900 gold and 100 copper — has a density of 17.16. These two standards are the ones most widely used in coinage.

Gold-copper alloys on exposure to air become tarnished, due to the oxidation of the copper. When the tarnished alloy is plunged into a dilute acid or an alkaline solution, the copper oxide is removed, and the effect of fine gold produced on the surface. This operation is known to jewelers as "blanching." Nitric or sulphuric acid dissolves copper from the alloys, if not less than 6.5 per cent. copper is present.

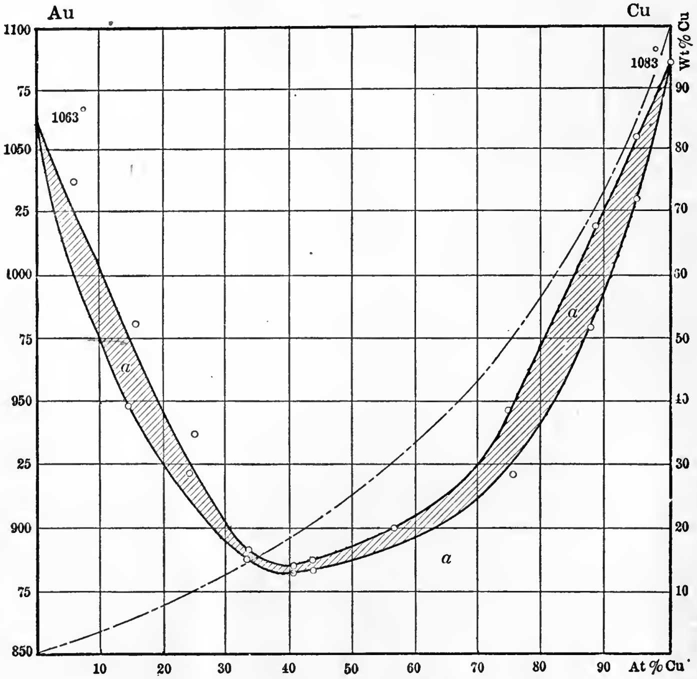

Fig. 31. — Copper-gold series.

The term "carat" is used by jewelers to indicate the fineness of gold alloys; fine gold, 1000 points fineness, is 24 carat fine. The English standard, 916.6, is 22 carat; 750 fine is 18 carat; 624.5 fine is 15 carat; and 375 fine is 9 carat. The most common jeweler's alloys are 18 and 14 carat fine. Jeweler's alloys in addition to copper frequently contain silver and at times iron. Copper-gold belonging to group *IAc*, forming a continuous series of mixed crystals, is not subject to segregation to any marked extent, as a eutectiferous alloy would be, and but little trouble is experienced in getting homogeneous metal for coinage purposes. If, however, but minute quantities of impurities, as lead or bismuth, are present, segregration is very pronounced.

ALLOYS OF CLASS IC*a* AND *b*

No. 1. — *Silver-Copper*. Silver-copper belongs to group *ICb*, a eutectic being present. In the solid state 90 per cent. silver will dissolve up to 10 per cent. copper to form a homogeneous mixed crystal, if opportunity be given by very slow cooling for equilibrium to establish itself. On the other hand, copper dissolves very little silver in the solid state. The eutectic composition is 39.8 atomic per cent. silver and 60.2 atomic per cent. copper, which freezes at 778° C.[1]

The silver-copper alloys ranging from 80 to 100 per cent. silver are of much importance industrially in the manufacture of silver articles, such as plate and jewelry and for coinage purposes. Many tons of silver are used annually for this purpose. The alloy used for plate in the various countries ranges from about 750 to 950 parts silver and 250 to 50 parts copper. The so-called "sterling silver," hall marked by the government assay offices in England, is 925 fine. In the United States the legal standard sterling silver is 900 fine.

Standard sterling silver is somewhat less ductile and malleable than pure silver, and harder, but it can readily be rolled into thin sheets and drawn into fine wire. It is the color of pure silver. Unlike the gold-copper alloy, silver-copper is subject to considerable segregation in cooling, and even in the alloys containing 5 to 10 per cent. copper it is practically impossible to obtain a uniform ingot.[2] This inhomogeneity of the alloys may be reduced to some extent by very slow cooling, viz., holding the ingot at a temperature near its melting-point for a

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[1] Friedrich und Leroux, Metallurgie, Vol. IV, p. 297 (1907).

[2] For a complete discussion of the freezing of alloys and the effect of segregation and diffusion, see H. M. Howe, Iron, Steel and other Alloys, pp. 85 to 116.

long time, permitting diffusion to come into full play. Ingots very quickly cooled show particularly strong segregation. The segregation of the silver-copper alloys is, however, abnormal, for it would be expected that the interior of the ingot be richer in copper than the walls of first frozen parts. The reverse, however, is true. The reason for this is at present unknown.

No. 2. — *Lead-Tin.*[1] This series of alloys is of importance industrially, being used for solders, manufacture of pewter vessels, and for toys and cheap jewelry. The most extensive application is for solders. The series is practically eutectiferous throughout, the eutectic occurring at 64 per cent. tin and 36 per cent. lead by weight, which freezes at 181° C. On either side of the eutectic, "excess" metal solidifies before the eutectic freezes, the excess metal being either lead dissolving approximately 12 per cent. Sn, or tin, depending upon which side of

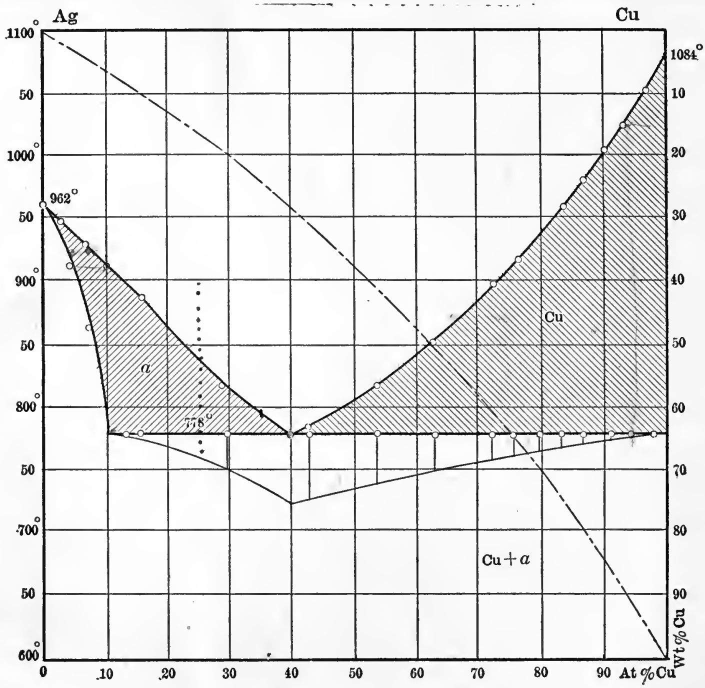

FIG. 32. — Silver-copper series.

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[1] Roberts-Austen, Engineering, 1897, Vol. LXIII, p. 223; P. N. Degens, Zinn-Bleilegierungen, Zeit. Anorg. Chem., LXIII, 207 (1909).

the eutectic the alloy is. The freezing of such an alloy therefore occurs during a temperature interval, during which it is in a pasty condition, permitting it to be worked, a very desirable property in a solder. Solders for tin are rich in tin, usually containing 2 parts of tin to 1 of lead, which is near the eutectic composition, while for soldering lead those rich in lead are employed, 2 parts lead to 1 of tin. The chief requirement of a good solder is a low melting-point and the property to alloy with the metal to be soldered at a comparatively low temperature. It also, for some purposes, should have considerable tensile strength. The tensile strength of the eutectic of tin and lead is about 9500 lbs. per square inch and is the maximum of the series, lead being about 2800 lbs. and tin 4000 lbs.

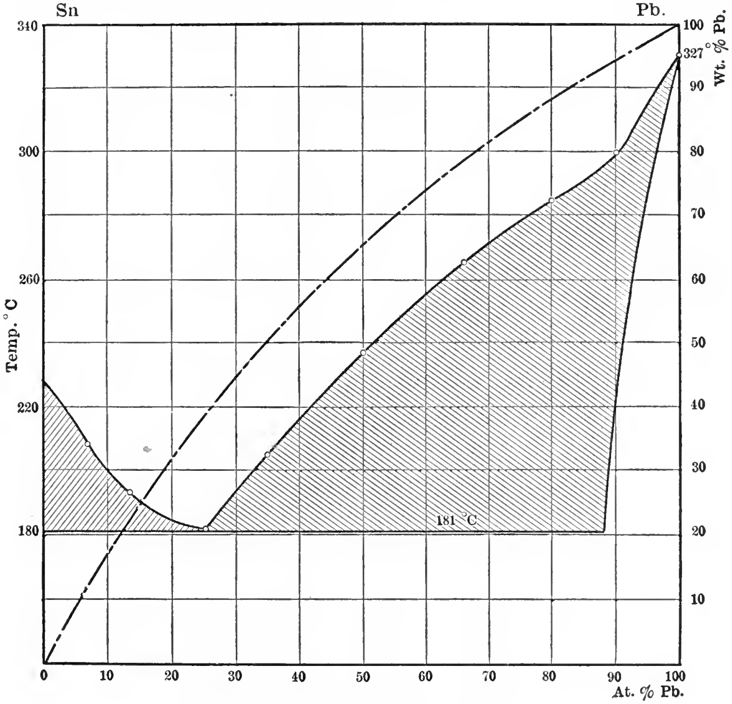

Fig. 33. — Lead-tin series.

Pewter is an alloy of tin and lead, the composition of which usually lies on the tin side of the eutectic, particularly when it is to be used in the manufacture of drinking vessels. There should be no lead present except that which is in the eutectic, as otherwise it would be corroded by acid liquids, possibly resulting in lead poisoning. The eutectic alloy of lead and tin solidifies with a very brilliant surface, and for this reason is used in the manufacture of imitation jewelry to a considerable extent.

No. 3.—*Lead-Antimony.*[1] The lead-antimony series is of interest as it forms the basis of some bearing metals and of type metal. The bearing metals are discussed in a separate section of this chapter. Lead-antimony resembles the lead-tin series very much. It is eutectiferous throughout, the eutectic composition being 87 per cent. lead and 13 per cent. antimony, by weight. Its freezing-point is 228° C. On the lead side of the eutectic the alloys consist of lead embedded in a mass of eutectic, while on the tin side they consist of antimony embedded in a mass of eutectic. The antimony is hard while lead is soft, so that by proper composition alloys may be obtained consisting of either a hard or a soft metal embedded in the eutectic mass, thus conferring distinct properties. For type metal the requirements are that the alloy shall give good sharp castings and that it shall resist the wear due to repeated use. Alloys of not more than 15 per cent. Sb expand on cooling and give sharp castings, but are too soft to wear. The addition of tin to antimony gives rise to a compound SbSn, which forms hard cubical crystals, these crystals furnishing the hard substance which takes the wear of the type. A common composition of type metal is 60 per cent. lead, 30 per cent. antimony, and 10 per cent. tin. For the best type an alloy of lead 50 per cent., antimony 25 per cent., and tin 25 per cent. is used. Antimonial lead is also used for constructing valves and pump parts employed in the transfer of corrosive liquids. The following table[2] gives the tensile and compressive stress of alloys used for this purpose:

TABLE XI. STRENGTH OF LEAD-ANTIMONY ALLOYS

Per cent. Lead	Per cent. Antimony	Tensile Strength Lbs. per sq. in.	Compressive Strength Lbs. per sq. in.
90	10	6460	15,180
87	13	6340	14,430
85	15	5780	14,980
80	15 + 5 per cent. Sn	5070	14,000

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[1] Roland-Gosselin, Gautier, Bul. de la Soc. d'Encouragement, etc., 1896.

[2] Goodman, Engineering, Sept. 21, 1906.

No. 4.—*Lead-Silver.*[1] This series of alloys is of interest in the bearing it has on the Pattinson process for the desilverization of lead and on the cupellation of lead-silver bullion.[2] The series is eutectiferous throughout, the solubility of silver in lead and vice versa being practically nil in the solid state. The eutectic occurs at a composition of 3.5 per cent. silver and 96.5 per cent. lead, the freezing-point of which is 303° C. In cooling alloys on the lead side of the eutectic, pure lead freezes out as excess substance when the temperature sinks to the freezing-point curve, the mother metal being enriched in silver until it reaches the eutectic composition. In the Pattinson process the silver-lead bullion containing 200 to 300 oz. of silver per ton —0.684 to 1.026 per cent.—is melted in iron kettles and care-

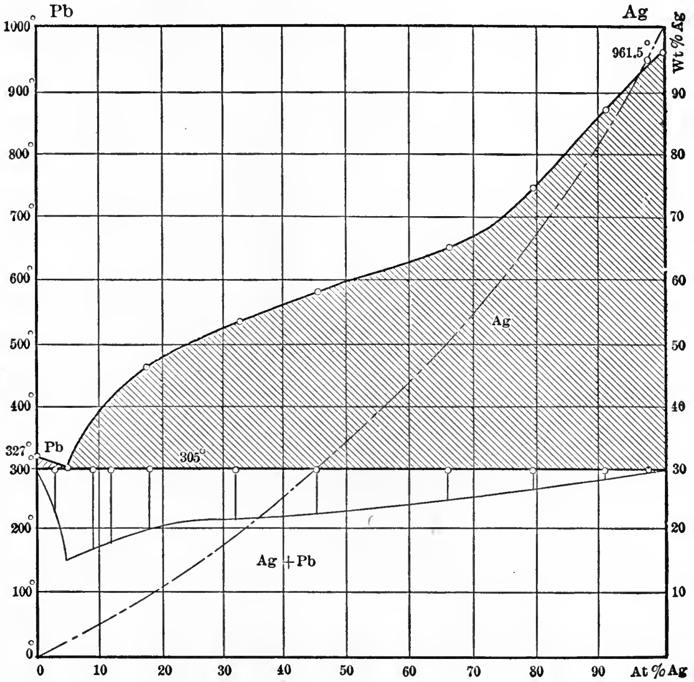

FIG. 34. — Lead-silver series.

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[1] K. Friedrich, Metallurgie, Vol. III, p. 396 (1906); Petrenko, Zeit. Anorg. Chemie, Vol. LIII, p. 200 (1907).

[2] Fulton and Anderson, Western Chemist and Metallurgist, Feb., 1908.

fully cooled through the range from 327° C., the freezing-point of lead, to 303° C., the freezing-point of the eutectic, pure lead freezing out. When about 315° C. is reached, the remaining mother metal (enriched in silver) is drained out, and the lead crystals removed from the kettle. These two products are then re-treated in the same way, the final products being nearly pure lead, not containing more than 0.2 to 0.3 oz. silver per ton, and an enriched lead containing about 2.5 per cent. silver—730 oz. per ton—which is cupeled for its silver.

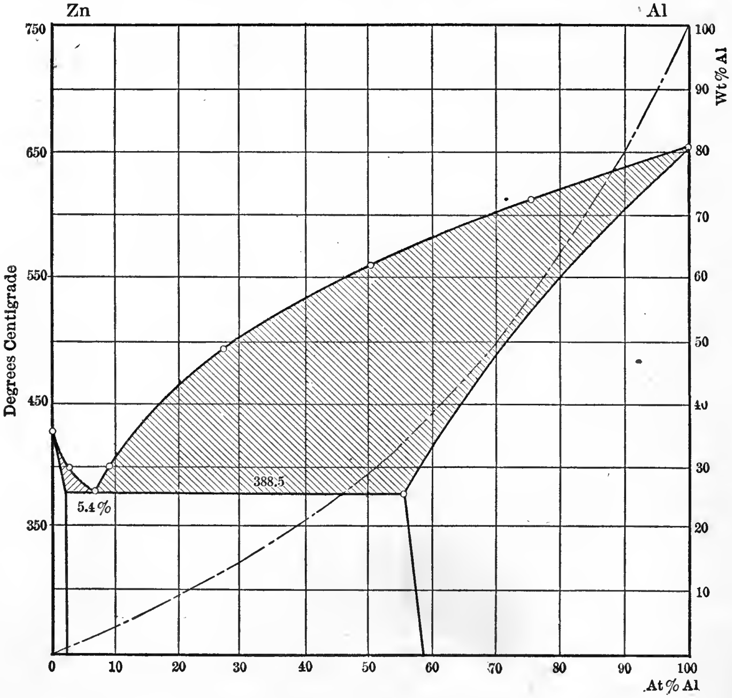

Fig. 35. — Aluminium-zinc series.

No. 5.—*Aluminium-Zinc.*[1] The two metals form mixed crystals with each other, zinc dissolving approximately 2 per cent. aluminium, and aluminium about 45 per cent. zinc. The eutectic composition occurs at 5.4 per cent. aluminium and 94.6 per cent. zinc, the freezing-point being 380.5° C. Aluminium zinc alloys are used in casting art objects in which lightness is an

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[2] E. S. Shepherd, Journal of Physical Chemistry, Vol. IX, p. 504 (1905).

object, but where pure aluminium cannot be used, as it does not make sharp, well-defined castings. Alloys up to 15 per cent. zinc can be rolled and drawn. Alloys between 25 and 50 per cent. zinc are very hard, approaching steel in hardness. Certain alloys are used in the manufacture of scientific instruments where lightness combined with strength is an object. They are also used extensively in the automobile industry. The industrial alloys contain less than 50 per cent. zinc.

ALLOYS OF CLASS II

No. 1.—*Iron-Carbon.*[1] Fig. 36 represents the equilibrium diagram of the series iron-carbon, which includes the very important group of ordinary carbon steels and cast iron. The subject of this system is an extensive one and the barest outline only is here given.

Iron in the molten state is capable of dissolving carbon in large proportion in the form of carbide of iron, Fe_3C (cementite). In the diagram, region 1 represents this condition. On cooling alloys of less than eutectic composition (4.2 per cent. carbon), a mixed crystal freezes out which, when saturated, contains about 2 per cent. carbon. This substance is called "austenite," and is stable only in the upper part of region 4 and in region 2. Austenite has been preserved in cold steel by a very sudden chilling from a high temperature. In the middle and lower parts of region 4 and in region 7, the solution of the carbide in iron is known as "martensite," and is derived from the austenite on cooling. To the right of the eutectic point, "primary" cementite freezes out as the excess substance, as is indicated by region 3. At a temperature of 1130° C., the eutectic freezes, consisting of saturated austenite and of cementite, the total carbon contents of the conglomerate being 4.2 per cent.

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[1] Based on: Howe, Das Zustands diagram des Systems Eisen-Kohlenstoff, Metallurgie, Vol. VI, pp. 65, 105 (1909); the Carbon-Iron Diagram, T. A. I. M. E. XXXIX, 3 (1908). Benedicks, "Über das Gleichgewicht und die Erstarrungs-strucktųren des Systems Eisen-Kohlenstoff," Metallurgie, Vol. III, p. 393 (1906). Goerens, Über den augenblicklichen Stand unserer Kenntnisse der Erstarrungs- und Erkältungs- Vorgänge bei Eisen-Kohlenstoff-Legierungen, Metallurgie, Vol. III, p. 175. Wüst, Über die Entwicklung des Zustandsdiagrams, etc., Metallurgie, Vol. VI, p. 512 (1909).

The curve *GHSP* represents the transformation curve of the mixed crystal austenite or martensite. On cooling, the point G = Ar_3 marks the change from gamma iron into beta iron; the curve H to S = Ar_2 marks the transformation of beta into alpha iron, alpha iron being magnetic and beta iron non-magnetic. The point S = Ar_1 marks the transformation of martensite, containing 0.9 per cent. carbon and called "hardenite," into the conglomerate "pearlite," which consists of cementite (Fe_3C) and ferrite, the latter practically pure iron. In cooling a mixed crystal of martensite containing say 2 per cent. carbon, cementite will form from it along the line *PS*, the martensite finally attaining a composition with 0.9 per cent. carbon, when it breaks up into "pearlite." A mixed crystal of martensite to the left of the point S will, on cooling, begin to separate out ferrite when it reaches a point on the curve *GHS*, the martensite meanwhile concentrating toward 0.9 per cent. carbon, at which point it will break up into pearlite. The point S is called a "eutectoid" point, and pearlite is termed a "eutectoid."

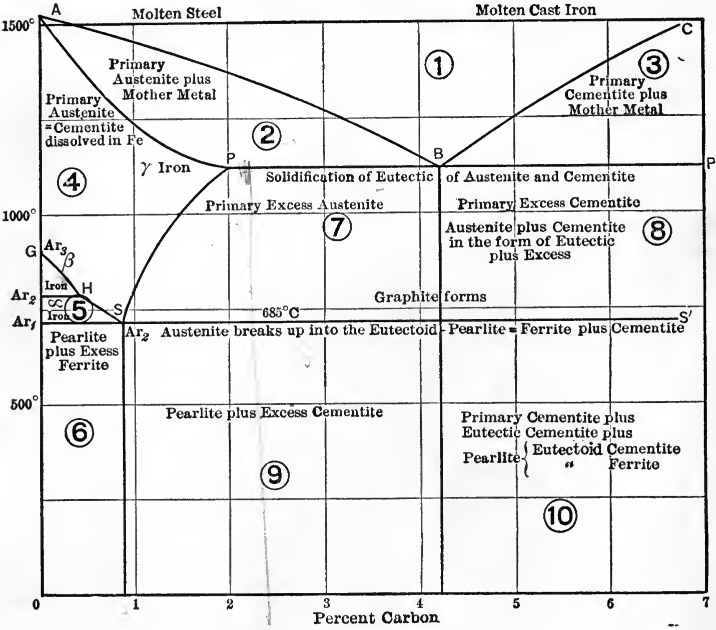

FIG. 36. — Iron-carbon series.

The resemblance of a eutectoid, which occurs in the solid state and is that composition which has the lowest transformation temperature, to a eutectic, which is the composition that has the lowest freezing-point, is apparent.

In region 6 the solid mass will consist of pearlite and excess ferrite. In region 9 it will consist of pearlite and excess cementite. Taking an alloy of the composition of 3 per cent. carbon, it will consist, just after cooling to 1130° C., of excess austenite and eutectic composed of austenite and cementite. On further cooling some of the cementite may break up into ferrite and graphitic carbon, graphite being a more stable form of carbon than the carbide of iron. Austenite will change into martensite, which in turn will change into "hardenite," with the separation of more cementite, the hardenite finally changing into pearlite, so that an alloy of this composition (3 per cent. carbon) will eventually consist of cementite, some graphite, ferrite, and the eutectoid pearlite, composed of ferrite and cementite. The amount of graphite which forms is dependent upon a number of conditions, primarily upon the nature of the impurities present, particularly silicon and sulphur. The freezing of an alloy to the right of the eutectic point B is similar except that the excess is cementite and the only austenite present is in the eutectic. It may be generally stated that the limit of occurrence of steel is fixed by the saturated mixed crystal austenite (2 per cent. carbon). Alloys containing more than 2 per cent. carbon fall in the class of cast iron. The change from martensite into hardenite and from thence into pearlite may be arrested by very sudden chilling from above the temperature Ar_1. In this case the product is hardened steel, the martensite being preserved in region 6 or 8, to which it is not normal. This hardened steel may be converted into the normal state by reheating to slightly above Ar_1. This process is called "annealing." For a further discussion of this series of alloys, reference is made to works on the metallography of iron and steel.

No. 2. — *Copper-Zinc.*[1] This is a very important series of alloys, as it contains the brasses, so widely used for many

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[1] V. E. Tafel, Konstitution der Zink-Kupfer-Nickel-Legierungen, und die binären Systeme, Cu – Ni; Cu – Zn; Ni – Zn; Metallurgie, Vol. V, p. 343, etc. (1908).

purposes. There is an extensive literature on the series, but the question of the exact constitution of the brasses has not yet been determined. The data used here represents the most recent research.

In range of physical properties, the zinc-copper alloys, as influenced by comparatively small differences of composition, resemble the iron-carbon (steel-cast iron) series very much. Small differences in composition bring about very decided changes in the strength, hardness, and ductility of brasses, and therefore, depending upon the purpose for which the alloy is to be used, its composition varies.

There is some discussion as to whether the zinc-copper series belongs in group *II* (*i.e.* that in which chemical compounds form) or to group *ICa* (mixed crystals series with a transition point). The number of entities in the series cannot, in the author's opinion, be satisfactorily explained, except on the basis that compounds exist.

The table gives the solid "phases" occurring in the series.

TABLE XII. CONSTITUENTS PRESENT IN BRASSES

Mixed Crystal	Range in Composition		Color	Nature		
	Cu.	Zn.				
	%	%				
Alpha	69 to 100	0 to 31	Yellow	Cu	dissolving	Cu_2Zn
Beta	39 " 62	38 " 61	Red	Cu_2Zn	"	Cu
Gamma	30 " 39	61 " 70	White	Cu_2Zn	"	Cu_2Zn_3
Delta	19 " 27	73 " 81	—	Cu_2Zn_3	"	Cu_2Zn
Epsilon	14 " 17	83 " 86	—	Cu_2Zn_3	"	Zn
Eta	0 " 2.5	97.5 " 100	—	Zn	"	Cu_2Zn_3

The range of these mixed crystals (solid phases) is readily seen from the equilibrium diagram (Fig. 37). Tafel considers the existence of the intermetallic compound Cu_2Zn_3 as established; its composition occurs at 39.33 per cent. Cu and 60.67 per cent. Zn. There is probably also a chemical compound of the composition Cu_2Zn (Cu = 66.02 per cent., Zn = 33.98 per cent.).

The following table shows the tensile strength, elastic limit and crushing strength of certain alloys of the copper-zinc series which are in ordinary use. (See table, page 108.)

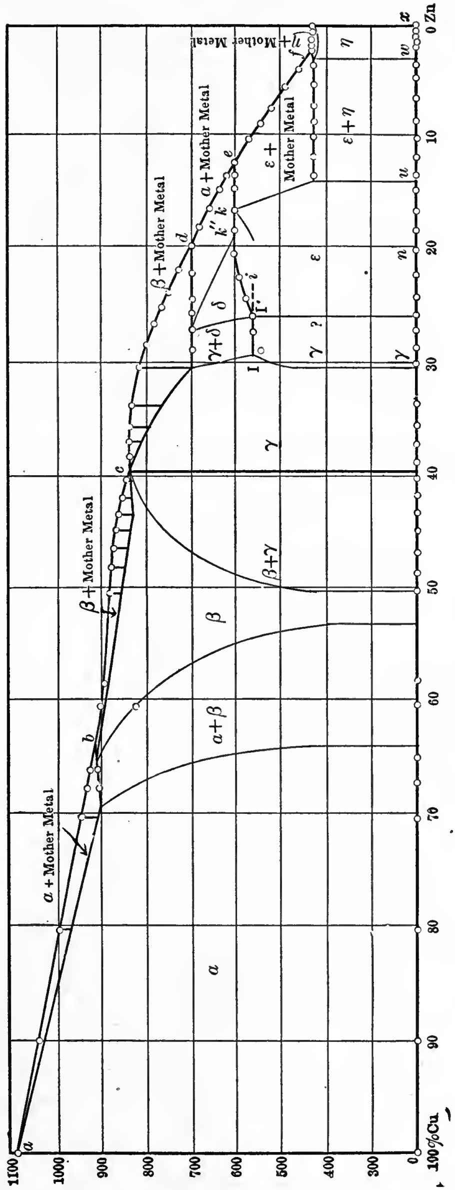

FIG. 37. — Copper-zinc series.

TABLE XIII. STRENGTH OF COPPER–ZINC ALLOYS

Microscopic Constituent	Copper per cent.	Zinc per cent.	Tensile Strength Lbs. per sq. in.	Elastic Limit Lbs. s. in.	Crushing Strength Lbs. s. in.	Elongation per cent.
Copper	100	0	27,000	14,000	41,000	7
Alpha	95	5	28,000	12,000	28,000	12
"	85	15	32,000	9,000	33,000	25
"	75	25	37,000	9,000	46,000	38
"	65	35	46,000	13,000	63,000	33
Alpha + Beta	60	40	49,000	17,000	74,000	19
Beta	50	50	30,000	24,000	116,000	4
Beta + Gamma	45	55	14,000	14,000	126,000	—

Wire brass has a composition of 72 per cent. copper, 28 per cent. zinc.

Common brass has a composition of 66⅔ per cent. copper and 33⅓ per cent. zinc, and is used for sheets, wire, tubes, pipe fittings, etc.

"*Muntz*" *metal* has a composition of 60 per cent. copper and 40 per cent. zinc. It is used for bolts, nuts, etc., and has the property of being malleable at a red heat.

Delta metal contains 56 per cent. copper, 42 per cent. zinc, and is used where strength is particularly necessary. Delta metal frequently contains a little iron.

Brasses range in composition from 90 per cent. copper and 10 per cent. zinc to 16 per cent. copper and 84 per cent. zinc, though most of the brasses contain more than 50 per cent. copper.

No. 3. — *Copper-Aluminium.*[1] This is an important series in that it contains the *aluminium bronzes.* The range of composition for industrial purposes is limited; for bronzes it lies between 100 to 89 per cent. copper and 0 to 11 per cent. aluminium, while on theot her end of the series the range is from 100 to 96 per cent. aluminium and 0 to 4 per cent. copper. It will be seen from reference to the diagram that the alloys of interest are: First, those in which copper and the intermetallic compound Cu_3Al are concerned, and second, those

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[1] H. C. Carpenter and C. A. Edwards, 8th Report Alloys Research Com., Proceedings of the Inst. of Mech. Engineers, Jan. 18, 1907.

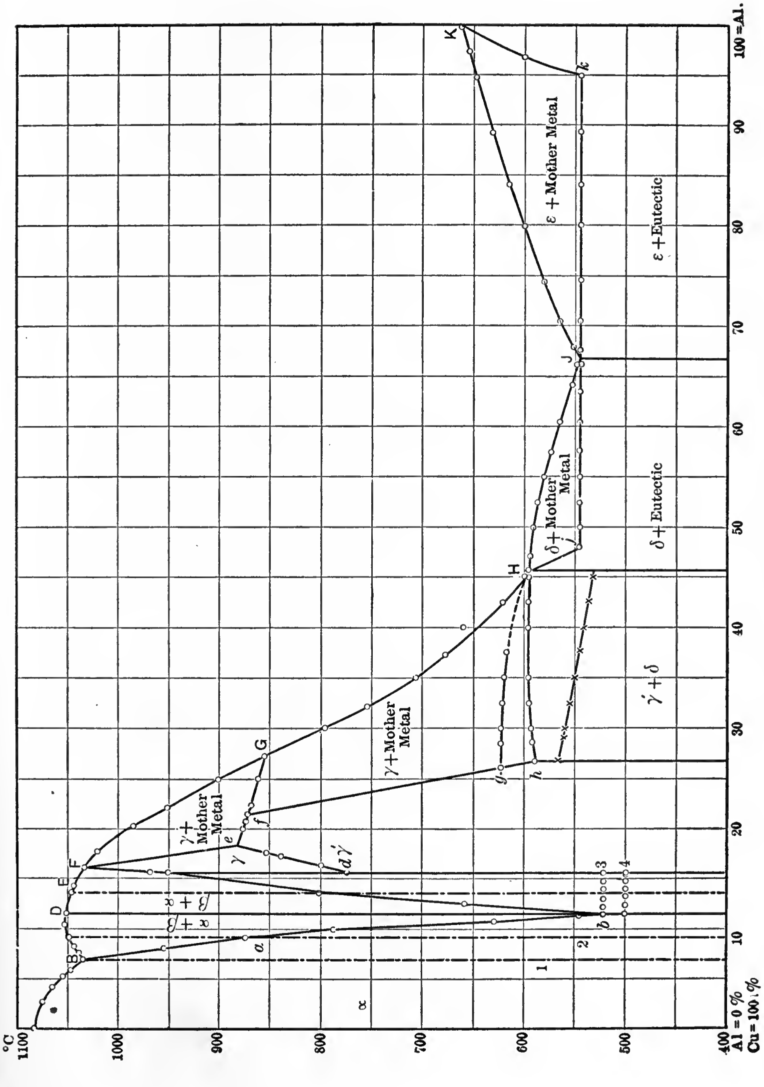

Fig. 38. — Copper-aluminium series.

containing the mixed crystal Epsilon (aluminium dissolving about 4 per cent. copper). The changes which take place during cooling in the alloys from 0 to 11 per cent. aluminium are not discussed here. They are similar to those occurring in the copper-tin series, in which changes of constitution of mixed crystals in the solid state, with consequent changes in physical properties, occur. These are fully discussed under copper-tin. Aluminium bronzes have great tensile strength, and are especially noteworthy in their capacity to resist rapidly repeated alternating stresses.

One per cent. of aluminium changes the color of copper to a "red brass" color; 2.5 per cent. of aluminium gives a gold color; 5 per cent. a pure yellow color, resembling gold very much; 7.5 per cent gives the color of so-called green gold; 10 per cent. gives a bright light yellow color; 15 per cent. gives a yellowish white alloy, which is too brittle to be of use. Table XIV shows the effect of increase of temperature on the strength of aluminium bronze.

TABLE XIV. EFFECT OF TEMPERATURE ON THE STRENGTH OF 10% ALUMINIUM BRONZE

Temperature Degrees Cent.	Tensile Strength Lbs. per sq. in.	Elongation Per cent.
15	76,000	19
100	74,800	22
150	72,800	21
200	70,200	22
250	67,000	21
300	63,000	19
350	52,800	15
400	33,000	21
450	14,200	23

Aluminium bronze[1] is softened or annealed by chilling from a red heat. Working the metal makes it stiff and hard, if it be not frequently annealed. To get bronze of maximum hardness it must be cooled slowly. Bronze is best worked (rolled)

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[1] Aluminium-copper alloys, in "Aluminium, Its Properties and Metallurgy and Alloys," J. W. Richards.

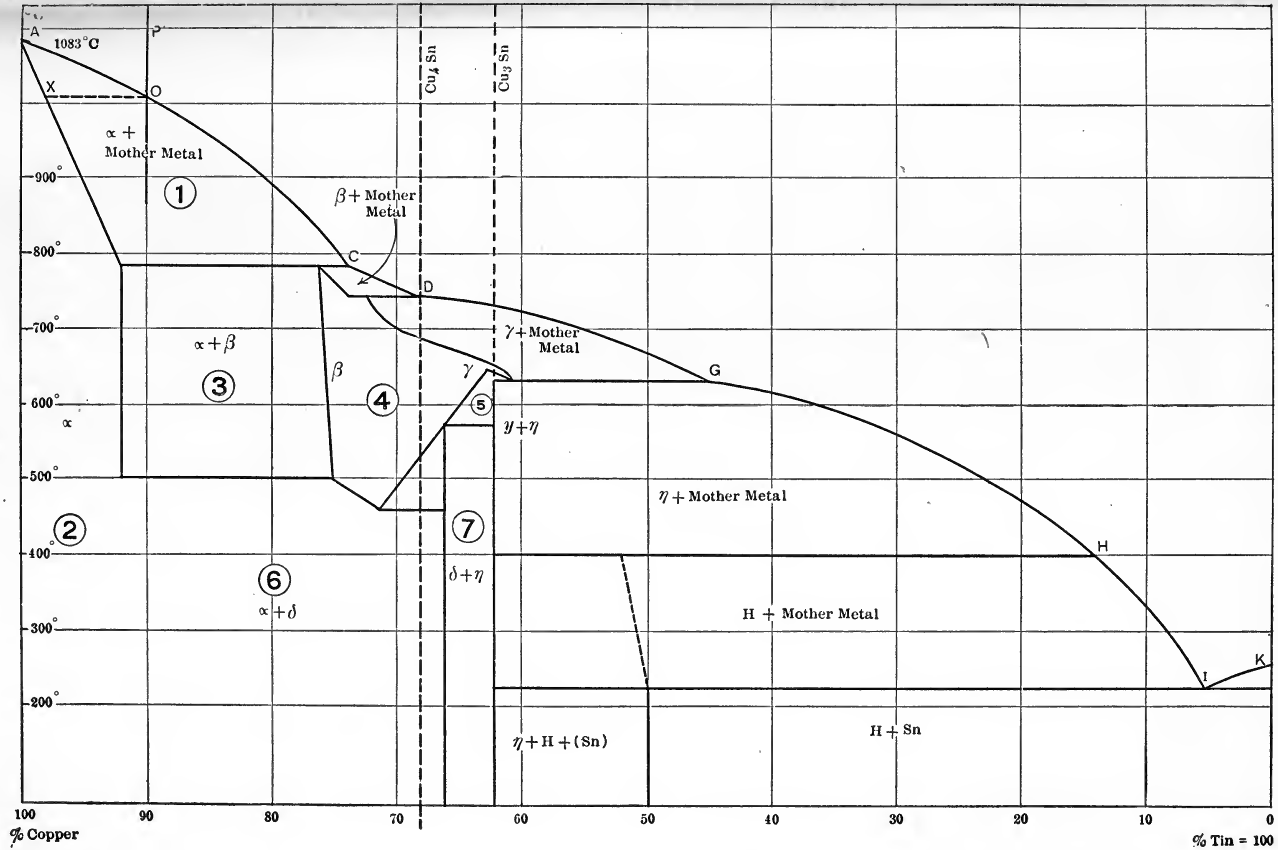

FIG. 39. — Copper-tin series.

at a full red heat, and the range of temperature in which it can be worked is small. It forges best at a low red heat. Aluminium bronze can be spun, stamped, or pressed like brass, if it be frequently annealed (*i.e.* softened by chilling). Aluminium bronze withstands corrosion about as well as brass; it is equally resistant to sea water as *Muntz metal* (Cu 60 per cent., Zn 40 per cent.). The casting of aluminium bronzes presents some difficulties, due to the shrinkage in setting and contraction on cooling. This must be especially provided for in the type of molds used. The alloy gives clean castings free from blow holes, as dissolved gases are absent. Certain makers of aluminium bronze add either silicon or phosphorus in small quantities, which are said to greatly increase the strength of aluminium bronze.

Alloys of aluminium containing up to 4 per cent. copper are used in casting statuettes, and aluminium apparatus. The alloy is stronger than pure aluminium and casts well, better than pure aluminium.

No. 4. — *Copper-Tin.* This series is of much interest as it contains the bronzes, so widely used for art castings, and certain industrial purposes. The literature on this series of alloys is large and it has been more thoroughly investigated than any other series, with the exception of iron-carbon. Fig. 39 represents the equilibrium diagram of the copper-tin series, based on the researches of C. T. Heycock and F. H. Neville[1] and Shepherd and Upton.[2] The interesting members of the copper-tin series are the bronzes ranging in composition from 70 to 100 per cent. copper and 0 to 30 per cent. tin. The bronzes, like cast iron and steel, are capable of having certain of their physical properties greatly altered by "heat treatment," *i.e.* quenching from certain temperatures, and reheating. By referring to that portion of the curve lying between 70 per cent. and 100 per cent. copper, it will be noted first that within this region occur three different types of mixed crystals, viz., alpha, beta, and gamma and the compounds Cu_4Sn and Cu_3Sn, termed Delta and Eta respectively. They are further defined in the following table:

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[1] Proceedings of the Royal Soc. of London, LXXI, 409 (1903).

[2] Journal of Phys. Chem., Vol. IX, p. 441 (1905).

TABLE XV. CONSTITUENTS PRESENT IN BRONZES

Substance	Composition	Constitution	Remarks
Alpha	Copper dissolving from 0 to 9 to 13% Sn.	Copper dissolving Cu_4Sn	Stable.
Beta	Copper dissolving from 22.5 to 27% Sn.	Cu_4Sn dissolving Cu	Unstable at room temperature unless preserved by chilling.
Delta	Cu_4Sn ?	Chemical compound 68% Cu–32% Sn	Stable.
Gamma ..	Copper dissolving tin, 28 to 57%.	Cu_4Sn dissolving Cu_3Sn	Unstable. Preserved by chilling.
Eta	Cu_3Sn	62% Cu–38% Sn	Stable.

The alpha crystals are stable and their range is evident from the diagram (area 2). In area 1, mixed crystals alpha and mother metal are in equilibrium as explained for the theoretical curves *ICb* in Chapter II. The discussion under that case also covers the method of the freezing of the mixed crystals alpha. In area 3, alpha and beta mixed crystals exist as a conglomerate, this area being the gap in the mixed crystal series (morphotropic series) as discussed in case *ICa*. In area 4, to one side of the compound line Cu_4Sn, exists the mixed crystal beta, while to the other side (right) the mixed crystal gamma exists. In area 5 there is the conglomerate of eta and gamma, caused by the gap in the second mixed crystal series, similar to area 3 above. In area 6 there exist alpha and delta conglomerate, the beta mixed crystal dissociating at about 500° C. as follows: beta = delta + alpha. In region 7 exist delta plus eta crystals as a conglomerate produced by the dissociation of gamma mixed crystals at about 585° C. as follows: Gamma = delta + eta. This manner of discussion is applicable to the rest of the equilibrium diagram.

Taking now an alloy of 90 per cent. copper, 10 per cent. tin, its freezing will be as follows, if the cooling be slow, so that all reactions can complete themselves and equilibrium be established.

When the temperature of the molten alloy reaches 855° C., alpha crystals of x composition separate out, while the mother metal concentrates in tin to the point C, when it solidifies to beta mixed crystals. This is at the temperature of about 790° C. The frozen alloy at this temperature will therefore consist of alpha and beta crystals. As it cools and reaches the temperature of about 500° C., the mixed crystal beta which has an approximate composition of 85 per cent. copper and 15 per cent. tin breaks up into alpha crystals (richer in copper and poorer in tin than beta) and delta, a chemical compound Cu_4Sn (poorer in copper and richer in tin than beta), so that the finally solidified alloy consists of alpha and delta. If the alloy be now quenched in water from the upper portion of region 3, the mixed crystal beta will be preserved in the cold alloy, and with it, its physical properties, which are different from those of delta. In order to get the full effect of the quenching the alloy should be held at the temperature of the upper portion of region 3 for a considerable time before quenching, in order to fully establish the equilibrium normal to that region.

The following conclusions may be drawn:

1. The tensile strength of bronzes consisting solely of alpha crystals is practically uninfluenced by heat treatment (alpha crystals rich in tin are stronger than those poor in tin).
2. Bronzes consisting of alpha and beta crystals (between 74 and 87 per cent. copper) have their tensile strength increased by reheating to above 510° C. for some time and then quenching from above the critical temperature of 510° C.
3. Reheating bronzes between 85 and 90 per cent. copper to above 540° C. for some time, and quenching, has also a marked effect of increasing the ductility of these bronzes.
4. Bronzes not heat-treated after casting show a steady decrease of ductility with a decreasing percentage of copper.

The strongest bronze (maximum tensile strength) occurs at about 80 per cent. Cu, 20 per cent. Sn, and consists mainly of beta crystals.

The maximum ductility occurs at about 88 per cent. Cu, 12 per cent. Sn, under heat treatment.

In color the bronzes vary from a red to a reddish yellow as the copper decreases from 100 per cent. to 90 per cent.

Ternary Alloys, Bearing Metals,[1] or Antifriction Alloys.—The alloys are very largely used as bearing metals for journals

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[1] Charpy, Contribution to the Study of Metallic Alloys, Metallographist, Vol. II (1899). Behrens and Baucke, Metallographist, Vol. III (1900).

of machinery, and according to the conditions of use vary widely in composition. Formerly, lead-antimony alloys were much used, but these have been largely replaced by the more complex ternary alloys. In a lubricated bearing, there should be no wear of metal on metal, but the thin sheet of oil between the bearing and the journal takes up the friction so that the friction is one between a solid and a liquid and not one between two solids. This condition, however, is more or less ideal, and requires a perfect adjustment, impossible to obtain in practice. It is therefore desirable to have the bearing surface of such a material as will readily adjust itself to the imperfections of the journal. A soft metal possesses this property in the greatest degree, but the coefficient of friction between a hard and soft metal is much greater than between two hard metals, so that from this point of view two hard metals would be preferable. This, however, does not fulfil the first condition of having a bearing that will adjust itself to the imperfections of the journal. If we can procure a substance consisting of hard particles in sufficient number imbedded in a rather soft and plastic matrix, the hard particles to take the wear and the soft matrix to adjust itself in shape to the journal, the conditions for a good bearing metal are fulfilled.

The table gives the composition and constitution of certain bearing metals in common use. (See table XVI on next page.)

German Silver. — This is a ternary alloy of copper, zinc, and nickel. The ternary series has been worked out by Tafel,[1] who states that no ternary metallic compound or ternary eutectic is present. The alloys of commercial importance consist with few exceptions of mixed crystals of one type or conglomerates of two. In the whole ternary system, two compounds occur, Cu_2Zn_3 and $NiZn_3$, which enter into mixed crystals of several types. Table XVII gives the composition of various kinds of German silver. (See table on next page.)

[1] Metallurgie, Vol. V, p. 413 (1908).

TABLE XVI. COMPOSITION AND USE OF BEARING METALS

No.	Composition						Constitution	Use
	Sn. %	Cu. %	Sb. %	Pb. %	Zn. %	P. %		
1.	88	4	8	—	—	—	Compound SnSb and SnCu$_3$ hard in soft matrix of tin.	Ordinary bearings.
2.	80	10	10	—	—	—	do.	Journals of railroad cars.
3.	67	11	22	—	—	—	do. Amt. much decreased.	do.
4.	5.9	—	16.8	77.7	—	—	Compound SnSb in Sb and hard free Sb in a matrix of soft lead.	Magnolia metal. Ordinary bearings.
5.	42	—	16.0	42.0	—	—	Compound SnSb imbedded in soft lead and tin matrix.	Railroad bearings.
6.	14	86	—	—	—	—	Bronze alpha crystals as matrix SnCu$_4$ imbedded hard crystals.	Locomotive bearings.
7.	28	58	—	—	14	—	—	Hard bearing metal.
8.	8	76.8		15		0.20	Cu$_3$P compound imbedded in alpha bronze crystal and lead as matrix.	Railroad bearings
9.	10	79.7		9.6		0.80	do.	Heavy machinery bearing.

TABLE XVII. COMPOSITION OF GERMAN SILVER

No.	Composition			Use
	Cu. %	Zn. %	Ni. %	
1.	50	25	25	Table ware.
2.	55	25	20	Art objects.
3.	60	20	20	Typical German silver. Can be rolled.
4.	56	5	39	White. Hard but ductile. High-grade tableware.
5.	50	31.25	18.75	Instruments.
6.	76	7	17	Tableware. Resembles silver very much.

CHAPTER V

THE PHYSICAL PROPERTIES OF ALLOYS

The physical properties of alloys are in most instances so radically different from those of the substances entering into the constitution of the alloy that a special treatment of the subject is necessary. The physical properties of alloys which will be discussed are:

1. Electric resistance and electric conductivity.
2. The expansion of alloys with increase of temperature.
3. Hardness and malleability.
4. Specific volume and specific gravity.
5. Magnetic properties.
6. Tensile strength and elastic limit.

Recent researches have established some general laws regarding physical properties of alloys, the properties varying with the constitution of the alloys as outlined in the different types mentioned. Most of the physical properties are dependent upon the following factors:

1. The formation of mixed crystals.
2. The formation of chemical compounds.
3. The formation of a conglomerate of two substances (eutectics or eutectoids).

These facts enable the physical properties of the alloys to be discussed on the basis of the equilibrium diagrams, outlined in Chapter II.

1. The two substances are completely reciprocally soluble in the molten state and form an unbroken series of mixed crystals (in this case true isomorphous mixtures) in the solid state. Cases: *IAa, IAb, IAc.*

2. The two substances are completely reciprocally soluble in the liquid state; but in the solid are capable of crystallizing together (either as partial isomorphous or as morphotropic crystals), only to a limited extent, forming a broken or interrupted series of mixed crystals of different kinds. Case *ICa,*

that in which the addition of one substance to the other lowers the freezing-point of the latter, but in which the addition of the latter substance to the first raises the freezing-point of this. Case *ICb,* in which the addition of either substance to the other lowers their respective freezing-points.

3. The two substances are completely reciprocally soluble in the liquid state, and in the solid state are not mixed crystals but consist of the pure components. Case *IB,* the addition of either substance to the other lowers their respective freezing-points.

4. The two substances are reciprocally soluble in each other only to a limited extent in the liquid state, and in the solid state are either incapable of crystallizing together, or crystallize together but to a limited extent. Case *IDa* and *IDb,* in which the addition of either substance to the other lowers the respective freezing-point. Case *IDc,* in which the addition of one substance to the other lowers the freezing-point of the latter, but in which the addition of the latter substance to the first raises the freezing-point of this.

5. One or more chemical compounds are formed in the series. The series then divides itself into a number of sub-series, viz., as follows: Suppose the two pure components are *A* and *B,* and the compounds formed are A_2B_3 and B_4A_2. The whole series may then be considered as divided into three individual series as follows: $A-A_2B_3$; $A_2B_3-B_4A_2$; and B_4A_2-B, each of which may have distinct characteristics and belong to certain members of the first group above discussed.

Cases *IIA* and *IIB* and various combinations of the two with each other and with types under Case *I.*

1. **The Electric Conductivity of Alloys.** — That particular resistance of a body to the passage of the electric current, referred to as a unit dimension (one cubic centimeter at zero degrees C.), is known as its *specific resistance,* or its *resistivity.*

This resistance is expressed in the unit of resistance, the ohm, or fractions of it, chiefly the microhm, equal to 0.000001 ohm, or in the c.g.s. unit, which is the bicrohm, equal to 0.00000001 ohm.

The standard resistance is that of 1 cc. of mercury at zero degrees C., and is equal to 94.08 microhms.

The electric conductivity of a substance is of course a direct function of its specific resistance, or resistivity, for a body of low resistivity has a high conductivity and vice versa.

The electric conductivity is therefore expressed as the reciprocal of the resistivity, as per the following formula:

Electric conductivity (as measured in ohms)

$$= \frac{1}{\text{Resistivity or specific resistance in ohms.}}$$

The result is best expressed as a factor, thus: $a \times 10^4$; in which "a" varies for each substance. The following table[1] shows

TABLE XVIII. ELECTRIC CONDUCTIVITY OF METALS

Metal	Conductivity	Metal	Conductivity	Metal	Conductivity
Aluminium.	32.4×10^4	Copper	55.4×10^4	Nickel	9.73×10^4
Antimony..	2.71×10^4	Iron	10.37×10^4	Platinum ..	5.97×10^4
Lead	5.04×10^4	Cadmium ...	14.60×10^4	Mercury ...	1.063×10^4
Gold	47.6×10^4	Cobalt[2].....	10.30×10^4	Bismuth ...	0.872×10^4
Silver	60.80×10^4	Magnesium .	24.47×10^4	Tin	9.99×10^4
				Zinc	18.6×10^4

the electric conductivity of a few metals, all for zero degrees C. temperature. Taking the conductivity of copper as 55.4×10^4, it is readily calculated back to resistivity as follows:

$$55.4 \times 10^4 = \frac{1}{\text{Resistivity in ohms}} \qquad \text{or}$$

$$\text{Resistivity in ohms} = \frac{1}{554000} \qquad \text{or}$$

$$= 0.000001805 \text{ ohms or } 1.805 \text{ microhms.}$$

Generally speaking, the resistivity of a substance increases with a rise in temperature, and decreases with a lowering of the temperature. Thus it has been demonstrated by Dewar & Fleming[3] that the specific resistance of metals when at very

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[1] Taken from Landolt und Börnstein, Chemisch-Physikalische Tabellen, (1905), pp. 716–717.

[2] At 20° C.

[3] Philosophical Magazine (5), Vol. XXXVI, p. 271 (1896).

low temperatures (−150 to −200° C.) is enormously decreased. The increase in resistivity per degree rise of temperature is known as the "temperature coefficient."

If w_0 is the resistivity at zero degrees C., at T it will be $w = w_0 (1 + aT + bT^2 + cT^3)$. The terms bT^2 and cT^3 can, in ordinary work, be disregarded so that the formula becomes $w = w_0 (1 + aT)$ where "a" is a constant for each substance, and is the temperature coefficient. This "a," however, holds only within a comparatively narrow range, approximately 100° C. The value of "a" for pure metals is very nearly 0.004 for all metals. When impurities are present, however, it will vary widely. Some alloys have an extremely small temperature coefficient practically negligible, as for instance, konstantan (copper-nickel) and manganin (copper-nickel-manganese) to which further reference is made.[1]

Guertler [2] states the following laws of electric conductivity as applying to alloys:

1. Alloys which in the solid state are entirely simple mixtures or conglomerates of the pure components (example Case *IB*), have a conductivity equal to the sum of the conductivities of its components. (*A*, Fig. 40.)

2. Alloys, the components of which form mixed crystals show a decided decrease of conductivity over that of the pure components composing the mixed crystals. Cases *IAa*, etc., *IC*. (*B* and *D*, Fig. 40.)

3. Alloys in the series of which chemical compounds occur, the compounds have a distinct conductivity of their own. This conductivity in all cases investigated to date is never greater than that of the pure components, but always less. There is thus a distinct change in the conductivity of the series where the compound occurs. (*C* and *E*, Fig. 40.)

These three laws cover fully all the equilibrium curves discussed, since the laws are based on the occurrence of either conglomerates, mixed crystals, or compounds, and these form the basis of the equilibrium curves.

Thus for Case *IC*, in which the solid alloy is composed of two types of mixed crystals, with a eutectic point and a given

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[1] Blood and Nichols, Amer. Jour. Science, 1890, Vol. XXXIX, p. 471.

[2] Über die Elektrische Leitfähigkeit der Legierungen, Zeit. Anorg. Chemie, Vol. LI, p. 397.

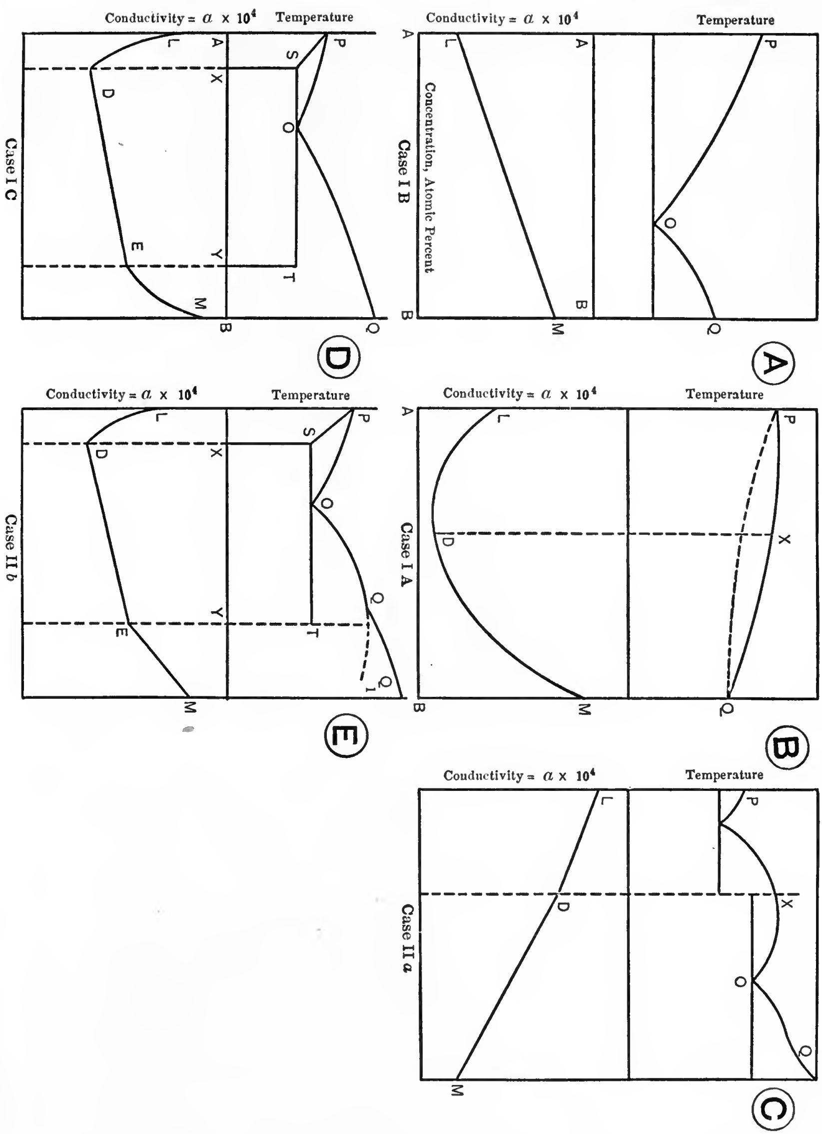

Fig. 40. — Freezing-point curves in relation to electric conductivity curves.

eutectiferous range, the conductivity curve will have the form as shown in *D*, Fig. 40.

In Figs. 41, 42 are shown accurate reproductions of conductivity curves of Cu–Ni; Ag–Au; Zn–Sn; Cu–Zn; Cu–Sn; Cu–Au. A temperature coefficient curve is also given.

General Considerations. — It will be noted that in some of the preceding diagrams concentration is represented by "atomic percentages" rather than by "percentages of weight" directly. This is on the theory stated by the periodic law of Mendelejeff & Newlands, that the properties of the elements are periodic functions of their atomic weights, and even more so, according to Lothar Meyer, of their atomic volume (atomic volume $= \frac{\text{atomic weight}}{\text{sp. gravity}}$). It is believed that the influence of one metal on another as regards certain physical properties, such as hardness, tenacity, electric conductivity, etc., is very largely a function of the relative atomic volumes.[1]

Atomic per cents. can readily be calculated to per cents. by weight, *e.g.* an alloy of 50 atomic per cent. of silver and 50 atomic per cent. of gold has a total weight of $50 \times 107 = 5350$, and $50 \times 196 = 9800$ or 15,150 units. The silver by weight per cent. is therefore $\frac{5350 \times 100}{15150} = 35.3$ per cent.; and the gold is $\frac{9800 \times 100}{15150} = 64.7$ per cent. The representation, therefore, of the concentration by atomic percentages enables one to inspect at once the atomic relationship of the particular alloy in question.

The subject of the electric conductivity of the metals and alloys is a very important one on account of their wide use for conductors, and resistance metal in the electrical industry. The problem of alloys for this purpose presents itself in several forms.[2]

1. It is desired to obtain a material of the highest conductivity for the transmission of the electric current, one which

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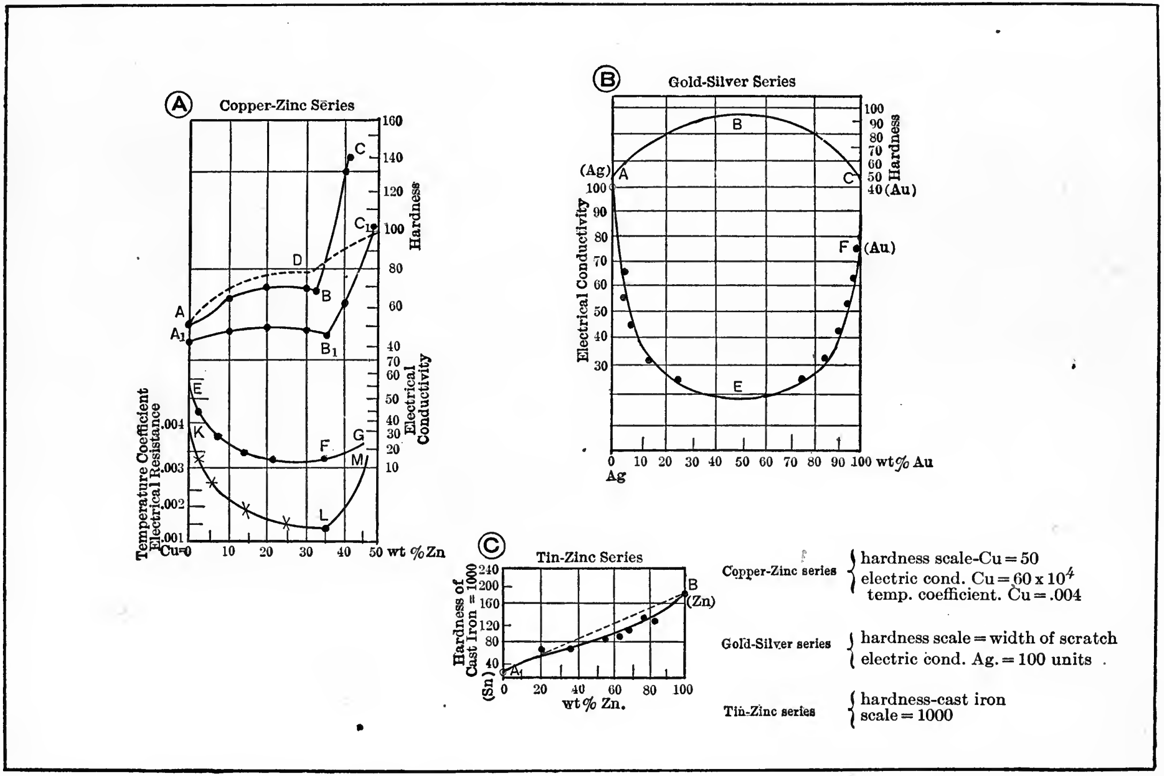
[1] Roberts-Austen, An Introduction to the Study of Metallurgy, 1902, p. 116; also, Phil. Trans. of Royal Soc., CLXXIX, p. 339. For interesting theory of the electric conductivity of alloys, based on the idea of atomic equivalent, see views of Matthews and Benedicks, The Metallographist, Vol. VI, p. 327, and Electrical World and Engineer, Oct. 4, 1902.

[2] W. Guertler, Folgerung für die Technik, etc., Metallurgie, Vol. V, p. 294.

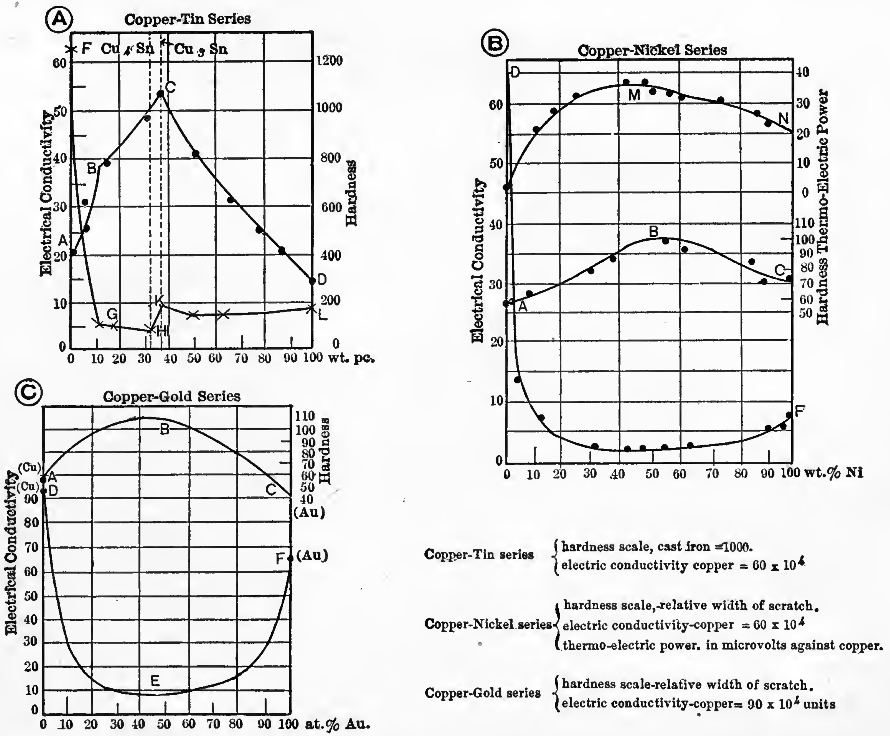


Copper-Zinc series { hardness scale-Cu = 50
electric cond. Cu = 60 x 10⁴
temp. coefficient. Cu = .004

Gold-Silver series { hardness scale = width of scratch
electric cond. Ag. = 100 units

Tin-Zinc series { hardness-cast iron
scale = 1000

FIG. 41. — Physical properties of alloys.



Copper-Tin series { hardness scale, cast iron =1000.
electric conductivity copper = 60 x 10^4

Copper-Nickel series { hardness scale,-relative width of scratch.
electric conductivity-copper = 60 x 10^4
thermo-electric power. in microvolts against copper.

Copper-Gold series { hardness scale-relative width of scratch.
electric conductivity-copper= 90 x 10^4 units

FIG. 42. — Physical properties of alloys.

can be obtained cheaply and in large quantities. It must possess certain physical properties, such as malleability and ductility (for wires) and the requisite tensile strength. It must resist corrosion under the conditions in which it is used. It has been stated that in alloys which are mixed crystals there is a profound lowering of the conductivity from that of the pure components, and moreover, very minute quantities of the alloying substance depress the conductivity very much. Therefore, it is evident that for the purpose of conductors it will be necessary to use pure materials generally, as for example, copper, aluminium, and iron, all of which are good conductors. (Consult Table XVIII for values.) Copper and aluminium are used for large currents such as are common in power transmission, while iron may be used for small currents common in telephony and telegraphy, though at the present day copper is mainly used even for this purpose. The case remains where two substances entering into a series may form one or more compounds, and as these compounds will have *specific properties* of their own, it might be expected that one would occur having a high electric conductivity; but as already stated, the compounds of a series as far as known have a conductivity below that of at least one of the pure components entering into their composition, or have a lower conductivity than that due to a calculation based on the proportional amounts of the pure components present. Among the metals available for conductors on account of cheapness — Cu, Fe, Ni, Al — and in their alloys with each other, no chemical compounds are known to form.

One other phase presents itself, viz., a material is available of high conductivity and reasonable price which does not possess the required tensile strength and ductility for the purpose to which it is to be put. This last property may be obtained by the addition of certain alloying substances, but of course at a sacrifice of conductivity. In the case where the gain from increased strength, etc., warrants the sacrifice in conductivity, such an alloy will be used. As an example — for trolley wires, great tensile strength is required, and still a high conductivity. Silicon bronze (copper 98.55 per cent.; tin, 1.40 per cent.; silicon, 0.05 per cent.), wires of 80,000 to 100,000 lbs. tensile strength per square inch and a conductivity of 70 per cent. of that of pure copper, have been used for this purpose[1] as well as for telegraph and telephone wires.

2. It is desirable to obtain a material of low conductivity, hence of high resistivity, for the purpose of rheostats or for electric safety fuses. In the first instance the material must have a high melting-point, so as to remain intact within the heating effects of the electric current; in the second instance the reverse is true. For this general purpose alloys are preëminently suitable, and the variety of binary, ternary, quaternary alloy combinations available is very large, and almost any special conditions may be met. Another phase of this question to be considered is that of the resistance alloys for electrical instruments of precision, such as bridges, potentiometers, galvanometers, etc. In this case the problem of practical constancy of resistivity with varying temperature is important, viz., the resistivity should not change with an increase of temperature, either due to condition of use, or to heating effects of current. That is, the "temperature coefficient" should be as nearly nil as possible. It has been noted that the "temperature coefficient" of mixed crystals is very low, and is practically proportional to the electric conductivity, so that when this is depressed the temperature coefficient is proportionately depressed. (See Fig. 41.) Thus, while the temperature coefficient of pure copper and iron is very nearly 0.004, the addition of comparatively small quantities of nickel or manganese to them depresses the temperature coefficient to approximately 0.0008. Even this, however, is not sufficient for instruments of very high precision, and two alloys have been found — konstantan (60 per cent. copper, 40 per cent. nickel) and manganin (copper 84 per cent., nickel 12 per cent., manganese 4 per cent.) — which have a temperature coefficient practically nil within any ordinary range of temperature, while their conductivity is reduced to about 0.05 of that of copper. This apparent violation of Matthiesen's law of the proportionality of the temperature coefficient is explained by assuming the existence of a mixed crystal at ordinary temperature which is normal to a higher temperature, *i.e.* a case similar to the preservation of the beta crystal in the bronze series by chilling. (See page 114.) This mixed crystal would have a conductivity normal to its true region which lies, as

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[1] Electrical Transmission of Energy, Abbott, p. 20 (1907).

regards temperature, above the one in which it exists, and hence would have no tendency to decrease its conductivity with rise of temperature (*i.e.* no temperature coefficient) until its temperature attains that region in which the mixed crystal is normal. This preservation of the mixed crystal in a region where it is not normal is, of course, a case of unstable equilibrium, which by heating will tend to change into stable equilibrium. This is found to be the case in the alloys mentioned, for after repeated use (heating effect of the electric current) the alloys develop a temperature coefficient in harmony with Matthiesen's law of proportion.[1]

Certain facts in regard to the electric conductivity of alloys are to be more particularly noted.

1. The shape of the electric conductivity curve in the case of *mixed crystals.* This in almost all cases drops away nearly vertically from the conductivity of the pure material so that *very small quantities* of the alloying substance have a profound effect on the electric conductivity. It follows from this that the investigation of the electric conductivity of a series of alloys will determine the existence of mixed crystals in the series, and also their limit of occurrence, viz., composition of saturated mixed crystals.

2. The occurrence of definite maxima or minima in the electric conductivity curve marks the position of intermetallic compounds in the series. This method, therefore, in conjunction with other means (microscopic examination revealing homogeneity of structure; occurrence of maxima; both true and hidden maxima in the freezing-point curve) assists in the fixing in position and in the identification of chemical compounds in the series of alloys.

3. The occurrence of allotropic conditions in a metal may also in certain cases be discovered by variations in the electric conductivity.[2]

2. The Expansion and Contraction of Alloys with Varying Temperature. — In general, when heat energy is added to a body its volume changes. The volume change is known as the

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[1] Blood and Nichols, American Journal of Science, Vol. XXXIX, p. 471 (1890).

[2] O. Boudouard, Journal Iron and Steel Inst., Vol. I (1903), and Metallographist, Vol. VI, p. 345.

cubical expansion. In this discussion expansion in one direction only will be considered, along a linear dimension of the body, which is known as the *linear expansion.* In crystals the coefficient of linear expansion along the several axes of the crystal may have different values, some of them may even be negative, producing a diminution of length with a rise of temperature.

If L_0 denote a unit length of the body at zero degrees C., then the effect of heat on the body will expand the length to L at t degrees. This fact is expressed by the equation, $L = L_0\ (1 + at)$ in which a is the *coefficient of linear expansion.*

This equation, however, does not hold true through all ranges of temperature, and the more general equation is

$$L = L_0\ (1 + at + bt^2 + ct^3).$$

There is no general law applicable to the expansion of alloys, and most of the experimental data available on expansion of alloys has reference to steel, and certain iron-nickel alloys, etc. The subject of the expansion of alloys is of importance for the industries and arts, as many instances are known in which two different materials used together should have similar coefficients of expansion; for instance, the junction of the light filament at the glass seal with the conductor in incandescent lamps. This junction material is embedded in the glass seal where it gets hottest, and in order to prevent rupture must have the same coefficient of expansion as the glass. In most lamps it is made of platinum, which has practically the same coefficient as glass, but platinum is very expensive and a suitable cheaper substitute would be welcome. Of course, the substitute must also possess certain other definite properties, such as a certain conductivity, a high melting-point, etc. In the manufacture of instruments of precision, such as theodolites, pendulum rods, parts of balances, it is desirable to employ a metal with a very small coefficient of expansion or, if possible, none at all, for obvious reasons. Such an alloy has been found in nickel steels of certain compositions.

Table XIX gives the coefficients of expansion of a number of carbon steels, in different temperature ranges.[1]

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[1] Georges Charpy and Louis Grenet, "Dilation of Steels at High Temperatures," Comptes Rendus de l'Académie des Sciences, March 3, 1902, and Metallographist, Vol. VI, p. 328.

TABLE XIX. EXPANSION OF CARBON STEEL

No.	Analysis of Annealed Steels					Coefficient of Expansion or Dilatation		
	C.	Mn.	Si.	P.	S.	15° to 200° C.	200° to 500° C.	500° to 650° C.
1.	0.03	0.01	0.03	0.013	0.023	11.8×10^{-6}	14.3×10^{-6}	17.0×10^{-6}
2.	0.25	0.04	0.05	0.010	0.010	11.5	14.5	17.5
3.	0.64	0.12	0.14	0.009	0.010	12.1	14.1	16.5
4.	0.93	0.12	0.05	0.005	0.010	11.6	14.9	16.0
5.	1.23	0.10	0.08	0.005	0.009	11.9	14.3	16.5
6.	1.50	0.04	0.09	0.010	0.010	11.5	14.9	16.5
7.	3.50	0.03	0.07	0.005	0.010	11.2	14.2	18.5

$$\text{Viz., } 11.8 \times 10^{-6} = \frac{11.8}{1000000} = 0.0000118 = a.$$

It is to be noted that the coefficient of expansion for the several temperature intervals indicated is the same whether the material be nearly pure iron (No. 1) or steel (Nos. 2, 3, 4, 5, and 6), of different carbon contents, or white cast iron, No. 7. The results are on annealed steels containing the greater amount of their carbon, as Fe_3C — carbide of iron or "Cementite," and show that probably iron and cementite have the same coefficient of expansion.

An entirely different case is presented by the iron-nickel alloys known as nickel steels, as Table XX indicates. (See table on page 130.)

In discussing these results it is essential to briefly inquire into the properties of the iron-nickel series of alloys. These belong to group *IAa*, which form a series of mixed crystals, the two metals being capable of crystallizing together in all proportions. Both iron and nickel are strongly magnetic in certain of their molecular modifications and non-magnetic in others.

The addition of nickel to iron has the effect of displacing the critical points of pure iron. Above 880° C. (Ar_3) gamma iron exists, which is non-magnetic. Between 880° C. and 780° C. (Ar_2), there exist isomorphous mixtures of beta and alpha iron, the more beta iron the nearer to 880° C. Beta iron is non-magnetic. Below 780° C. alpha iron only exists, which is magnetic. Depending on the percentage of nickel present, the

TABLE XX. EXPANSION OF NICKEL STEEL

No.	Analysis of Steel			Coefficients of Expansion				
	Ni.	C.	Mn.	Between 15° and 100° C.	100–200° C.	200–400° C.	400–600° C.	600–900° C.
1.	26.9	0.35	0.30	11.0×10^{-6}	18.0×10^{-6}	18.7×10^{-6}	22.0×10^{-6}	23.0×10^{-6}
2.	28.9	0.35	0.36	10.0	21.5	19.0	20.0	22.7
3.	30.1	0.35	0.34	9.5	14.0	19.5	19.0	21.3
4.	34.7	0.36	0.36	2.0	2.5	11.75	19.5	20.7
5.	36.1	0.39	0.39	1.5	1.5	11.75	17.0	20.3
6.	32.8	0.29	0.66	8.0	14.0	18.0	21.5	22.3
7.	35.8	0.31	0.69	2.5	2.5	12.5	18.75	19.8
8.	37.4	0.30	0.69	2.5	1.5	8.5	19.75	18.3
9.	25.4	1.01	0.79	12.5	18.5	19.75	21.0	35.0
10.	29.4	0.99	0.89	11.0	12.5	19.0	20.5	31.7
11.	34.5	0.97	0.84	3.0	3.5	13.0	18.75	26.7

critical points Ar_3 and Ar_2 occur at a lower temperature. With about 30 per cent. Ni present, Ar_2 (the change of non-magnetic to magnetic iron) occurs at about—70° C., so that at room temperature this alloy is non-magnetic. Now nickel also has a transformation point where non-magnetic nickel changes to magnetic nickel in cooling. This occurs at 320° C. The effect of iron on the critical points of nickel, up to a certain per cent., seems to be similar to that of nickel on iron, *i.e.* there is a reciprocal lowering of the temperatures at which the critical points occur, so that an alloy of two magnetic components may be non-magnetic at ordinary temperatures, *i.e.* room temperatures.

The transformation of a non-magnetic iron-nickel alloy to the magnetic form may be made to occur by cooling to a sufficiently low temperature. It seems evident that the presence of nickel preserves at a low temperature the substance, gamma iron (non-magnetic). It is an example of a substance existing in a state not truly normal to the region in which it is ordinarily found. The bearing of this theory on expansion is briefly as follows:[1] Gamma iron, which is normal above 880° C. only,

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[1] C. E. Guillaume, Non-Expansive Alloys, Metallographist, Vol. VI, p. 162, and original article. Recherches sur les Aciers au Nickel, Comptes Rendus, March 11, 1908.

has undergone a certain expansion in heating from room temperature or alpha iron to 880° C. or gamma iron. If now by any means gamma iron be preserved at room temperature, it is in a molecular condition corresponding to its normal region above 880° C., but in an unstable condition of equilibrium. It is reasonable to believe, therefore, that it will not expand upon heating until it reaches the region in which its constituents are normal.

The presence of carbon in nickel-iron alloys, making the nickel steels, has also a certain influence on the transformation points. Nickel steels from 0 to about 26 per cent. nickel are called, according to Guillaume, "irreversible alloys," and those containing 26 per cent. and more nickel are the "reversible alloys." This distinction is based on their laws of expansion, viz., the reversible alloys expand with a certain coefficient of expansion on heating, and contract again on cooling at the same coefficient. This is the normal condition for most metals and alloys. The irreversible alloys do not follow this law, but expand and contract in the manner illustrated by Fig. 43.

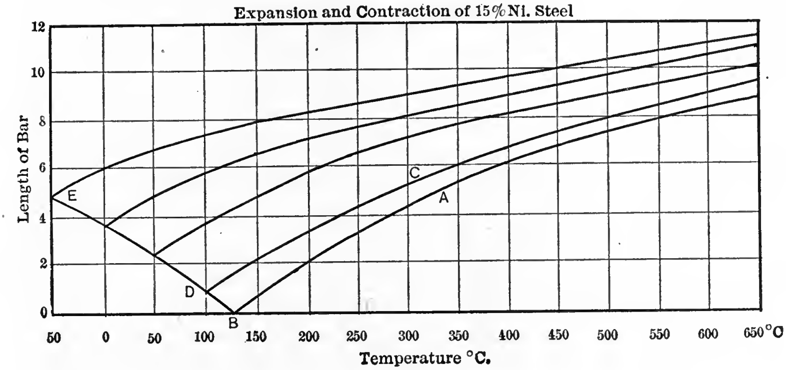

Fig. 43. — Expansion and contraction of 15% Ni steel.

When an alloy of the *irreversible type* is heated to about 700° C. and slowly cooled, it will contract regularly until it reaches about 130° C. (for 15 per cent. nickel), when, instead of further contracting, it now expands along the line *BE*. If, when it reaches 100° C., it again be reheated, it will not now contract along *EB* from *D* to *B*, but will at once expand along *DC*.

If now it be again allowed to cool, it will contract along the line CD, and when it reaches D will on further cooling expand along the line DE, until it reaches E, where the expansion is practically nil. The phenomena of contraction and expansion are intimately associated with the gain or loss of magnetism, which in turn is dependent on the molecular state as already stated. The exact relationship has not been completely worked out. Some further reference to this is made under the magnetic properties of alloys.

The reversible alloys of nickel and iron, or more truly nickel-steel, have a regular coefficient of expansion and contraction. The data for the same is found in Table XX. It will be seen that alloys of about 36 per cent. nickel have a coefficient of expansion which is practically nil. It is possible, therefore, taking this alloy as a basis, to obtain an alloy of almost any desired coefficient of expansion by adding to it either nickel or iron.

3. **Hardness.** — (1) Mineralogical hardness is the resistance offered by a smooth body to abrasion. It has also been defined as (2) the resistance which a body offers to permanent deformation by the application of an outside force, by means of pressure or impact, or (3) the resistance which a body offers against a penetration into its interior by a second and harder body.

These definitions, however, do not completely cover the case and the property of hardness is still to be more closely defined.[1]

Hardness is measured in a number of ways, the two chief of which are:

1. *The Sclerometer Method.*[2] — By means of an instrument, the sclerometer, consisting of a suitable apparatus by means of which the polished surface of a substance may be scratched or bored by a needle point of given dimensions under a given load. The width of the scratch or depth of the hole measured by micrometer methods is a measure of the hardness. In delicate measurements the scratches are microphotographed, with

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[1] Über Härteproben, Thos. Turner, Metallurgie, Vol. VI, p. 371; Über Härtebestimmungen mittels der Brinnell'schen Kugeldruckprobe und verwandter Eindruckverfahren, Paul Ludwik, Metallurgie, Vol. V, p. 100, and Vol. IV, p. 633; Journ. Iron and Steel Inst., Vol. LIX, p. 269 (1901).

[2] Turner's Sclerometer, Birmingham Phil. Soc., Dec., 1886; Jaggar's Microsclerometer, Am. Jour. Science, Vol. IV, p. 399 (1897).

a given magnification, and then their width is measured on the negative The hardness (H) is then expressed as follows:

$$H = \frac{\text{Magnification in diameters}}{\text{Width of scratch in mm.}}$$

2. *Brinell's Method.* — Carried out by a suitable apparatus by means of which a hard steel sphere 10 mm. in diameter is pressed against the polished surface of the material to be tested by a static load of 3000 kgs. The hardness is measured by the area of the surface of the depression formed by the penetration of the steel sphere. This can be directly determined by reading a scale on the instrument.

The hardness is expressed as follows:

Number on scale of hardness

$$= \frac{\text{Pressure in kilograms}}{\text{Area of surface of depression in sq. mm.}}$$

The sclerometer method is applicable to all substances; Brinell's method, only to non-brittle substances. All measures of hardness are relative only. Some efforts at defining absolute hardness have been made, but are not in use.

The ordinary measure of hardness is based on the mineralogic or Mohs' scale, as follows: (See table on page 134.)

In Brinell's scale cast copper is 51[1]; annealed copper, 42; and manganese, 50.

N. S. Kurnakow and S. F. Zemczuzny[2] have formulated the following laws of the hardness of alloys, according to their constitution, based on the classification of the alloys as outlined in this work:

1. The formation of mixed crystals of two metals is accompanied by an increase of hardness.

2. The changes in hardness occurring in an unbroken series of mixed crystals of two metals of the type IAa may be graphically depicted by a continuous curve possessing a definite maximum.

3. In the type IA, this maxima corresponds to the minima of the curve of electric conductivity for the series.

4. In the case of a non-continuous series of mixed crystals

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[1] A. Kurdjumow, Monograph on Copper-Zinc Alloys, pp. 409, 425.

[2] Die Härte der festen Metallösungen und der bestimmten chemischen Verbindungen, Zeit. Anorg. Chemie, Vol. LX, p. 1 (1908).

TABLE XXI. HARDNESS OF SUBSTANCES

The standards of Mohs' scale are marked with an *.

Substance	Hardness	Substance	Hardness
Zinc	2	Iron	4 – 5
Agate	7	Steel	5 – 8.5
Topaz *	8	Brass (bell metal)	4
Aluminium	2	Gold	2.5 – 3
Nickel	4	Magnesium	2
Antimony	3 – 3.3	Iridium	6
Cadmium	2	Iridosmium	7
Stibnite *	2	Copper	2.5 – 3
Apatite *	5	Brasses	3 – 4
Arsenic	3.5	Palladium	4.8
Lead	1.5	Phosphor bronze	4
Diamond *	10	Platinum	4.3
Cobalt	4	Platinum–Iridium	6.5
Quartz *	7	Silver	2.5 – 3
Bismuth	2.5	Tin	1.8 – 1.5
Talc *	1	Calcite *	3
Fluorite *	4	Corundum *	9

of the type *ICa, ICb,* the curve of hardness shows inflections at the points of occurrence of the saturated mixed crystals of each kind.

5. In the case of an intermetallic compound in the series, there may occur either a maximum or a minimum in the curve of hardness, though this may be of a "hidden nature," similar to that discussed for the freezing-point curves of series in which chemical compounds occur.

These laws may be represented graphically in a way similar to that used for depicting the electric conductivity of alloys.

Case IA. The two components form a continuous series of mixed crystals. (Fig. 44 *A.*)

Case IB. The two components form no mixed crystals, but the alloys consist of conglomerates of the pure components. (Fig. 44 *B.*)

Case ICb, etc. The two components form two distinct sets of mixed crystals.

The line *bc* marks the gap in the mixed crystal series and the range in which a conglomerate of both occur. (Fig. 44 *C.*)

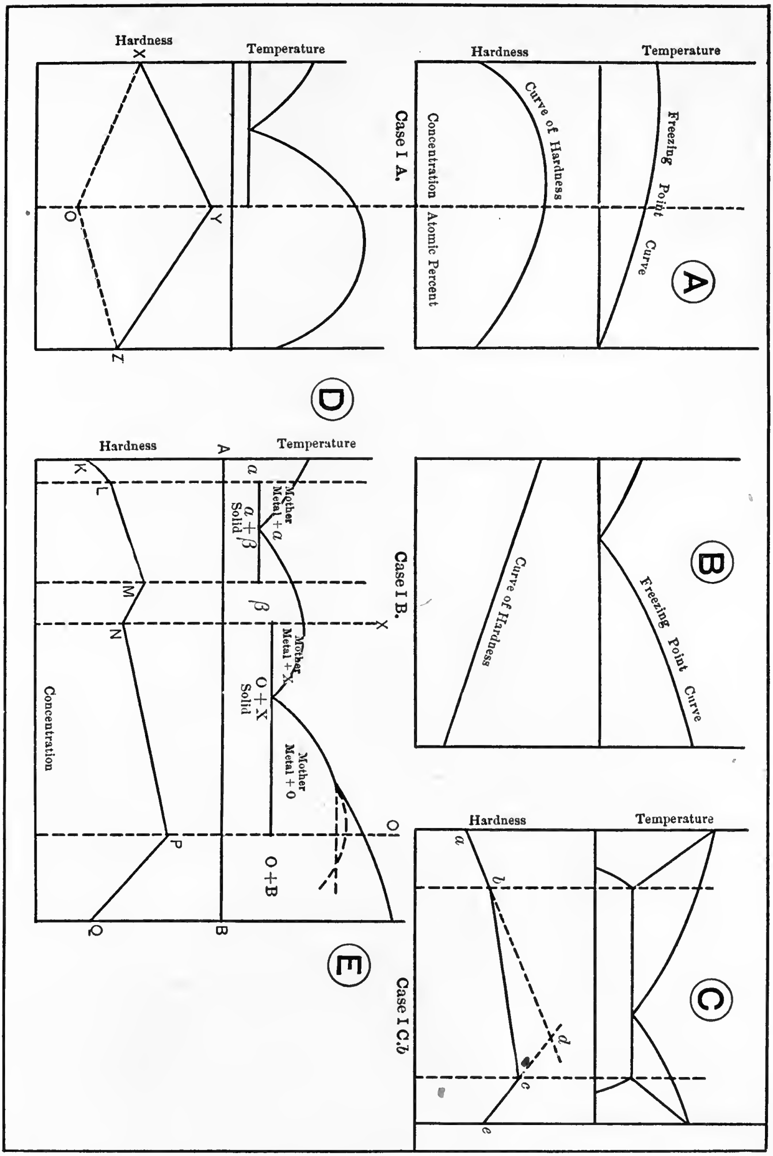

FIG. 44. — Hardness curves in relation to freezing-point curves.

Case II. Chemical compounds are formed in the series. Fig. 44 *D* represents the simplest case, of one compound in the series with no mixed crystals forming. *XYZ* represents the case in which the compound has a hardness superior to that of the components; and *XOZ*, that in which its hardness is inferior, both of which cases may occur. Fig. 44 *E* represents the theoretic hardness curve in the case in which several compounds are present and mixed crystals occur in the series. This curve is practically a combination of the simple curves above discussed. The compounds *X* and *O* exist in the series, the compound *X* entering into the formation of the mixed crystals alpha and beta. Between *X* and *O* no mixed crystals are formed. The curve of hardness of the series is represented by *KLMNPQ*, the points *L* and *M* marking inflections corresponding to the saturated mixed crystals alpha and beta respectively. The minimum *N* marks the occurrence of the chemical compound *X*, and the maximum *P* the occurrence of the compound *O*.

The property of hardness is an important physical property in itself, and many alloys in industrial use must fulfil certain conditions in this respect. The property of hardness is, however, not definitely related to either brittleness or tensile strength, though hardness and brittleness are more closely related than hardness and tensile strength. Very hard bodies are often brittle, while very soft bodies usually have a rather low tensile strength.

One feature in connection with hardness is of interest, viz., that the critical points in the hardness diagram correspond rather closely to the critical points in the electric conductivity curve. As already pointed out, the maximum hardness in a series of the type *IA* corresponds with the minimum electric conductivity for that series. The critical points in the hardness curve, due to compounds, are likewise reflected in the electric conductivity curve.

It will thus be seen that the property of hardness furnishes a means of analysis, when aided by other data, as electric conductivity, freezing-points, etc. In Figs. 41, 42 are reproduced the hardness curves of several binary series of alloys.

The Malleability of Alloys, based on the equilibrium diagrams. L. Guillet[1] has investigated this subject and formulated

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[1] Comptes Rendus, Vol. CXLIV, p. 1273 (1907).

the following rules. *For case IB,* in which the metals separate out as pure components in the form of excess substance and eutectic, the following holds true:

1. If both of the 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 series is largely dependent on the malleability of the eutectic. If the eutectic point lies between the middle of the diagram and the ordinate representing the non-malleable metal, the eutectic will be non-malleable or but little so. Example, Pb–Bi. If, on the other hand, the eutectic lies between the middle of the diagram and the ordinate representing the malleable metal, the eutectic will be malleable. Example, Pb–Sn. Further, if the alloy then consists of a malleable eutectic and the malleable metal of the series, it will be malleable. The alloys consisting of the malleable eutectic and the non-malleable metal will be malleable only when the amount of the non-malleable metal as "excess" is small.

For Case ICa and b. The two metals form an interrupted series of mixed crystals when solid. 1. If both metals of the series are malleable, the whole series of alloys is malleable. 2. If one metal only is malleable, those alloys which are rich in the metal are malleable. Example, Cu–Ag; Ni–Au.

For Case IIA. The two metals form compounds represented in the freezing-point curve by maxima, and which enter into the composition of mixed crystals in the series. All alloys of a series in this class are non-malleable.

For Case IIB. The two metals form compounds which dissociate before they melt; *e.g.* the freezing-point curves show inflections. Generally speaking, alloys coming under this case are non-malleable. It is very noticeable that a malleable metal is made decidedly brittle by the addition to it of a small amount of compound into which it enters as a constituent and with which it can form mixed crystals. Example, Cu–Cd.

An alloy consisting of a conglomerate of two types of mixed crystals, the first of which only is rich in a malleable metal, can itself be malleable only when the second mixed crystal is present in small amount. Example, Cu–Sn; Cu–Zn. Instances, however, arise where certain alloys under this case, while not malleable at ordinary temperatures, may be malleable at high temperatures. Example, certain alloys in the Al–Cu series.

For Case IAa, b, c. The two metals form a continuous series of mixed crystals. If the two component metals are malleable, the whole series into which they enter is malleable. Example, Cu–Ni; Ni–Co; Cu–Pd; Ag–Au. If but one metal of the series is malleable the alloys rich in this metal are malleable. When neither metal of the series is malleable, not any of the alloys are malleable. Example, Bi–Sb.

4. Specific Gravity and Volume of Alloys. — The specific volume is defined as the reciprocal of the specific gravity.

Thus, the specific gravity of lead = 11.376. The specific volume is $\frac{1}{11.376} = 0.08791$.

In the case of *IB*, viz., the two component metals form a conglomerate of the pure substances, the specific gravity curve and the specific volume curve are straight lines. (Fig. 45 *A*.)

In the case of the formation of mixed crystals there is a slight contraction of the specific volume from that which is to be expected from the mixture of a given proportion of the two components. Fig. 45 *C*. represents the curve of specific volume in this case.

In the case of chemical compound forming (Cases *IIA* and *IIB*), the formation of the chemical compound is usually accompanied by a contraction of the specific volume, although there may be an increase of the specific volume, hence an increase in specific gravity and the hardness. Fig. 45 *D*.

5. Magnetic Properties of Alloys.—Certain magnetites (lodestone) possess the property of attracting iron and nickel and cobalt. These are called the natural magnets. Their magnetism is permanent. Pure iron, nickel, and cobalt will become magnetized when in contact with a *permanent* magnet, or by means of induction by the electric current, but when the exciting cause is removed, their magnetism ceases. They become *magnets*, due to a superior permeability to the so-called lines of force. Certain alloys of iron, such as medium and high carbon (1.5 per cent.) steels, and tungsten and molybdenum steels, have, however, in distinction to pure iron, the property of becoming *permanent magnets*. Their permanent retention

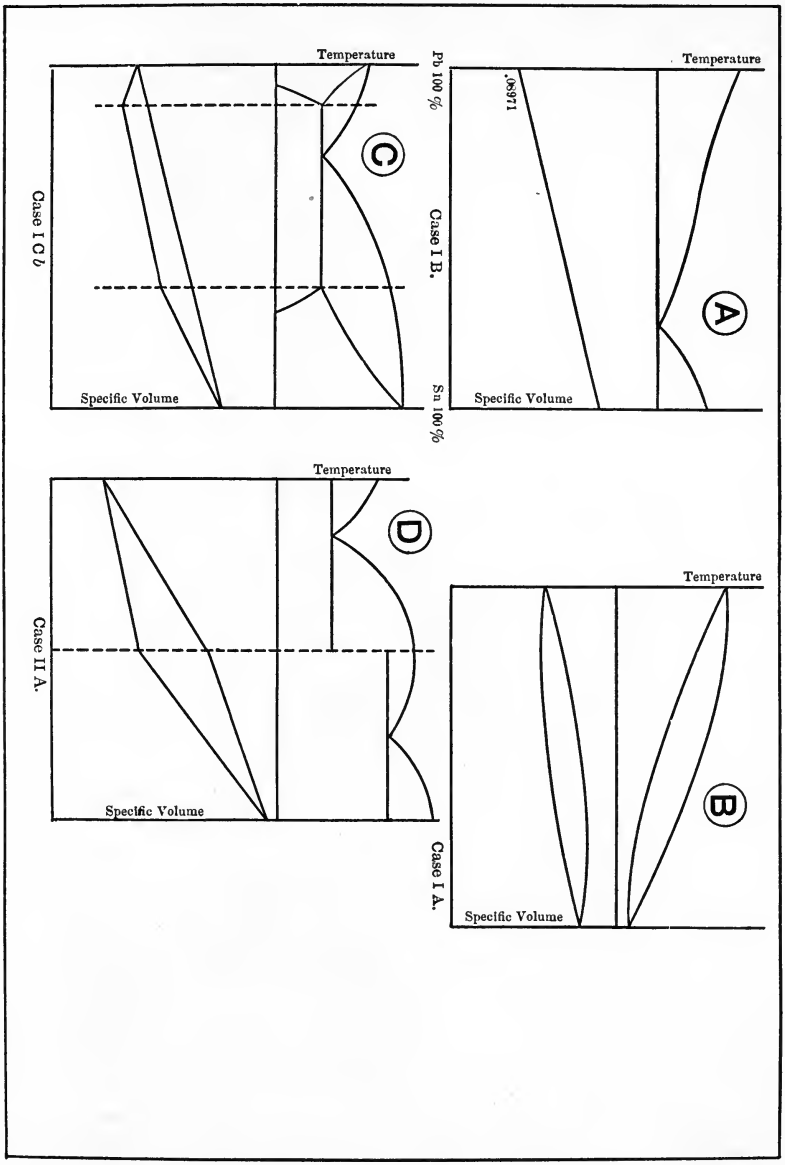

Fig. 45. — Specific volume curves in relation to freezing-point curves.

of magnetism is due to what is rather vaguely called their "coercive force." Alloys of this kind are of great value in the electrical industry for the construction of permanent magnets. The most common material for this purpose is a steel containing from 0.8 per cent. to 1.2 per cent. carbon. Tungsten steels[1] containing from 1.0 per cent. to 0.6 per cent. C and 3 per cent. to 5.5 per cent. W are also much used, largely for physical magnetic and electric apparatus. Molybdenum steels containing from 1 per cent. to 1.25 per cent. C and 3 to 4 per cent. Mo are also employed for the same purpose.

Chromium, copper, nickel, and silicon in steels of low carbon contents, less than 0.5 per cent., increase the intensity of the residual magnetization somewhat, but have not this effect on high-carbon steels.

Manganese up to 2 per cent. has practically no influence. Hadfield's manganese steel (13 per cent. Mn) in the quenched condition (viz., chilled in water from a high temperature) is not magnetizable, and in the annealed condition (viz., reheated) only slightly so. If I_r denote the "intensity of residual magnetization" per cu. cm., viz., permanent magnetism, in c. g. s. units (dynes), which, however, varies with a number of factors, chiefly the shape of the magnet, the relative value of different materials for permanent magnets is shown below.

TABLE XXII. MAGNETISM OF STEELS

Substance	I_r (in dynes)
Steel containing 0.06 per cent. carbon	30
" " 0.49 " " "	208
" " 1.21 " " "	460
" " 1.07 " " " and 3.40 Cr.	530
" " 1.02 " " " " 2.07 W.	540
" " 1.59 " " " " 5.50 W.	560
" " 1.24 " " " " 4.00 Mo.	530
" " 1.72 " " " " 3.90 Mo.	560

In order to produce permanent magnets from the above steels it is essential that they be quenched from somewhat above

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[1] Madame Sklodowska Curie, Bul. de la Soc. d'Encourgement pour l'Industrie Nationale, Jan., 1898, and Metallographist, Vol. I.

their "critical temperatures" Ar_2-Ar_3, viz., that at which the alloy changes from a magnetic to the non-magnetic condition on heating. This critical point varies with the nature of the alloy, since carbon and the other alloying substances shift its position. Roughly, it will lie between about 700° and 900° C. If it be quenched from below the critical temperature the residual magnetism will be comparatively slight.

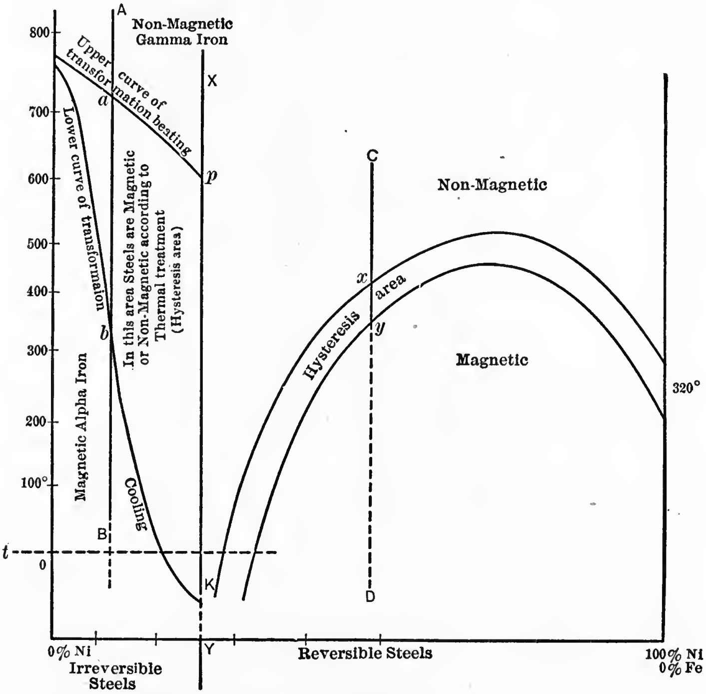

Fig. 46. — Magnetic diagram of nickel-steel.

As already stated under the caption "Expansion of Alloys," certain metals added to iron modify its magnetic properties. Chief among these substances are nickel and manganese. In Fig. 46 is shown a somewhat diagrammatic curve of the magnetic critical points of the iron-nickel series. It will be noted that the alloys are divided into the "reversible," over 26 per cent. nickel, and the "irreversible," under 26 per cent. nickel. Taking an alloy of the composition A–B, about 10 per cent. nickel[1] in a normally cooled state at temperature $t°$ (room temperature), it will be magnetic. On reheating it, it will not change its magnetic properties on passing the point b on the lower curve, but will cease to be magnetic on passing the point a on the upper curve. If now the same alloy be cooled, it will not change its magnetic properties on passing a, but will become magnetic on passing b on the lower curve.

Again taking an alloy of $X-Y$ composition, about 26 per cent. nickel, in a normally cooled state at the temperature $t°$ it will be non-magnetic. If it now be heated to 600° C., *e.g.* to p, it will not change its magnetic properties and, on cooling down again to $t°$, will pass through no change in its condition. If now, however, it be cooled to the point K, somewhere below zero degrees, it will become magnetic, and stay so, on reheating, until it passes the point p on the upper curve, when it will become non-magnetic.

This peculiar state of things seems to be due to a very decided "lag" in the reaction of the change of gamma iron to alpha iron and vice versa, which is an instance of "hysteresis," mentioned briefly in Chapter II. The hysteresis increases with the percentage of nickel up to 26 per cent.

With steels over 26 per cent. nickel the hysteresis seems to be constant (about 50°). For instance, a steel containing $C-D$ per cent. nickel is non-magnetic to the point y, on cooling, and then becomes magnetic. On reheating it will change from the magnetic to the non-magnetic state at x.

Recurring again to a steel of about 24 per cent. nickel, it will be seen that if cooled from a high temperature to room temperature, it will be non-magnetic, but if it should be now cooled to just below zero, it will become magnetic and stay so at room temperature and above. Steels of this approximate composition may therefore be either magnetic or non-magnetic at ordinary temperatures, dependent upon the thermal treatment they have passed through.

In further reference to the expansion of the irreversible

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[1] Hopkinson, Magnetic Properties of Iron-Nickel Alloys, Proceedings Royal Society, Vols. XLVII, 23, XLVIII, 1, 442, and L,121. Guillaume, Recherches sur les Aciers au Nickel, Comptes Rendus, March, 1898; also, Guillet, Les Aciers au Nickel, Bul. de la Soc. d'Encouragement, etc., May 31, 1903.

nickel alloys mentioned in this chapter as connected with the magnetic properties, it has been noted that when alloys of this class pass the lower transformation curve on cooling, *i.e.* pass from gamma to alpha iron, an increase in volume occurs.[1] The 15 per cent. nickel alloy contracts on cooling until it reaches 130° C., where it crosses the lower transformation curve, and then it expands, as the gamma iron changes to alpha iron, and keeps expanding until all of the gamma iron is transformed.

An interesting occurrence of magnetic alloys composed of non-magnetic metals is that of Heusler's magnetic alloys.[2] It has a bearing on the theory of magnetism, in so far as their existence may be considered to furnish proof that magnetism may not be a property inherent in a particular body, but is the result of certain forms of molecular groupings. Heusler's magnetic alloys are alloys of manganese-copper alloyed with certain percentages of aluminium. Table XXIII gives some typical analyses.

TABLE XXIII. ANALYSES OF HEUSLER'S ALLOYS

Number	1	2	3	4	5	6
	%	%	%	%	%	%
Silicon	0.08	0.07	0.02	0.16	0.17	0.05
Lead	0.07	0.07	0.13	2.03	3.14	3.84
Copper	64.49	70.14	75.83	59.43	65.22	73.68
Manganese	20.39	18.03	14.66	22.60	19.76	13.73
Aluminium	13.25	10.03	8.64	14.50	11.13	8.33
Iron	1.05	0.99	0.55	1.31	0.67	0.46

The basis of the magnetic alloys is an alloy of 30 per cent. manganese—70 per cent. copper, to which varying amounts of aluminium are added. The magnetic property of these alloys depends upon the amount of aluminium present and the heat

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[1] Guillaume, *ibid.*

[2] Fr. Heusler, W. Stark und E. Haupt, Verhandlung der Physikalischen Gesellschaft, Vol. V, p. 219 (1903); Zeit. Anorg. Chemie, Vol. LXI, p. 265, A. D. Ross und R. C. Gray, Zeit. Anorg. Chemie, Vol. LXIII, p. 349; Experiments on the Heusler Magnetic Alloys, K. E. Guthe and L. W. Austin, Bul. Bureau of Standards, Vol. II, p. 297.

and mechanical treatment through which the alloy has passed. (See iron-nickel.) The manganese-copper alloys themselves are non-magnetic. The greatest magnetic intensity occurs when 13 per cent. aluminium are added to 87 per cent. of manganese-copper. Heusler believes that the magnetic properties of these alloys are due to the presence of isomorphous mixtures of the compounds $AlCu_3$ and $AlMn_3$ which are supposed to be strongly magnetic.

6. The Tensile Strength and Elastic Limit of Alloys. — No well-defined laws of tensile strength or elastic limit of alloys as based on their constituents are known. It is well established that the addition of very small quantities of alloying substances very materially affects the strength of various metals, either increasing or decreasing the same. A well-known example of this is steel, an alloy of iron and carbon in certain proportions, in which comparatively small amounts of carbon (0.15 and 0.20 per cent.), combined with minute quantities of other substances (Mn, P, S, and Si), affect enormously the ultimate strength, elastic limit, etc. of the iron. This alloy is not treated further in this volume as it is practically a subject in itself. Examples of the tensile strength of alloys are given in Chapter IV.

Sir William Roberts-Austen[1] has conducted an elaborate investigation of the influence of certain small amounts of other metals on the tensile strength and ductility of gold, gold being chosen as it is obtainable in a very pure state, is not subject to oxidation, and does not contain much occluded gas. The amount of foreign substance added did not exceed 0.21 per cent. of the weight of the gold, an exceedingly small quantity. The following table gives the data of these experiments:

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[1] Proc. Royal Society, Vol. XLIII (1888), p. 425, and Phil. Trans., Vol. CLXXIX (1888), A. p. 339.

TABLE XXIV. EFFECT OF IMPURITIES ON GOLD

Name of Element Added	Ultimate Tensile Strength Lbs. per sq. in.	Elongation Per cent. (on 3 in.)	Impurity Per cent.	Atomic Volume of Impurity
Pure gold	14,000	30	None	—
Potassium	Less than 1,000	Not perceptible	Less than 0.2	45.1
Bismuth	1,000	" "	0.210	20.9
Tellurium	7,760	" "	0.186	20.5
Lead	8,340	4.9	0.240	18.0
Thallium	12,420	8.6	0.193	17.2
Tin	12,420	12.3	0.196	16.2
Antimony	12,000	?	0.203	17.9
Cadmium	13,760	44.0	0.202	12.9
Silver	14,200	33.3	0.200	10.1
Palladium	14,200	32.6	0.205	9.4
Zinc	15,080	28.4	0.205	9.1
Rhodium	15,520	25.0	0.21	8.4
Manganese	15,980	29.7	0.207	6.8
Iridium	15,980	26.5	0.290	15.3
Copper	16,440	43.5	0.193	7.0
Lithium	17,740	21.0	0.201	11.8
Aluminium	17,740	25.5	0.186	10.6

CHAPTER VI

THE MEASUREMENT OF HIGH TEMPERATURE

THE measurement of high temperature is rapidly becoming recognized as a matter of much importance in metallurgical and other industrial operations. Brick and pottery works, cement plants, glass works, galvanizing and tinning works, and certain chemical works employing comparatively high temperatures, habitually measure temperatures of certain operations. Many iron and steel plants use pyrometers constantly in heating and annealing furnaces; for the determination of the temperature of hot blast for blast furnaces; for occasional determinations of the temperature in rolling rails and structural iron; and other occasional temperature determinations. Metallurgic plants treating other metals than iron use pyrometers for the determination of temperatures of ore roasting furnaces; temperature of gases in flues. Tool works use them for temperature determinations of annealing and tempering and case-hardening operations; galvanizing and tinning works, for the determination of galvanizing and tinning baths, and many other plants also use them wherever the working temperature of the process employed is an essential feature. In general it is becoming recognized that an accurate knowledge and record of the temperatures employed in certain processes is vital to the production of a high-grade uniform product.

The types of pyrometers employed are many, amongst which the following are the most important:

1. Gas pyrometers; based on the change of pressure of a mass of gas at constant volume when subjected to varying temperature, and other similar types.

2. Calorimetric pyrometers; based on the determination of the total heat in a mass of metal.

3. Radiation pyrometers; based on either the total heat radiated by the hot body to be measured, or the photometric

measurement of radiation of a given wave length of a definite portion of the visible spectrum.

4. Electric resistance pyrometer; based on the variation of electric resistance of platinum with temperature.

5. Thermo-electric pyrometer; based on the measurement of the e.m.f. developed by the difference in temperature of two similar thermo-electric junctions opposed one to the other.

6. Contraction pyrometer; based on the permanent contraction of clayey materials when submitted to somewhat high temperature.

7. Fusible Seger cones; based on the fusing points of various definite mixtures of certain substances.

In this work only those methods generally and widely applicable are discussed in detail as regards principle and application — namely:

1. The thermo-electric pyrometer.
2. The platinum resistance pyrometer.
3. The radiation pyrometer, measuring total radiant energy.
4. Seger cones.

Temperature Scales. — Temperature is the "heat effect" or the "heat pressure" of a body and is strictly not a measurable quantity. The assignment of numerical values to temperature involves several steps, and not only that of choosing a unit of measurement as in measuring length or mass. It is essential that we have: First, some substance to serve as the thermo-metric body; second, the choice of some property of the body which changes with the temperature; third, two standard thermal states which are constant under given conditions, *e.g.* melting ice, and boiling water; fourth, the scale or number of units between these standard temperatures, or thermal states. The normal thermometer, to which practically all thermometers are standardized, is the hydrogen gas thermometer under the following conditions: Hydrogen gas at 1000 mm. pressure, the effect measured is the change of pressure at constant volume; the two standard thermal scales are melting ice, and vapor arising from boiling water at normal atmospheric pressure; the scale chosen between these points is 100 units, melting ice being taken as zero, and the scale is called Centigrade or Celsius.

In the normal thermometer hydrogen is used, since the coefficient of expansion $a = \frac{1}{273}$ in the laws of Mariotte & Gay Lussac; viz.,

$$\frac{p_1v_1}{p_0v_0} = \frac{1 + a\,t_1}{1 + a\,t_0} \text{ or } pv = R\left(\frac{1}{a} + t\right) = RT,$$

does not vary with pressure as it does slightly with other gases. In this instance the temperature t_1 and t_0 are assumed as those of known thermal states, viz., melting ice and boiling water, the interval comprising 100 units, which are not those indicated by the mercury thermometer, but closely approximate it. These points thus furnish the basis of the gas scale, which then, from the nature of the gas laws, is a uniform scale even for very high temperatures.

Hydrogen is, however, not a suitable gas to use for the measurement of *high* temperatures, and air and nitrogen have been employed in gas pyrometers, the temperature being carried up to 115°C. by Holborn & Day, with a constant volume nitrogen gas pyrometer. At these temperatures the coefficient a does not vary materially from that of hydrogen. From what has been said it is evident that as the estimation of temperature depends upon a considerable number of factors, the temperature indication of the several methods of pyrometry, viz., thermo-electric couples, platinum resistance pyrometers, radiation pyrometers, must be related to the normal scale of temperatures, viz., the gas scale. This establishment of relationship implies the determination of the fixed thermal states such as boiling water, boiling sulphur, melting-point of certain metals by both the standard methods, viz., the gas pyrometer, and the other method in question, and then relating the data by proper formula, in which are involved the parameters of temperature and that property of the body undergoing change with temperature which is measured, as for instance, in thermo-electric couples, the electromotive force, and in the platinum resistance pyrometer the variable electric resistance.

This work has been done by Holborn & Day up to 1150° C. for the thermo-couple, and by J. Harker up to 1000° C. for the platinum resistance pyrometer. Above these temperatures the thermo-couple scale and the platinum resistance scale are based on the assumption that the laws relating to temperature and the specific property of the pyrometric substance measured, are true above the stated temperature as they are below it. This is very nearly true for the thermo-couple to about 1500° C. (as checked by radiation measurements referred to further on), but above 1100° C. we have no laws relating the gas scale to the platinum resistance scale, so that this latter form of pyrometer is practically limited to this temperature.

The Thermo-Couple.[1]

General Theory. — Let Fig. 47 represent a thermo-couple, one wire of which is of pure platinum and the other of platinum alloyed with 10 per cent. rhodium. If the junction *A*, called the hot junction, be heated to T°, and junction *B*, at room temperature t°, be called the cold junction, then a certain current will flow through the closed circuit, induced by an electro-motive force *E*. Following the general convention that the current flows along the positive wire and returns by the negative wire, it will be seen that the electro-motive force originating at junction *A* induces a current flowing to the right in the direction of the arrows, while the electro-motive force originating at junction *B* induces a current flowing to the left in the direction of the arrows. It follows, therefore, that the electro-motive force of the couple which causes a current to flow is

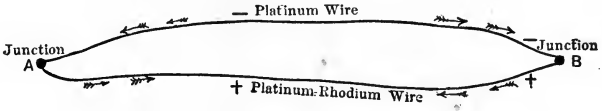

Fig. 47. — Diagram of thermo-couple.

$$E' - E''$$

E' being the electro-motive force due to junction *A*.
E'' being the electro-motive force due to junction *B*.
Therefore, $E = E' - E''$, or $E' = E + E''$.

The definite or specific electro-motive force of any couple is a function of the materials of which the couple is composed and the difference in temperature between the two junctions.

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[1] For complete data consult Franz Peters, Thermoelemente und Thermosäulen, W. Knapp, Halle, 1908.

In order, therefore, to determine the temperature T (above O^0 C.) of the hot junction A, it becomes essential to find the e.m.f. $-E'$, since the e.m.f. E, which is ordinarily measured, is due to the algebraic sum of two electro-motive forces, and does not represent that of the hot junction A. The simplest method of determining the value of T above $O°$ C. is to reduce the temperature of the junction B to zero degrees; for since the electro-motive force is a function of the difference in temperature between the two junctions, then in this case the measured electro-motive force E is that due to the temperature of the hot junction T above $O°$ C., viz., what we desire.

The relation between electro-motive force and temperature is expressed by Holman by means of the following formula for temperatures above 250° C. For platinum–platinum rhodium, and platinum – platinum iridium couples, with the cold junction at $O°$C., $\log e = a \log t + b$, in which $e =$ e.m.f. expressed in microvolts (millionths of a volt), $t =$ temperature of hot junction in degrees C. above $O°$, a and $b =$ constants depending on the composition of the couple. This represents very nearly a straight line.

The equation does not apply to temperatures below 250° C., a region in which the thermo-couple is comparatively insensitive. For the lower temperatures a rather complicated parabolic formula applies, so that the ratio between e.m.f. and temperature as observed at the higher temperatures no longer is true. In this lower range the electro-motive force comes up relatively much slower than the rise of temperature. It is evident that if the curve were a straight line throughout, viz., from zero degrees C. on, then in the measurement of any temperature, at which the cold junction was not at zero, it would be correct, in determining the temperature of the hot junction, to read the electro-motive force, convert it into temperature by means of the formula, and add to this the *temperature* of the cold junction, in order to get T, or the temperature of the hot junction above zero degrees. This, however, is not correct for the reasons stated, and it is customary, in order to obtain the temperature of the hot junction above zero degrees, to add to the temperature obtained by the e.m.f. reading one-half of the temperature of the cold junction.

Even this, however, is by no means rigorously correct, and leads often to appreciable error, as the above correction factor of 0.5 is based on the constants of a specific couple. The constants a and b given in the preceding equation are apt to vary with *each individual couple,* although supposed to apply to all couples of the same composition. This is no doubt due to the fact that it is practically impossible to obtain any amount of a metal or an alloy of the nature employed in couples of absolute homogeneity.

Offerhaus and Fischer[1] recommend, in accurate temperature determinations, the taking of the e.m.f. reading, due to the difference in temperature between the hot and the cold junction, and then adding to this the e.m.f. due to the temperature of the cold junction, calculated by means of a parabolic formula as mentioned, from the temperature of the cold junction, and from this sum, determine the temperature of the hot junction above zero degrees C.

It is, however, more desirable, whenever possible, to keep the cold junction at zero degrees C. and avoid any error, due to inaccurate correction factors, or to avoid calculation. The cold junction is again referred to in the following pages.

The Galvanometric Method of Measuring Temperature.— In Fig. 48 let Axy represent a thermo-couple of platinum and platinum-rhodium having its hot junction A in a heated space (furnace, crucible, etc.), and at x and y let it be joined by suitable connectors to the copper leads xo and yp, which in turn are connected to the binding posts of the galvanometer R_1. The resistance of the wires of the thermo-couple is expressed by r' and will vary, as during the heating of the junction a portion of the wires will become hot and their resistance increases as the temperature rises. The resistance of the copper conductors, which are of ample cross-section, is r; the resistance of the galvanometer is R_1. In the figure there is shown a second large resistance R, which is usually absent, but is inserted in this instance for the purpose of illustration.

If the junction A now be heated, an electro-motive force is generated at A, which will cause a current to flow through

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[1] Cold Junction Temperature Corrections, Electro-Chemical and Met. Ind., Vol. VI, p. 362.

the circuit. This current (amperage) will cause a deflection of the galvanometer needle. Let it be assumed that the junction A is heated to $T°$, which will cause an e.m.f. E to be generated, the value of which is dependent on the *difference* in temperature between A and that of the cold junction. (What the cold junction is in this case will be explained.) The current flowing in the circuit is expressed by Ohm's law as follows:

1. $C = \dfrac{E}{r' + r + R_1 + R}$. The current C causes a deflection of the galvanometer needle of say a degrees. If now the resistance R is cut out, the above equation becomes

2. $C^1 = \dfrac{E}{r' + r + R_1}$ and the deflection of the galvanometer needle is a^1 degrees. Now noting that there has been no change in E (e.m.f.), it becomes at once apparent that we may define

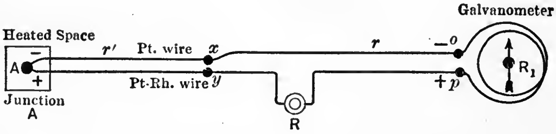

FIG. 48. — Galvanometer method of measuring temperatures.

certain conditions for this method, in order to be able to measure temperatures by means of it, viz., as follows:

That to have the galvanometer deflect solely in accordance with the electro-motive force, viz., the current generated, the resistance of the galvanometer must be proportionately very large to that of the rest of the circuit, so that any change in the resistance of the leads of the thermo-couple, due to increasing temperature of the wires, or a change in the resistance of the copper leads, due to a shortening or lengthening, as the set-up may require, will have practically no influence on the current generated by the fixed e.m.f.

That is, R_1 must be so large, in comparison to r and r', that even if these later change, the value of the fraction in equations 1 and 2 above is practically not affected. This is easily accomplished if R_1 is between 350 and 400 ohms, and $r + r'$ does not vary more than between 1 and 2 ohms, for E is always very small, rarely exceeding 20 millivolts (0.020 volts), so that the above equations become, in this instance,

$$1.\quad C = \frac{20}{1000\,(400 + 1)}$$

$$2.\quad C^1 = \frac{20}{1000\,(400 + 2)}$$

viz., practically identical.

In this method it is to be noted that the electro-motive force is measured in terms of current (amperage), and in this way is dependent on the resistance as shown. The type of galvanometer most frequently used is a high-resistance needle galvanometer of the D'Arsonval or swinging coil type, which is readily made aperiodic or "dead beat," the coil coming to rest instantly when the current is put on or off.

These instruments are standardized by the manufacturers and provided with a scale reading in millivolts, up to 18 millivolts, a millivolt being 0.001 volt. Each of the eighteen divisions is again subdivided into ten minor divisions, corresponding to 0.0001 volt or 100 microvolts. Some of the galvanometers have, above the millivolt scale, a corresponding temperature scale, calculated from the equation for the couple to be used with the galvanometer. It is to be noted that this temperature scale holds true only for the specific couple, or couples made from one mass of metal thoroughly homogeneous, and cannot be used indiscriminately for any couple. The equation for any given couple is worked out further on in this chapter.

The Cold Junction. — What is meant by the cold junction, and what is its significance, has already been defined. It remains to discuss the cold junction for the set-up shown in Fig. 48. If we consider a thermo-couple whose cold junction ends, instead of being soldered together, to be joined by a very short piece of copper wire, we could consider this copper wire as the cold junction of the circuit; it follows, therefore, that if this wire be very materially lengthened and a galvanometer included in its course, the whole circuit from the thermo-couple leads onward may be considered the cold junction, rather than any one point. We preferably call this a "cold circuit." In order to realize a true junction, an extra wire of platinum is necessary, as shown in Fig. 49. This, however, is of no practical importance, and experimentally will show no difference in results from that of the ordinary set-up. In order to conform rigidly to theoretic requirements, the *whole* cold circuit should be of *uniform temperature,* and as already outlined, is best held at zero degrees C. The reasons for a uniformity of temperature of the cold circuit are as follows: We have at the point x (Fig. 48), a junction of Pt and Cu; at the point y, a junction of an alloy Pt–Rh with Cu; near the points o and p, the junction of Cu with German silver (of the galvanometer). Each of these junctions represents a thermo-couple and unless the whole circuit be of uniform temperature, electro-motive forces may originate at these points, which will give rise to so-called "parasite currents," which may seriously influence the result due to the main hot junction A. It follows, therefore, that the more nearly we confine ourselves to the use of one metal for conductors and galvanometer, the more completely will errors from this source be eliminated.

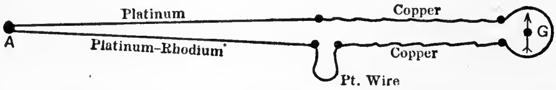

FIG. 49. — Cold junction, connections.

It is, of course, usually impossible to keep the whole of the cold circuit at zero degrees C., and by experience it is found sufficient to keep the junctions of the couple leads with the copper conductors at a uniform *known* temperature, preferably as nearly zero as possible. It is absolutely essential that the junctions x and y be at precisely the same temperature. This is best done by the device shown in Fig. 50, which is self-explanatory.

An accurate thermometer is placed in each test tube for the readings of the junctions and to insure their uniformity. It is sometimes necessary to place ice into the test tubes themselves to get the temperature of the junctions to zero degrees C. If the junctions are not at zero degrees but near it, it will be sufficiently accurate to add one-half the reading of the cold junction to that obtained for the hot junction by the calculation of temperature from the measured e.m.f. There are on the market jacketed copper-ice vessels for the cold junction arrangement. (See Fig. 52.) The "cold circuit" not included in the "cold junction" should be kept at a uniform room temperature.

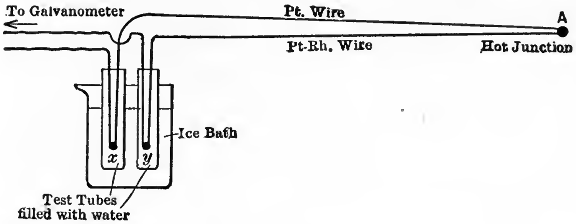

Fig. 50. — Cold junction set-up.

General Data on Platinum-Platinum Alloy Thermo-Couples.— As already stated, we have no common formula applying to all Pt, Rh – Pt, or Pt, Ir – Pt couples relating temperature to electro-motive force, but in the general equation

$$\log e = a \log t + b$$

the constants a and b must be determined for a given couple. With these determined, a curve may be constructed with temperatures as ordinates and e.m.f. as abscissæ, from which temperatures corresponding to any given indicated e.m.f. can be directly read off. The fixed temperature points against which any given couple is standardized are the boiling-point of sulphur (444.6° C., at 760 mm. pressure with a variation of 0.095° per mm. change of mercury pressure); the freezing-point of pure zinc (419° C.); the freezing-point of pure gold (1065° C.); and the freezing-point of pure copper under reducing conditions (1084° C.).

The highest temperature to which the thermo-couple may safely be applied is about 1600° C. It is sometimes desirable to have a fixed point above that of copper to standardize to, and in this case pure platinum is used — 1753° C. This point is determined by a special method described further on.

The metals and the alloys of Pt–Rh and Ir, are used for thermo-couples, because they may be obtained in states of great purity, give a comparatively high electro-motive force for a given temperature, are practically unoxidizable and unattacked by other agents than oxygen, and withstand a high temperature.

Platinum and platinum alloys are made brittle by heating for a *long time* to 1000 to 1200° C. The brittleness is probably due to crystallization. Pt–Ir is especially susceptible to this; Pt–Rh, to a less degree, and pure Pt to a still less degree. This brittleness may cause changes in the e.m.f. of the couple, and prolonged heating of couples should be avoided if possible. Where it is necessary, as in certain industrial uses, the couples must be restandardized at comparatively frequent intervals or renewed.

Couples in frequent use suffer strain by bending at sharp angles and become hardened in spots. This unequal molecular condition throughout the length of the couple wires may change the e.m.f. of the couple. It is desirable, therefore, to have the couples annealed throughout their whole length by heating to 1200° C., and cooling in air, before use. This is particularly necessary for Pt, Pt–Ir couples.

The thermo-couples must be rigorously protected against reducing gases, particularly those containing CO, hydrocarbons, and hydrogen, as these gases at the high temperatures at which the couples are used rapidly attack platinum and cause alterations which very seriously affect the e.m.f. of the couple. An oxidizing atmosphere, even at high temperatures, is not injurious to the couple.

The couples must also be protected against the vapors of the volatile metals, such as Cu, Zn, Ag, Sb, etc., and their oxides, also against the vapors of P and Si, and certain silicides and phosphides. All of these prove rapidly destructive to the thermo-couples.

Neither can the thermo-couple be put into direct contact with most molten metals as the platinum will alloy with them, and destroy the couple.

Thermo-couples are protected against the above described conditions by means of iron, Berlin porcelain, and fused silica tubes, closed at one end. As it is essential in pyrometric measurements by the thermo-couples to prevent short-circuiting of the wires, two tubes, an inner and an outer one, are generally used. The tubes should be of as small a diameter as is consistent with the wires used. The outer tube is closed at one end, while the inner one, open at both ends, fits into the large tube.

Iron tubes can be used, under conditions in which they are not seriously attacked, and up to temperatures of 800° to 900° C. In order to avoid short-circuiting, iron is used only for the outer tube, while for the insulating tube porcelain, glass, or quartz is used. Where iron can be used for the protective tubing, it has the advantage, due to the high conductivity of the iron, of establishing temperature equilibrium between the source of heat and the instrument in a very short time, thus largely doing away with the "lag" in the galvanometer indications, which must be accounted for when other tubing is used.

Porcelain and fire-clay tubes are used when the temperature to be measured is above 900° C., or the conditions call for a tube that is not attacked. Porcelain tubes possess a very decided disadvantage in that they are very fragile and break very easily when unequally heated, or when rather suddenly heated or cooled, a condition, especially in industrial work, difficult to avoid. Tubes of this kind are made which serve to determine temperatures of 1500° to 1600° C.

The most serviceable protective tubes are the fused silica and quartz tubes recently placed on the market. The former are known as the "electro-quartz" tubes. The coefficient of expansion of this material is very small, so that even very sudden temperature changes cause no breakage. Tubes of this material may safely be used up to 1400° C., at which temperature the material softens; it will melt at about 1600° C. It is practically impenetrable to gases and metal vapors below 1300° C., and thoroughly protects the thermo-couple wires. Its heat conductivity is also greater than that of porcelain or fire clay.[1]

The closed tubes may be had of the following diameters of bore: $\frac{1}{8}$, $\frac{3}{16}$, $\frac{1}{4}$, $\frac{3}{8}$, $\frac{1}{2}$, and $\frac{5}{8}$ in., and in lengths of 3 to 5 ft. The insulating tubes come in similar sizes, the smallest having a $\frac{1}{16}$ in. bore. Special sizes are also obtainable.

It is usually desirable to employ tubes of as small a diameter as possible, and for ordinary laboratory work, outer tubes of $\frac{3}{16}$ to $\frac{1}{4}$ in. bore, and inner tubes of $\frac{1}{16}$ to $\frac{1}{8}$-in. bore, are most frequently used.

In place of inner tubes for insulation, asbestos thread braided about the couple wires so as to prevent their contact may be used. This arrangement is very flexible, but cannot be used

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[1] P. Schoen, Metallurgie, vol. V, p. 635.

for temperatures above 1200° C., the approximate melting-point of asbestos. By use of asbestos thread small diameter tubes can be used, making the couple very sensitive.

In certain industrial work it is sometimes necessary to afford greater protection to the couple wires than can be done by means of the tubes mentioned, and for this purpose especially heavy graphite and fire-clay tubing may be used. When this is the case, considerable time must be allowed for temperature equilibrium to establish itself between the junction of the thermocouple and the source of the temperature to be measured.

Manufacturers of pyrometer installations of the thermocouple type for industrial purposes sell the thermo-couple protected by various special forms and designs of protective tubing, provided with handles and binding posts, etc., but the application of these forms is so limited, that except for very special and constant use purposes under certain conditions their purchase is not recommended. It is much better to have reasonably long couples, and an assortment of tubing of the types mentioned, by means of which any desirable set-up suitable to the conditions may be obtained.

Resistance of Couples and the Making of a Junction. — It has been pointed out that the question of resistance of the circuit plays an important part in the galvanometric method of measuring the temperature by thermo-couples, and in this connection the resistance of the couple wires is of interest.

The specific resistance[1] of pure platinum is 7.9 michroms at zero degrees C., and of the alloy 90 per cent. Pt–10 per cent. Rh is 27.0 michroms. For increasing resistance with temperature, Holborn & Wien[2] give the following formula:

$$R \text{ (specific rest.)} = 7.9\,(1 + 0.0031\,t) \text{ between } 0° \text{ and } 100° \text{ C.}$$

$$R = 7.9\,(1 + 0.0028\,t) \text{ between } 0° \text{ and } 1000° \text{ C.}$$

and for the platinum-rhodium alloy, LeChatelier gives

$$R = 27\,(1 + 0.0013\,t) \text{ between } 0° \text{ and } 1000° \text{ C.}$$

The most common size of couple wire used is 0.5 mm. diameter, although 0.3 are now also frequently used. For a couple of 0.5 mm. diameter wire and 1 meter length, the resistance is about 2 ohms cold. This is practically doubled at 1000° C.,

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[1] See chapter V, p. 118.

[2] LeChatelier and Boudouard, High Temperature Measurements, 1904, p. 135.

but it must be borne in mind that usually but a portion of this length is heated.

The junction of the platinum and the platinum-rhodium wire may be made by firmly twisting the two wires together for a distance of a few millimeters, but the method is uncertain as during heating they may become untwisted in part and make a poor contact, increasing the resistance of the circuit greatly and giving rise to false measurements. The best way is to fuse the two wires together, making what is known as the autogene junction. This is best done by the oxy-hydrogen blow-pipe flame, obtaining a small steady flame, touching the ends of the wires together in the flame and instantly removing them when fused. The little ball formed by the fusion should not exceed about 2 mm. in diameter. The fusion may also be carried out by means of oxygen and illuminating gas, but this is more difficult as the temperature attained is not so high as with the oxy-hydrogen flame, and the operation requires more care. The joining of the wires must sometimes be frequently performed, due to injury to the lower end of the couple, by prolonged heating at high temperature, or by metallic vapors or reducing gases. When this injury has occurred, the injured portion of the wires should be cut away and a fresh junction made. The joining may also be made by means of palladium or gold, when the temperature for which the couple is to be used is not very high; the gold junction cannot be used above 1000° C. A small strip of palladium or gold is firmly twisted about the ends of the wires, and these held in the flame of a blast lamp on a stick of charcoal properly hollowed out.

The Calibration of Thermo-Couples. — *First Point.* Boiling sulphur. The accompanying figure shows a sketch of the apparatus required, which is:

1. A thin glass tube similar to a test tube, but with a bulb near the top, about 10 to 12 in. long and 0.5 to 0.75 in. in diameter.

2. A plaster of Paris muff, to prevent radiation, about 6 in. long and 4 in. in diameter. This is easily made by forming the plastic plaster of Paris around the tube in a rough cardboard mold, and withdrawing the tube with a twisting motion before the plaster has set, slightly enlarging the opening so that when the plaster has hardened the tube can readily be reinserted.

3. An ordinary Bunsen flame.

4. A ring stand and clamps similar to those shown in the illustration.

5. The thermo-couple, which is best about 24 to 36 in. long.

6. The cold junction vessel with an accurate thermometer, and the galvanometer, with suitable copper leads and binding screws to make proper connections.

The necessary precautions as to cold junction and connections have already been fully discussed. It is essential to set up the galvanometer in such a way that it will be free from vibration such as is caused by persons walking across the floor.

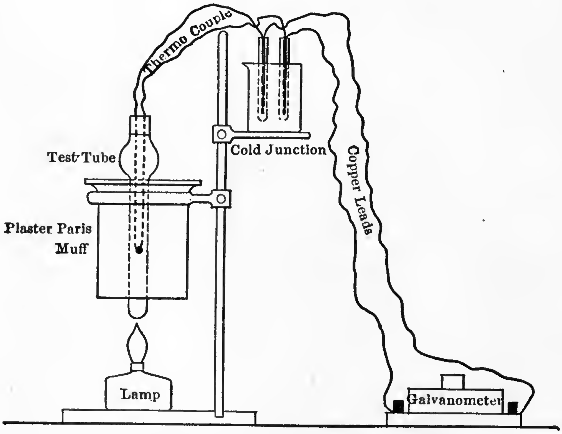

Fig. 51. — Set-up for determination of sulphur boiling-point.

The galvanometer should be known to record accurately and it is essential that it does not "hang," *e.g.* the needle be arrested by friction, etc. If the needle is not at zero, it should be adjusted to it. The set-up must be perfectly level. It is well also from time to time to break the galvanometer connections and note whether the needle returns to zero, as it should. Care must be taken to connect the proper wires to the plus and minus binding post; this may be done by trial. The platinum or softer wire is the *negative*, and the platinum-rhodium, or the platinum-iridium, is the *positive* pole.

The thermo-couple need not be protected by the tubes for the sulphur boiling-point determination, but for insulation purposes the inner tube is best used. Chemically pure sulphur is quite readily obtained; this is placed into the test tube so that when molten it fills it to the depth of about 1.5 in. The tube is then heated until the sulphur boils gently, when the flame is so adjusted to keep it just boiling. The thermo-couple is then plunged into the vapor just above the boiling liquid at a point protected by the plaster muff, and the galvanometer watched and read when the needle gives the maximum deflection and comes to rest; the *millivolt* reading is carefully recorded, reading as closely as possible.

Connections are broken and reestablished a number of times to get a series of readings. The thermometers in the cold-junction tubes are also read and the readings recorded. The cold junction should be kept as near zero degrees as possible. The barometer reading at the time of the experiment must also be recorded. As an illustration, let it be assumed that the data for this experiment is as follows:

A. The average of five closely agreeing galvanometer readings is 3.2 millivolts.

B. The barometric reading is 680 millimeters. The boiling-point of sulphur at 760 mm. is 444.7° C.[1] A correction of 0.095 ° C. is to be added or subtracted for each millimeter difference in pressure as the barometer reads above or below 760 mm. This gives a correction of (760-680) × 0.095 = 7.6° C., to be deducted from 444.7° C., giving 437.1° C. as the boiling-point of sulphur at 680 mm. pressure.

Thus, 3.2 millivolts corresponds to 437.1° C. The cold junction was at zero degrees C. This data gives one set of figures for the determination of the curve of the couple.

The second set of figures may readily be determined by taking the freezing-point of pure electrolytic copper.

The apparatus for this determination is shown in Fig. 52.

A small gas furnace is well adapted for work of this kind, although special small electric furnaces are very well adapted.

If no furnaces of these types are available, copper may be melted and superheated in a small graphite crucible under a layer of charcoal in a wind or muffle furnace. When removed from the furnace, this is placed in a somewhat larger fire-clay

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[1] LeChatelier and Boudouard, High Temperature Measurements, 1904, p. 296; Determination of Chappius and Harker.

crucible to protect against too rapid radiation, and covered with a sheet of asbestos with a hole in it through which the pyrometer tube can be passed. The set-up of the pyrometer and galvanometer should be in readiness when the crucible is brought from the furnace so that no time is lost, as the copper will chill quickly. In order to carry out this method, the superheating must be considerably above the melting-point of copper, and all the apparatus in instant readiness for the insertion of the quartz protective tube carrying the couple, and the reading of the galvanometer.

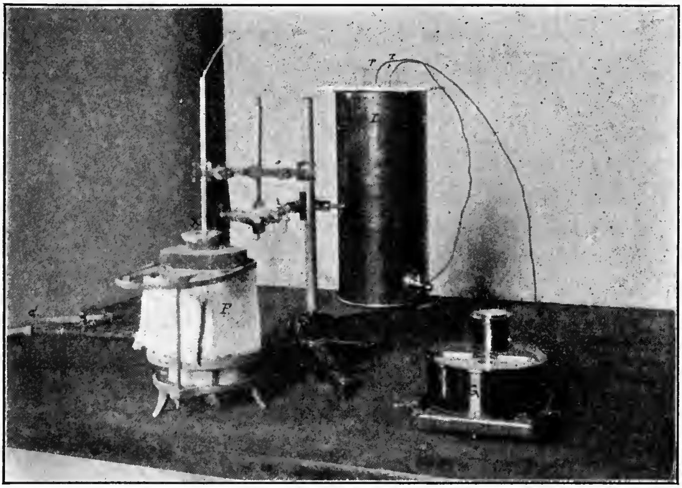

FIG. 52. — Set-up for the calibration of the thermo-couple, and the taking of freezing-points.
F, gas funace; D, cold junction vessel; G, galvanometer; T, thermometers.

The furnace method is carried out in a similar manner. About 20 to 25 grams of pure copper are melted in a small graphite crucible under charcoal in a small gas or electric furnace, and superheated 50 to 100° C. above its melting-point. The quartz protective tube in which is the couple is then inserted into the molten copper, reaching about two-thirds of the distance into the molten mass. Proper connections are made and the galvanometer read. After temperature equilibrium in the instrument has been attained, the gas or current is shut off and the furnace and its contents allowed to cool. The cooling curve of the copper is then taken, the galvanometer readings being noted at intervals of every 10 to 30 seconds, both time and millivolt readings being recorded. As for example:

Table XXV. Record for the Cooling-Curve of Copper

Time			Millivolts	Temperature Cold Junction
Hrs.	Min.	Sec.		
2	10	—	10.20	0° Cent.
2	10	30	10.10	do.
2	11	—	10.00	do.
2	11	30	9.78	do.
2	12	—	9.78	do.
2	12	30	9.78	do.
2	13	—	9.60	do.

The arrest point occurring at 2 hrs. 11 min. 30 sec. to 2 hrs. 12 min. 30 sec., with an indication of 9.78 millivolts, is the freezing-point of copper. (Consult cooling curves in Chapter II.) The experiment is repeated several times in order to confirm the results. Pure copper under reducing conditions freezes at 1084° C.[1] Under oxidizing conditions, the freezing point of copper (copper-copper oxide) is 1065° C.

We have then the following data: Freezing-point of copper, 1084° C.; millivolt reading, 9.78; cold junction, zero degrees C. From the data of the sulphur and copper experiments it is now possible to deduce the equation of the particular couple in use from the general equation

$$\log e = a \log t + b$$

in which e = microvolts = millivolts × 1000.
t = degrees C. above zero.
a and b = constants to be determined.

From sulphur we have

1. $\log e\ (3200) = a \log t\ (437.1) + b.$

From the copper we have

2. $\log e\ (9780) = a \log t\ (1084) + b.$

or

1. $3.50515 = a \times 2.6405 + b.$
2. $3.99034 = a \times 3.03502 + b.$

---

[1] Holborn and Day's determinations.

Subtracting 1 from 2,

3. $0.39452\,a = 0.48519$ or $a = 1.23$.

Substituting this value in No. 1, we have

3. $3.50515 = 3.2478 + b$, or $b = 0.25734$.

The general equation then becomes

$$\log e = 1.23\,t^\circ + 0.25734,$$

which is the specific equation for the couple in use.

From this equation is then constructed the curve for this couple, plotting the temperatures as ordinates and the e.m.f. in microvolts, derived by computation from the formula for the corresponding temperature, as abscissæ. In plotting the curve it is well to check up by several other fixed point determinations, such as pure lead (327°), and pure silver (961.5° C.).[1] This latter figure is for the metal under strictly reducing conditions. For silver in air, 955° C. is to be used as the admixture of silver oxide lowers the melting-point of the metal similar to the case of copper. Silver is not very desirable as a fixed point, but will serve as a check. The boiling-point of naphthaline, 218.0° C., with a correction of 0.06° C. for every mm. change in pressure of barometer from 760 mm., or the tin freezing-point, 232° C., may be used as fixed points.

A higher, but somewhat indefinite fixed point, may be obtained by the fusion point of platinum, 1753° C. This is best obtained at the time the "autogene" junction of the couple is made, utilizing the platinum wire of the couple, which melts before the alloy wire. The gas-oxygen flame is best used, and a tall flame should be obtained. The wires of the couple are twisted together for a distance of 5 to 10 mm. and held about 2 in. above the nozzle of the blast lamp, a strong stream of oxygen is turned on, and then gas, endeavoring to obtain a steady flame. One person watches the flame and the other the galvanometer; when fusion takes place there will be a momentary halt in the motion of the galvanometer needle, followed by a sudden jump. The halt indicates the fusion point. This method can, however, give only approximate results, and is dependent upon the obtaining of a very steady flame, as it is evident that irregularities in the heating power of the flame will have the same effect on the galvanometer needle as the fusion of the metal.

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[1] Holborn and Day's figures.

The "set-up," described for sulphur, serves also for the determination of naphthalene, and that for copper for any of the metals mentioned, viz., tin, silver, lead, zinc, etc.

The Opposition Method of Measuring Temperature by Means of the Thermo-Couple. — The galvanometric method has been shown to be not an absolutely rigorous method, due to the fact that a varying resistance of circuit influences the result. It is, however, amply accurate for all industrial purposes to which the thermo-couple is applicable, and all ordinary scientific measurements of temperature. Where, however, more than ordinary correctness is required, the "opposition method" by means of the potentiometer, viz., the direct measurement of the e.m.f. of the couple, independent of the resistance of the circuit, is to be used. The apparatus required for this set-up is also very serviceable for the checking up of galvanometers used in the galvanometric method.

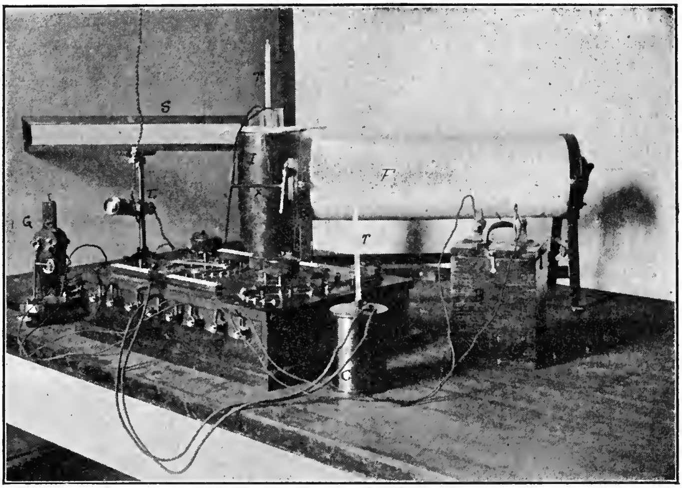

FIG. 53. — Set-up for the potentiometer or opposition method of measuring temperature by the thermo-points.

Fig. 53 shows a sketch of the set-up required for this method. *P* is a potentiometer capable of measuring differences of potential (e.m.f.) up to 30 millivolts.

B is a battery furnishing a definite e.m.f., in the particular instrument under discussion, between 1.8 and 2.14 volts.

C is a standard cell, best a Clark cadmium cell.

G is a delicate reflecting galvanometer of the Thomson type. A suitable lamp and proper scale on which to project the galvanometer mirror deflections must also be provided. (*S*, *L*.)

X, *I* represents the thermo-couple, cold junction, and copper connecting leads. *F* is an electric furnace containing the hot junction of the couple.

The potentiometer, the description of which follows, is made by the Cambridge Scientific Instrument Company of Cambridge, England. Similar instruments are made by the Leeds-Northrup Company of Philadelphia. This instrument is an apparatus for accurately measuring small differences of unknown potential, by balancing the same directly against an adjustable known potential, standardized in millivolts, by means of a standard cadmium cell. The adjustment can be made by direct reading to 0.01 millivolt and by estimation of tenths to one microvolt. The arrangement of the potentiometer circuit is shown diagrammatically in Fig. 54.

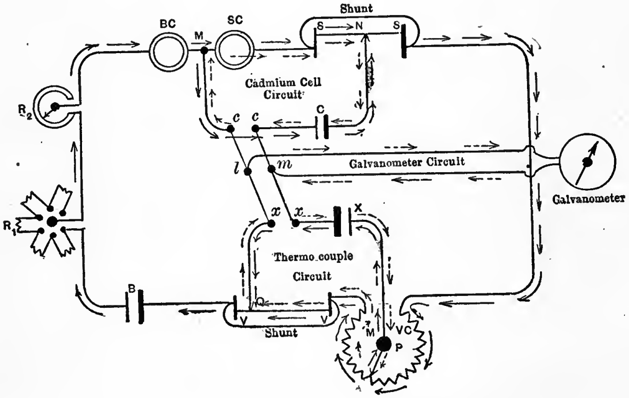

FIG. 54. — Diagrammatic sketch of potentiometer connections. Full arrows indicate battery current. Dotted arrows indicate thermo-couple and cadmium cell current.

The accumulator cell *B*, generating an e.m.f. of from 1.8 to 2.14 volts (no greater variation is permissible), furnishes the current to the main circuit. Starting from the plus pole of the battery, the current passes through the adjustable resistances R_1 and R_2, the resistance coils *BC* and *SC* and the graduated wire *SS*, then through the resistance coils *MVC* and the graduated wire *VV* to the negative pole of the cell.

The total resistance in the circuit is arranged so as to give a fall of potential of about one volt per 50 ohms circuit resistance, and the resistance coils *BC* and *SC* are so adjusted that the fall of the potential from the point *M*, to a point *N* on the wire *SS*, is approximately equal to the e.m.f. of the cadmium cell. The adjustable resistances R_1 and R_2 are introduced as a means of adjusting the resistance of the main circuit, as may become necessary as the voltage of the battery varies from 1.8 to 2.14 volts; R_1 gives a rough adjustment with a range of 10 ohms and R_2 gives a fine adjustment with a range of about 2.5 ohms.

The wire *SS* is graduated so that the reading shown at any point on it is the potential difference between that point and the point *M* on the basis of a fall of exactly one volt per 50 ohms resistance in the circuit. If, therefore, a standard cadmium cell *C* is connected with the circuit between the points *M* and the point *N* on the wire which marks its e.m.f. at the existing temperature, and an exact balance be obtained (by means of the adjustable resistances R_1 and R_2) between the e.m.f. of the cell and the potential difference between the points *M* and *N*, the whole circuit becomes accurately adjusted to a fall in potential of one volt per 50 ohms of circuit resistance.

For the following is true — the total resistance of the potentiometer circuit is made up as follows:

Adjustable resistance coil R_1	total resistance	10.000	ohms
Adjustable resistance coil R_2	total resistance	2.5	"
Resistance coil BC	total resistance	42.5	"
Resistance coil SC	total resistance	51.0	"
Slide wire SS (adjustable resistance)	total resistance	0.125	"
Coil MVC	total resistance	1.45	"
Slide wire VV (adjustable resistance)	total resistance	0.06	"
Resistance of connecting wires	total resistance	—	
	Total	107.635	ohms

The battery furnishing the current may have an e.m.f. of from 1.8 to 2.14. Then assuming the last figure to be true, we have from Ohm's law, $C = \frac{E}{R}$

$$C = \frac{2.14}{107.635} = 0.0198 \text{ amperes,}$$

or substituting again for $R = 50$ we have $CR = E$.

$0.0198 \times 50 = 0.99 +$, or a drop of potential of one volt approximately for 50 ohms of circuit resistance.

Or the second case of an e.m.f of 1.8 and leaving out the two adjustable resistances BC and SC amounting to 12.5, the total resistance of the circuit now is $(107.635 - 12.5)$ or 95.135 ohms, and

$$C = \frac{1.8}{95.135} = 0.0189,$$

or substituting again for $R = 50$ we have $CR = E$.

$0.0189 \times 50 = 0.945$, or again a drop of potential of approximately one volt for 50 ohms circuit resistance.

The slide wire SS, as already stated, is accompanied by a scale on which is marked the e.m.f. of the cadmium cell for given temperatures. Suppose this e.m.f. for the room temperature is 1.098, then if the sliding contact is placed on this mark on the slide wire SS, thus fixing the point N, then the drop of potential of the current furnished by the cadmium cell, between the points M and N, is exactly in the ratio of one volt per 50 ohms of circuit resistance. With the battery connected, a current is constantly flowing through the whole circuit, in a given direction, the cadmium cell is shunted into this circuit between M and N in such a way that the two currents oppose each other in the cadmium cell circuit as shown in Fig. 54. If now the key *lm* is thrown to connect into this circuit the galvanometer, this will indicate the difference in strength of the currents, and if now resistance be put into the main battery circuit by means of the adjustable coils R_1 and R_2 until the galvanometer indicates zero, it is evident that the current flowing between M and N in the cell circuit due to the battery is just balanced by that from the cadmium cell, and as this latter is such as to cause a drop of potential of exactly *one volt per* 50 *ohms of circuit resistance,* the battery current is standardized to this, and may be used, while the cadmium cell current can be cut out by releasing the key *lm*.

The coil *MVC* is a continuous coil of twenty-nine sections, each of which is accurately adjusted to a resistance of 0.05 ohms. On the basis of 50 ohms circuit resistance for each drop of potential of one volt, the fall of potential in each section is thus exactly one millivolt. Similarly the resistance of the wire *VV* being 0.06 ohms, the fall of potential along its length is 1.2 millivolts. Thus, in the portion of the circuit between the points *P* and *Q* in the thermo-couple circuit, including the coil *MVC* and the wire *VV*, there is an available fall of potential of 30.2 millivolts. If the thermo-electric couple is shunted into the circuit with the poles connected as shown at *X* in the figure, between the points *P* and *Q* and the galvanometer thrown in by the key *lm* connecting the posts *l* and *x* and *m* and *x*, the galvanometer will show a deflection due to the thermo-couple current, which may now be brought to zero again by putting in resistance against the thermo-couple current by means of the coil *MVC* and the slide wire *VV*, but cutting out resistance to the battery current, thus letting battery current pass to the thermo-couple circuit shunt, in an opposite direction to the current from the thermo-couple until this is neutralized and the galvanometer again registers zero. As the resistance put in is accurately standardized to drop of potential it is graduated directly in millivolts and thus reads directly the e.m.f. of the thermo-couple which has been neutralized.

In operating by this method the cold-junction device is used as described for the galvanometric method. The following points also should be observed: The galvanometer, which should be a reflecting one of Thomson type, very delicate and sensitive, and of low resistance, should be placed on a firm foundation, not subject to vibration caused by walking about the room, etc. The reflecting lamp used to obtain the beam of light may be of any suitable type; the author uses a small Nernst lamp in a brass tube which throws the image of a wire on the galvanometer mirror. A suitable scale on which the mirror throws the image is used. As already stated, the battery used to furnish the current for the circuit is best an accumulator cell and its e.m.f. must be carefully chosen for the potentiometer in use. For the instrument described, the cell used should have an e.m.f. of not less than 1.8 and not more than 2.14 volts. In using the instrument, after making the proper connections, and standardizing the battery current by means of the standard cadmium cell which furnishes an e.m.f. of 1.095 volts at 18 degrees C. with a decrease or increase of 0.00002 volts for each degree of rise or fall of temperature of the air surrounding it, the thermo-couple circuit is thrown in by pressing the key *lm* to make proper connections, and then the resistance thrown in in the coil *MVC*, the final adjustment to a zero reading of the galvanometer being made by the contact on the slide wire *VV*. The e.m.f. of the couple is then read off directly on the coil *MVC* and the scale accompanying the slide wire. Cooling curves can readily be obtained by this method by taking the time accompanying each reading, keeping a record of the temperature of the cold junction. The method is an extremely sensitive one, and possesses the advantage of being independent of the resistance of the thermo-couple circuit, as the e.m.f. flowing in a closed circuit is reduced to zero. It also does away with possible error of indication by the high-resistance galvanometer used in the galvanometric method, due to variable zero in the instrument, and other causes.

Base Metal Thermo-Couples. — Of recent years, certain base metal thermo-couples have come into wide use for the measurement of temperatures in industrial works where great accuracy is not required. The advantages in the use of these couples are to be found in their cheapness, and their robustness, *i.e.* the wires can be made of large cross-section and the indicating instrument, the galvanometer, need not be a very delicate or costly one. The most common form of base metal thermo-couple, is the iron-konstantan and the copper-konstantan, konstantan being an alloy of copper and nickel. The exact proportions are usually held secret by the manufacturers. This alloy is the negative wire of the couple, while pure iron, or pure copper, is the positive wire. Base metal thermo-couples of this type are quite reliable and remain constant in e.m.f. to a considerable degree of accuracy for low temperature, say up to 1000° F. = 537° C. Above this temperature, the couples are not reliable. When temperatures between 1000 and 2000° F. (537 to 1075° C.) are to be measured by base metal thermo-couples, other couples must be used; for instance, for the negative wire an iron-wolfram alloy containing from 5 to 25 per cent. of wolfram, and for the positive wire, pure nickel. Nickel steel and chrome steel wires, as the negative element, and pure nickel as the positive element, have also been used, as well as a number of other metals and alloys. For the thermo-couples with konstantan as one wire, for low temperatures, a total accuracy of reading within 2 per cent. may be obtained. The error increases with time of use, due to the changes taking place in the couple, particularly that due to oxidation. The base metal thermo-couples for measuring higher temperatures are subject to a considerably greater error. The electro-motive force of base metal thermo-couples varies widely with small differences of compositions of the wires, and practically each couple must be standardized. The wires of base metal thermo-couples should be thoroughly annealed at temperatures of about 500° C. before use. Wires commonly in use are $\frac{1}{16}$ in. in diameter, one wire being completely covered by an asbestos jacket. The curve relating e.m.f. to temperature is a straight line. For an iron-konstantan couple, the following data shows the relationship:

Degrees Fahrenheit	e.m.f. Millivolts
0	0
180	5
360	10
540	15
720	20
880	25
1000	28

The Platinum Resistance Pyrometer

This method of measuring temperatures is based on the variable resistance of a definite amount of pure platinum wire with temperature, which variation of resistance follows definite laws. Since *electric resistance* can be measured very accurately with comparative ease, the method affords a ready means of measuring temperature.

Laws[1] Relating the Resistance of Pt to Temperature. — Let R_0 = the resistance of a particular piece of *Pt* wire at 0° C.

Let R_1 = the resistance of the same piece of *Pt* wire at 100° C.

Let R = the resistance of the same piece of *Pt* wire at T° C. (Gas scale.)

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[1] Callender and Griffiths, Phil. Trans. Royal Soc., 1892, p. 119.

Let pt = the temperature on the Pt scale of temperature = to $T°$ on the gas scale of temperatures.

Then assuming that the resistance varies proportionately to the temperature, we have

$R - R_o$ = the resistance at $T°$ or pt (platinum scale).
$R_1 - R_o$ = the resistance at 100° (on both scales).

From which follows:

$$a. \quad (R - R_o) : pt = (R_1 - R_o) : 100 \text{ or } pt = 100 \frac{(R - R_o)}{(R_1 - R_o)}$$

The value of pt depends upon the purity of the platinum.

From experimental work, Callender and Griffiths have shown that the following relation exists between the platinum scale and the air pyrometer scale up to 600° C., and later by Harker,[1] up to 1000° C. and somewhat above.

$$b. \quad d = T - pt = \delta\left(\left\{\frac{T}{100}\right\}^2 - \frac{T}{100}\right)$$

The value of δ depends upon the purity of the platinum; d indicates the difference between the air and platinum scales. From the above formula is deduced the following:

$$1. \quad T = pt + \delta\left(\left\{\frac{T}{100}\right\}^2 - \frac{T}{100}\right) \text{ or}$$

$$2. \quad T = \left(\frac{5000}{\delta} + 50\right) - \sqrt{\left\{\frac{5000}{\delta} + 50\right\}^2 - \frac{10000\, pt}{\delta}}$$

From this equation (2) a table may be calculated giving the value of "pt" in terms of T, and from this a curve may be plotted with $(T - pt)$ in terms of T, abscissæ, and pt as ordinate. This will at once give $d = (T - pt)$, which must be added to "pt," the platinum temperature, in order to get T, or the reading on the normal gas scale, as shown in Fig. 55.

The value of δ for any given pyrometer may be determined with ample accuracy by standardizing the instrument against a known point, usually boiling sulphur, 444.5° C. at 760 mm. pressure, and substituting this value of T and the observed value of "pt" corresponding to T in formula b, and calculating δ. The value of δ can also be checked by making another similar determination as above, with silver as the fixed point. (See remarks about silver under the thermo-couple.)

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[1] Proc. Royal Soc., Vol. LXXIII (1904), p. 217.

The denominator in equation *a*, $(R_1 - R_0)$ is known as the "*fundamental interval*" of the resistance pyrometer and is expressed in ohms.

The "*fundamental coefficient*" expressed by the letter C is the mean temperature coefficient of change of resistance between zero degrees and 100° C., and is expressed as follows:

$$C = \frac{R_{100} - R_0}{R_0 \times 100}$$

From what has gone before it is evident that the platinum temperature scale is expressed in terms of electric resistance. If now the platinum pyrometer be so constructed that the increase in resistance of the coil of platinum wire acting as the pyrometer be of such diameter and length that the increase of resistance between zero degrees and 100° C. (fundamental interval) be just one ohm, then 0.01 ohm will be equal to one platinum degree, and a special Wheatstone bridge apparatus may be designed so as to measure in units of 0.01 ohm and thus record platinum degrees directly. It is evident that the resistance measuring apparatus need not be calibrated to measure absolutely standard ohms, since all that is necessary is to have the "fundamental interval"

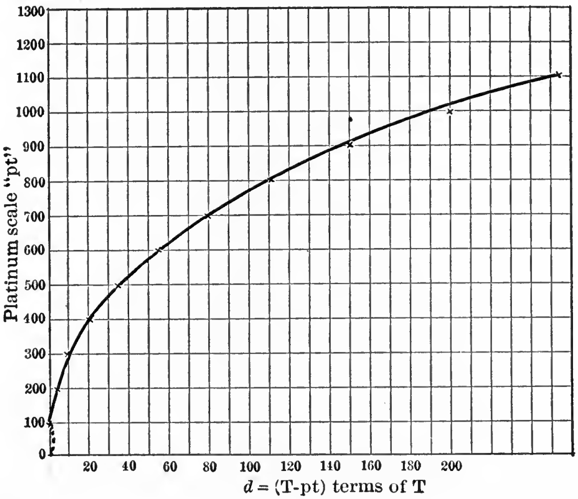

FIG. 55.—Curve relating the gas scale to the platinum scale.

a certain definite resistance and then take for units one hundredth part of this. It is, however, essential to have the various resistance coils of the instrument and the calibrated wire of the bridge standardized in terms of the "fundamental interval" so that the various resistances are strictly comparable.

A formula relating directly the temperature T and resistance R of any given piece of platinum wire is

$$\frac{R}{R_0} = 1 + aT + bT^2, \text{ or } R = R_0\,(1 + aT + bT^2)$$

In this formula, $a = C\left(1 + \frac{\delta}{100}\right)$, and $b = \frac{-C\,\delta}{10000}$

In order to solve the equation, resistances of the wire at zero degrees C. and at 100° C., viz., at melting ice and boiling water, must be known, so as to be able to calculate the "fundamental coefficient" C, and the value of δ.

Design of the Pyrometer. — The electric resistance pyrometer is due to Werner von Siemens,[1] who first proposed it in 1871. Its development as an accurate scientific instrument is largely due to Callender and Griffiths.

The main consideration in the platinum resistance pyrometer is to keep the resistance of the platinum constant. It is found that heating platinum in the presence of silica, or clay, or iron, or directly in furnace gases, or in presence of hydrogen, particularly when SiO_2 is also present, causes very great changes in the electric resistance, so as to practically make the instrument worthless. Heating above 1200 °C. causes a slight volatilization of the platinum, which increases the resistance of very fine wires. It is found that when the platinum wire is wound around a spool of pure mica, formed by two strips of mica set crosswise, and enclosed in a porcelain tube, that the resistance of the coil undergoes no change and may be used an indefinite number of times with concordant results. Fig. 56 shows the construction of platinum resistance pyrometers. A coil of platinum wire, usually from 0.10 to 0.3 mm. diameter of wire and of certain length (the coil should not be more than 1 to 1.5 in. long in most cases, *so as to localize the temperature it measures*), is wound on mica plates, and connected by its terminals by "autogene" junctions to heavy copper or platinum leads (these latter preferred),

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[1] W. Siemens, Proc. Royal Soc., Vol. XIX (1871), p. 351.

insulated from each other by thin fire-clay tubes, and passing out to binding posts on the handle of the instrument as shown in Fig. 56. The whole is protected by a porcelain tube, which may be enclosed in an iron tube.

Since the temperature is measured by the increase in resistance of the platinum coil only, and the instrument is immersed in the furnace in such a manner that parts of the conducting leads, through which the current enters and leaves the coil, are also heated and thus increase in resistance, the instrument is provided with "compensating leads" of the same size as the "conducting leads," and extending down as far as the top of the coil. These "compensating leads" are eventually connected with the Wheatstone bridge which measures the resistance, but to the opposite

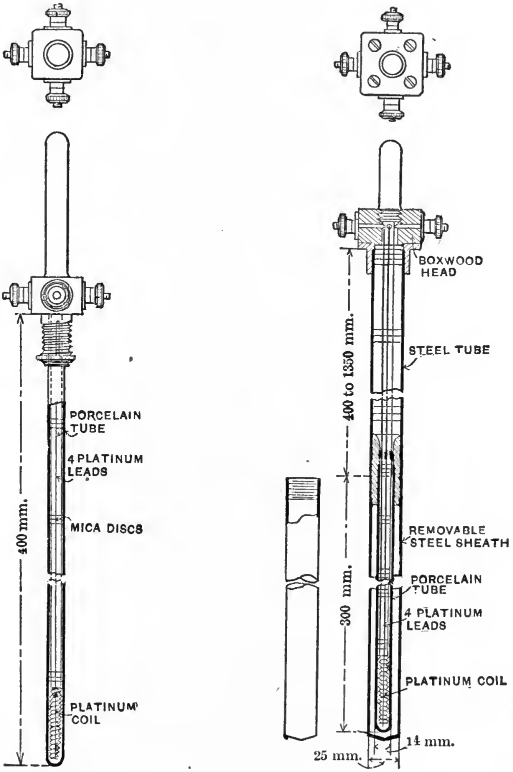

Fig. 56. — Platinum resistance pyrometers.

arm from that to which the leads from the platinum coil are connected, so that the two resistances, the "conducting leads" from the *top* of the coil to the Wheatstone bridge and the compensating leads from the top of the coil to the bridge, are just equal and therefore balance each other, the bridge then measuring only the resistance of the platinum coil. Fig. 57 showing a diagrammatic sketch of the set-up will make this explanation plain. The platinum conductors leading from the resistance coil and carrying the current of the battery to the coil are connected to one arm of the Wheatstone bridge apparatus by heavy copper leads, and in the same way the "compensating leads" are connected to the

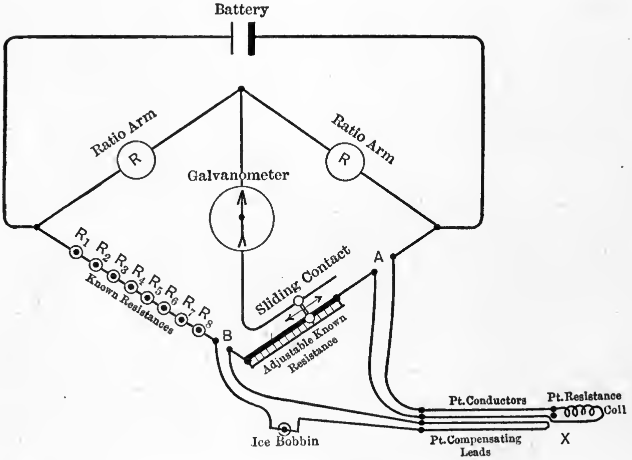

FIG. 57. — Diagrammatic sketch of platinum resistance pyrometer set-up.

opposite arm of the bridge, the conditions being that the total resistance of the circuits from X to A and from X to B are exactly equal. The "ice bobbin" is a spool of manganin wire inserted into the compensating leads as shown, and is of such resistance as to just equal the resistance of the platinum resistance coil at zero degrees C. It is therefore evident that the resistance of the two circuits leading from the instrument (pyrometer) are equivalent. If now the platinum resistance coil be exposed to the source of temperature and the battery current turned into the system by throwing a suitable switch and the "ratio arms" of the Wheatstone bridge are of equal resistance, the increased resistance of the platinum resistance coil due to temperature can be measured by adjusting the various known resistances, including the sliding contact, until the galvanometer shows zero reading. If the Wheatstone bridge is calibrated in platinum degrees as explained, and the "ice bobbin" is used, the reading will be the temperature of the coil above zero degrees C. in platinum degrees, which can then be converted to degrees on the standard gas scale by means of the formula. If no "ice bobbin" is used, it will be necessary to determine the resistance of the coil at zero degrees C. (in melting ice) on the bridge and then subtract this constant from all readings of temperature in platinum degrees. When temperatures below zero degrees C. are to be determined, it will be necessary to omit the "ice bobbin," determine the resistance of the coil at zero degrees C., set this resistance, then immerse the instrument in the source of temperature, adjust the galvanometer to zero again by adjusting resistances, and subtract the last reading from the reading at zero. The difference will give the temperature below zero in platinum degrees, which can be converted as stated. Fig. 58 shows a complete set-up of apparatus for the determination of temperature by the platinum resistance pyrometer.

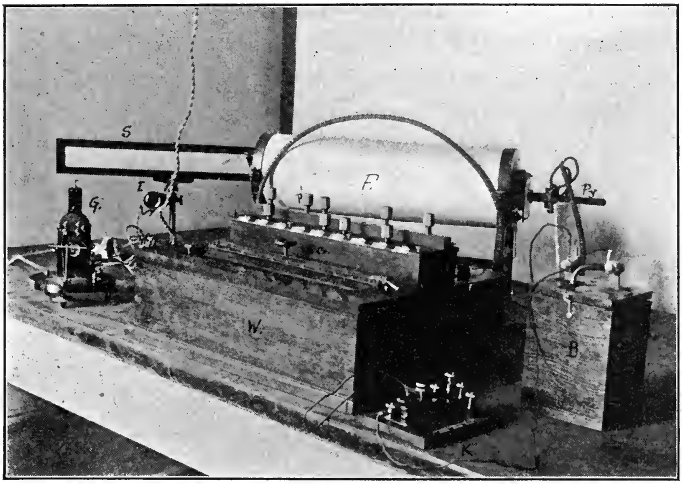

Fig. 58. — Set-up of platinum resistance pyrometer. *Py* is the pyrometer in electric furnace, *F*; *W* is Wheatstone Bridge, *G* is the reflecting galvanometer, *B* is the battery.

The pyrometer in this instance has a "fundamental interval" of 1.0005 ohms, the resistance at zero degrees C. = R_0 is 2.712 ohms, and the difference coefficient = δ = 1.50. This value is practically that for very pure platinum.

The Wheatstone bridge used is of special form for high accuracy of the Callendar and Griffiths design. All of the resistances are immersed in an oil bath to avoid any correction for "temperature coefficient" of the resistances, although these are of manganin wire, except the "bridge wire," which is of platinum silver. By means of this bridge, platinum temperatures can be measured to 0.01 C.

THE FÉRY RADIATION PYROMETER

The principle of this pyrometer is based on the Stefan-Boltzman radiation law, viz., that the total energy radiated by a "black body" is proportional to the fourth power of its absolute temperature, or, $E = K(T^4 - T_0^4)$, in which E is the total energy radiated by the body at T to a precisely similar body at T_0, and K is a constant dependent upon the units used. A brief consideration of some of the principles of radiation is essential to the following discussion.

The amount of radiant energy emitted by a unit of surface of a body per unit of time for any given temperature measures the intensity of radiation at that temperature, and is called the *emissivity* of that body. This emissivity varies with the temperature, but also with the nature of the surface of the body, so that different bodies at the same temperature do not emit necessarily the same total amount of energy per unit of surface. In other words, the emissivity of the bodies for the same temperature is different. If a body be considered which from its nature is capable of absorbing all radiant energy thrown upon it without *reflecting* any portion of it or *transmitting* another portion, it is called a *black body.*

The emissivity of a "black body" for any given temperature is unity; the emissivity of any body not a "black body" is always less than unity. But if we add to its emissivity its reflective and transmissive powers their sum will be equal to unity. It follows from the above that if we have a "black body" at a certain constant temperature, receiving upon it a given quantity of energy per unit of time, it must radiate the same amount of energy per unit of time in order that the temperature may remain constant. Theoretic "black body" conditions are very closely realized by such things as glowing solid coal, hot solid iron covered with oxide, hot solid copper under the same conditions, etc. Molten iron and molten copper, however, differ widely from "black body" conditions. It has been demonstrated that while the emissivity of solid iron covered with oxide is practically unity, that of molten iron is but 0.28 and molten copper but 0.14.[1]

Such substances as polished silver, platinum, or magnesia, all have emissivities much less than that of a "black body." "Black body" conditions are also realized by the interior of an enclosed space coated on the inside with lampblack and uniformly heated by any suitable means. The interior of this space will radiate through any suitable opening in it, according to the laws of "black bodies," viz., according to that of the Stefan-Boltzman law already mentioned. In practice, this "black body" condition is realized by the interior of muffles, furnaces, kilns, etc. Furthermore, any body placed within such an enclosed space essentially becomes a "black body" as regards its radiating powers after it has assumed the temperature of a space within which it is.

It is a well-known fact that temperatures are roughly judged by the nature of the light emitted by an incandescent body. This method, however, is correct only when the incandescent body is under "black body" conditions, viz., is within a uniformly heated space, such as a furnace, etc. The nature of the radiant energy emitted by bodies not black for any given temperature varies with different bodies. Thus, in the total energy emitted by one body at a given temperature there may be much more light radiations than in those emitted by another and different body at the same temperature. If we thus judge the temperature of the body by the eye according to the light emitted, we would assign a much higher value to the temperature of the second than to the first body, but wrongly so. As already stated, the total radiation (heat and light radiations, etc.) from a "black body" or a body under "black body" conditions, is strictly a function of its temperature, so that if an instrument is available for measuring the intensity of total radiation from a substance under "black body" conditions, a very accurate estimation can be made of its temperature. The chief difficulty with an instrument of this

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[1] C. B. Thwing, "Physical Review," February, 1908.

type is the realization of the "black body" conditions. As already stated, if such an instrument were sighted upon a mass of molten iron in a ladle standing in the open air, its indications would be far from giving the correct temperature of this molten iron, for the reason stated. If, however, this molten iron be within a furnace and be sighted on through a suitable opening in the furnace, the correct temperature can be determined. The instrument thus gives what is termed the "black body temperature," which may be the true temperature if the body be under "black body" conditions. It is therefore seen that the instrument is to be used with caution and its readings interpreted accordingly.

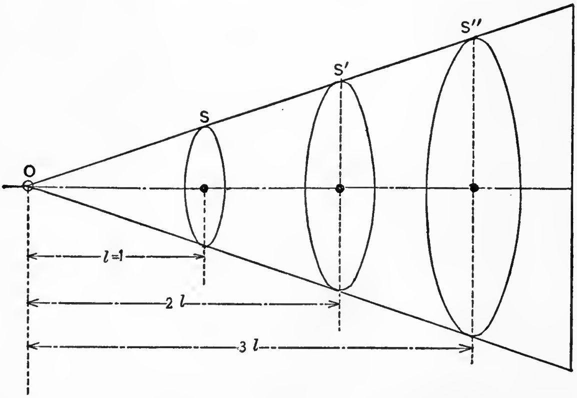

FIG. 59. — Diagram showing distribution of radiant energy.

Theory of the Total Radiation Pyrometer. — Let O be a source of radiant energy and let S be a unit surface at unit distance l, receiving a quantity of radiant energy q. Then in the above figure S is to S' as l^2 is to $(2l)^2$, or

$$\frac{S}{S'} = \frac{l^2}{(2l)^2} \text{ or } \frac{S}{S^1} = \frac{1}{4} \text{ or } S' = 4\,S$$

The amount of radiant energy on S' is the same as on S, therefore a unit surface on S' receives one-fourth of the radiant energy as the unit surface at S. The radiant energy therefore varies inversely as the square of the distance.

Considering now a concave mirror M receiving radiant energy[1]

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[1] The discussion which follows is strictly valid only when the object radiating energy is at a distance from the mirror, which is large as compared with the focal distance of the mirror.

(total) q' from the radiating source at S, the focus of the mirror being at l distance from S, it will form an image of S at I, whose area is indicated by S'. All the energy received by the mirror M is then concentrated in the image I and the intensity of energy in the image will be expressed by the quantity $\frac{q'}{S'}$. If now the focus of the mirror is removed to a distance $2\,l$ from the source of radiant energy, and the image focused at I', its size will be S'' and, according to the laws of optics, I' will be one-fourth the size of I, since the area of the image varies inversely as the square of the distance of the object from the focus. The mirror in its new position M' will receive one-fourth the radiant energy that it did at M and this energy will be concentrated in the image I'. If q'' is the amount of radiant energy that the mirror receives at M', and S'' the size of the image, then the intensity of energy in the image is $\frac{q''}{S''}$, but as $q'' = \frac{q'}{4}$ and $S'' = \frac{S'}{4}$, we have, substituting, $\frac{q''}{S''} = \frac{q'}{4} \times \frac{4}{S'} = \frac{q'}{S'}$, or the intensity of energy in either case is the same. If now a means is provided for measuring the intensity of energy in the image of the mirror, we can determine the temperature of the source S from the Stefan-Boltzman radiation law, provided we first standardize the instrument containing the mirror against a known temperature. The intensity of the energy will be measured by a sensitive thermo-couple placed in the focused image and completely covered by it; in fact the image must overlap the junction

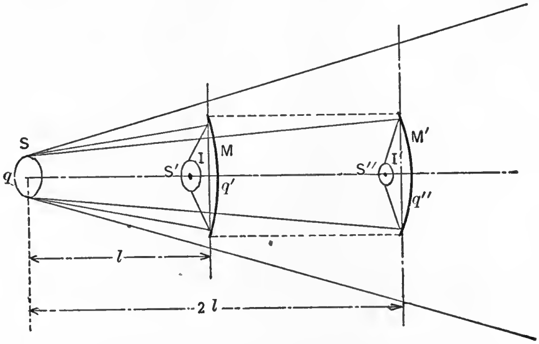

FIG. 60. — Diagram of mirrors receiving radiant energy.

of the couple, since we are measuring the effect of intensity of the energy in the image. If the junction be sufficiently small, there will be no difficulty in doing this with the instrument within any reasonable distance from the radiating object.

The thermo-couple will be connected by leads to a sensitive high-resistance galvanometer, and when the instrument containing the mirror is now focused upon the source of energy in such a way as to fulfil the above conditions, the temperature set up in the image by the intensity of radiations received from the source S will cause an e.m.f. in the couple which will cause a current to flow through the circuit of the couple and give rise to a definite deflection of the galvanometer needle, which will be called R. Let it be supposed that the temperature of the source S be known, in this instance, for the purpose of calibration, it having been measured say by means of a thermo-couple or a resistance pyrometer and expressed in the *gas scale* as T_1.

We have now the Stefan-Boltzman law: $E = K\ (T^4 - T_0^4)$ in which T is the absolute temperature of the source S; T_0, the absolute temperature of the receiving surface, the mirror; and E the intensity of energy of radiation of the source. K = constant dependent upon the units used.

In this particular instance of calibration let T be the known temperature T_1, and let the intensity of energy in the focus of the mirror cause a galvanometer deflection of R. Then we can say

1. $E_1 = R_1 = K\ (T_1^4 - T_0^4)$

and for another case at a higher temperature T_2, but unknown

2. $E_{''} = R_{''} = K\ (T_2^4 - T_0^4)$

and since for ordinary accuracy the absolute temperature of the receiving source, the mirror, is negligible, we have

$$E_1 = R_1 = K\ (T_1^4) \qquad \text{or } R_1 = K\ (T_1^4)$$
$$E_{''} = R_{''} = K\ (T_2^4) \qquad R_{''} = K\ (T_2^4)$$

or $$K = \frac{T_1^4}{R_1} \text{ and } K = \frac{T_2^4}{R_{''}} \quad \text{or} \quad \frac{T_1^4}{R_1} = \frac{T_2^4}{R_{''}}$$

or $$T_2^4 = T_1^4 \times \frac{R_{''}}{R_1} \text{ or } T_2 = T_1\sqrt[4]{\frac{R_{''}}{R_1}} \qquad (3).$$

Then as R_1 and T_1 are known values, as is also $R_{''}$, by observation of the galvanometer the temperature T_2 can be calculated. In this manner the scale of the galvanometer can be so constructed as to indicate directly the temperature of the radiating source, and temperatures read off directly from the galvanometer deflections. In considering the instrument, the following facts must be taken into consideration:

1. It has been shown that the indications of the instrument are independent of distance as long as it is possible to have the focused image of the incandescent object, formed by the mirror, overlap to some extent the thermo-couple junction, so that this will fully measure the intensity of the radiations.

2. That the intensity of radiations are measured by a suitable thermo-couple, and since the e.m.f. of a thermo-couple is a function of the difference in temperature of the two junctions, hot and cold, as shown previously in this chapter, the galvanometer deflection will be that due to the difference in temperature between that of the hot junction and that of the "cold junction" (in this case the galvanometer at room temperature), but this difference is exactly the increase of temperature of the hot junction in the image due to the radiant energy received, which is the temperature it is desired to measure. For this reason there are no "cold junction" factors to be considered in this instance, provided that before use there is no difference in temperature between the telescope and the galvanometer. The temperature of the image is rarely more than 80° C. above the room temperature.

3. The mirror of the instrument may be replaced by a suitable lense, as is done in the laboratory form of the instrument. This lense must fulfil the condition that the ratio of radiation transmitted to those absorbed be constant, in order that the instrument may obey Stefan's law. Fluorite is a suitable material in this sense for radiations above 900° C. The amount of radiant energy received by the lense or mirror and brought to focus in the image is dependent upon the diameter of the opening of the telescope. With this factor fixed, a certain temperature of the incandescent source causes a given deflection of the galvanometer. With high temperatures the scale of the galvanometer will have insufficient length to record the deflection. This difficulty may be obviated by providing the opening of the telescope with a shutter provided with a diaphragm as shown in Fig. 62, so that the amount of radiations reaching the mirror may be regulated. It is readily deduced from what has gone before that the intensity of radiations in the image will be directly proportional to the area

of the opening. The instrument may be calibrated with any given size opening and a second scale established on the galvanometer. Instead of reducing the size of opening of the telescope, recourse may be had to placing the galvanometer on a shunt of known resistance (thus decreasing the current in this part of the circuit and reducing the galvanometer deflection) in the circuit, instead

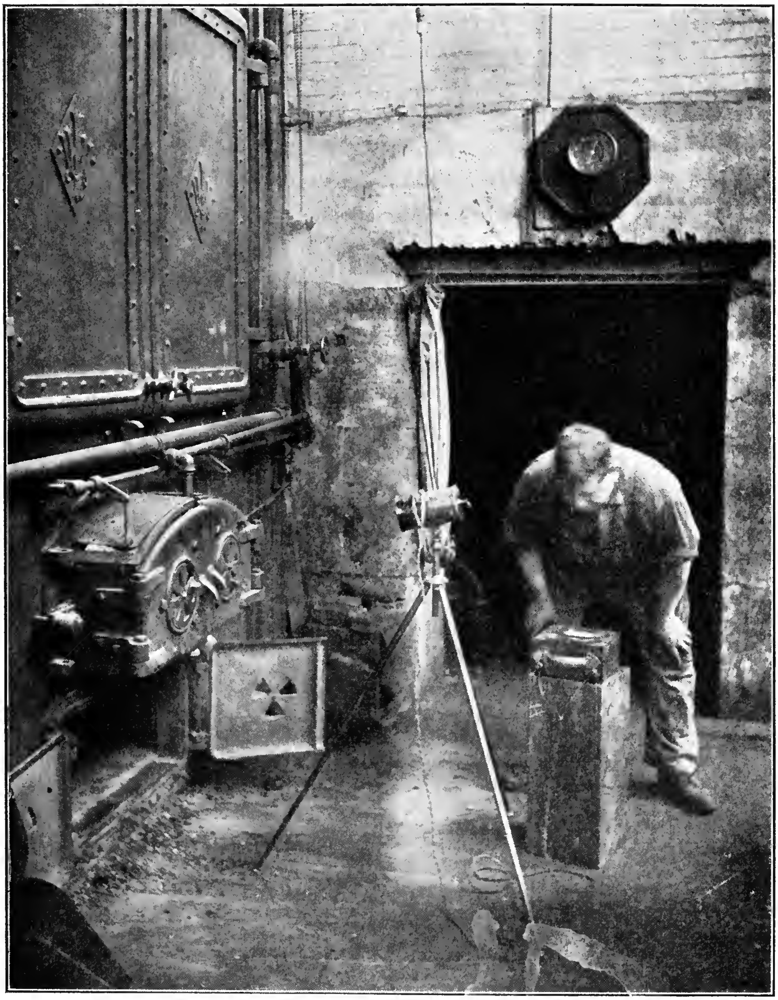

FIG. 61. — Féry pyrometer set up for an observation.

of directly in series, and thus establishing a second scale for the higher temperatures.

Fig. 61 shows the instrument set up for an observation.

In Fig. 62 is shown the telescope, within which on a rack and pinion is fixed the concave mirror *M* with an opening through the center. The rack and pinion device is operated by the thumb screw *p*, by which means the image of the incandescent object is focused upon the junction of a copper konstantan thermo-couple at *X* in the optic axis of the telescope. The junction of this thermo-couple, which is but a few thousandths of a millimeter wide, is in the form of a cross and is soldered to a silver disc. The two wires of the thermo-couple are attached to two brass strips, *D* and *R*, which lead to the insulated terminals *b* and *b′*. These terminals connect by leads with the galvanometer. Two *small mirrors* placed close to the couple reflect the *image* of the incandescent object formed by the concave mirror, to the eye piece *O*, and are arranged in such a way as to split the field of view into an upper and lower half which conform only when a focus has been reached. When focused, the junction of the couple which appears as a black disc in the center of the field is overlapped by the conformed halves of the image. *B* shows the front of the telescope with the shutter up and *A* the telescope with the shutter down. The galvanometer employed is a sensitive one of the D'Arsonval type, similar to that used in the galvanometric work with thermo-couples, as already described. It is graduated with special temperature scales, derived in the

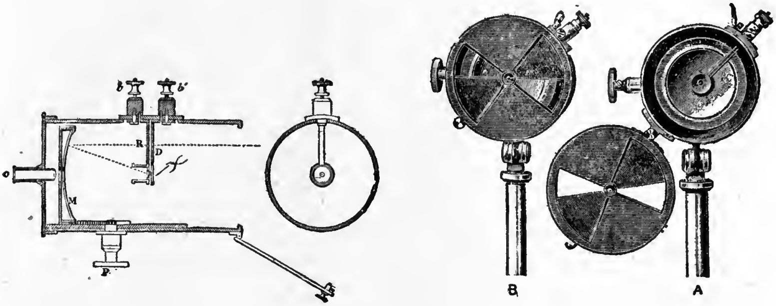

FIG. 62. — Construction of the Féry radiation pyrometer *B*, *A*, diaphragm for reducing the aperture of the telescope.

manner outlined under the discussion of the theory of the radiation pyrometer.[1]

Fusing-Point Pyrometry. Fusible Seger Cones. — The idea of determining temperatures by means of the melting-points of metals and alloys is an old one. The application of metals to this purpose, however, is limited, as in most instances the conditions of use would specify a non-oxidizable metal, in order to be certain of an unchanging melting-point. The unoxidizable metals, platinum, gold, palladium, silver, are much too costly for ordinary use. Most *alloys* also have no definite melting-point, but melt through a temperature interval, as has been fully explained in Chapters II and IV. For these reasons, metals and alloys are not in use for temperature determinations at the present day. Certain definite chemical salts could be well employed for this purpose as many are very stable and have very definite melting-points. Mixtures of two salts (except the eutectic ratio) suffer from the same objection as alloys by melting in many cases through a temperature interval.

The only fusing-point pyrometers in constant use are the "Seger cones," made of mixtures of either silica, or boric acid, or both, and the bases, soda, potash, lime, alumina, and ferric oxide. The original Seger cones were made of mixtures containing various proportions of quartz sand, feldspar, carbonate of lime, and kaolin as pure as procurable. The Seger cone mixtures do not possess a definite fusing-point, but soften, then bend, and finally melt into a liquid. It is therefore essential to define a certain softening and bending of the cone as corresponding to a given temperature. The "cones" are made in the form of triangular pyramids 50 mm. high, with a side of the base triangle 15 mm. long, and have a number, corresponding to a certain melting-point, stamped on one side, near the base. When the cones bend under the influence of heat, this number usually remains uppermost so that it can be identified. In the accompanying table the temperature assigned to each cone corresponds to that necessary to bend over the cone so that its tip will practically touch its base. However, the manner and rapidity of heating have their influence on the bending of the cone as well as the temperature, and the figures given are those for slow heating. In

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[1] See Principle and Operation of Féry Radiation Pyrometer, C. H. Wilson and Fred Maeulin, S. of M. Quat., Vol. XXVIII, p. 353.

determining temperatures with the Seger cones, the method used is to place a number of the cones, of successive melting-points, fastened by clay to a fire-clay tablet, into the furnace, where those cones with a lower melting-point than the temperature of the furnace will melt down, while those of the higher melting-point will remain unaltered. That cone which is bent in the manner described above indicates the highest temperature reached. The cones listed in the accompanying table, up to number 7, are calibrated against the platinum-rhodium thermo-couple and are made from certain feldspars and kaolin. If cones are made of local material, it may be necessary to recalibrate, as small amounts of impurities, or small changes in composition, especially in the alkalies, will quite materially alter the melting-points.

It is evident from the foregoing that temperature determinations carried out by means of Seger cones are approximate only. The method in many cases furnishes a rapid and cheap way of temperature measurement which in individual cases may answer fully as well as more expensive and elaborate methods.

Table XXVI. Seger Cones[1]

No. of Cone	Composition	Melting-point C°
022	0.5 Na_2O, 0.5 PbO, 2.0 SiO_2, 1.0 B_2O_3	590
021	“ “ 0.10 Al_2O_3, 2.2 “ “	620
020	“ “ 0.20 “ 2.4 “ “	650
019	“ “ 0.30 “ 2.6 “ “	680
018	“ “ 0.40 “ 2.8 “ “	710
017	“ “ 0.50 “ 3.0 “ “	740
016	“ “ 0.55 “ 3.1 “ “	770
015	“ “ 0.60 “ 3.2 “ “	800
014	“ “ 0.65 “ 3.3 “ “	830
013	“ “ 0.70 “ 3.4 “ “	860
012	“ “ 0.75 “ 3.5 “ “	890
011	“ “ 0.80 “ 3.6 “ “	920
010	0.3 K_2O, 0.7 CaO, 0.20 Fe_2O_3, 0.30 Al_2O_3, 3.5 “ 0.50 “	950
09	“ “ “ “ 3.55 “ 0.45 “	970
08	“ “ “ “ 3.60 “ 0.40 “	990
07	“ “ “ “ 3.65 “ 0.35 “	1010
06	“ “ “ “ 3.70 “ 0.30 “	1030
05	“ “ “ “ 3.75 “ 0.25 “	1050
04	“ “ “ “ 3.80 “ 0.20 “	1070
03	“ “ “ “ 3.85 “ 0.15 “	1090
02	“ “ “ “ 3.90 “ 0.10 “	1110
01	“ “ “ “ 3.95 “ 0.05 “	1130

TABLE XXVI SEGER CONES[1] (*Continued*)

No. of Cone	Composition					Melting-point °C.
1	0.3 K_2O,	0.7 CaO,	0.20 Fe_2O_3,	0.30 Al_2O_3,	4 SiO_2	1150
2	"	"	0.10 "	0.40 "	4 "	1170
3	"	"	0.05 "	0.45 "	4 "	1190
4	"	"	0.5 "		4 "	1210
5	"	"	0.5 "		5 "	1230
6	"	"	0.6 "		6 "	1250
7	"	"	0.7 "		7 "	1270
8	0.3 K_2O,	0.7 CaO,	0.8 Al_2O_3,		8 SiO_2	1290
9	"	"	0.9 "		9 "	1310
10	"	"	1.0 "		10 "	1330
11	"	"	1.2 "		12 "	1350
12	"	"	1.4 "		14 "	1370
13	"	"	1.6 "		16 "	1390
14	"	"	1.8 "		18 "	1410
15	"	"	2.1 "		21 "	1430
16	"	"	2.4 "		24 "	1450
17	"	"	2.7 "		27 "	1470
18	"	"	3.1 "		31 "	1490
19	"	"	3.5 "		35 "	1510
20	"	"	3.9 "		39 "	1530
21	"	"	4.4 "		44 "	1550
22	"	"	4.9 "		49 "	1570
23	"	"	5.4 "		54 "	1590
24	"	"	6.0 "		60 "	1610
25	"	"	6.6 "		66 "	1630
26	"	"	7.2 "		72 "	1650
27	"	"	20 "		200 "	1670
28			1 "		10 "	1690
29			1 "		8 "	1710
30			1 "		6 "	1730
31			1 "		5 "	1750
32			1 "		4 "	1770
33			1 "		3 "	1790
34			1 "		2.5 "	1810
35			1 "		2 "	1830
36			1 "		1.5 "	1850

These cones can be procured from Prof. Ed. Orton, Department of Ceramics, Ohio State University, Columbus, Ohio; and from Eimer and Amend, 3d Ave. and 18th St., New York.

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[1] Hecht, Ton Industrie Zeit., 1885, etc.

A Comparison of the Various Forms of Pyrometer Described. — The methods of pyrometry described in the foregoing pages are essentially the chief ones used both in the laboratory for scientific investigation and in the works as industrial instruments. The other methods outlined briefly at the beginning of this chapter are but rarely used, with the exception of some of the forms of optical radiation pyrometers, of which a number of good instruments exist, such as the Wanner pyrometer, that of Mesure & Noel, and that of LeChatelier, and others. These instruments, however, possess certain very definite disadvantages, so that it requires considerable scientific skill to get results of which the operator can be certain. They are used to a considerable extent in the laboratory but practically not at all in practice.[1]

The most accurate method of measuring high temperatures is that using the resistance of platinum. It is coming rather widely into use in an industrial form for measuring temperatures up to 1000° C. The highest limit to which it can be safely used, as already outlined, is about 1200° C. It serves excellently to determine ordinary furnace temperatures, temperature of hot blast, temperature of gases in flues, for which latter purpose it can be arranged as shown in Fig. 63, so that the temperature read will be practically an integration of that existing over the area, giving the average temperature of any given cross-section of the flue and not merely the temperature of some small localized area. In the laboratory the method serves very well for extremely accurate measurements of temperature, such as the temperature of the recalescence of steel, the temperature in roasting experiments, etc. As the temperature is measured by the increase of electrical resistance of a coil of platinum wire, which occupies an appreciable space, it is evident that this method does not serve as well as the thermo-electric method, for the determination of temperatures closely localized, such as the condition existing in the determination of the melting-points of alloys or metals. Furthermore, the resistance pyrometer must always be protected by suitable tubing, no matter what conditions are, since the wire

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[1] For a description of optical pyrometers and the principles upon which they are based, reference is made to High Temperature Measurements by LeChatelier, Boudouard and Burgess, 1907, chapter on the "Optical Pyrometer," and to "Optical Pyrometry" by C. W. Waidner and G. K. Burgess, Bul. Bureau of Standards, Washington, Vol. I, No. 2, p. 189.

and frame upon which it is wound are very delicate. The thermo-couple in many cases can be used without protection, and even though it is used with protecting tube, this in most cases can be very much smaller than that used in the resistance pyrometer; for this reason — the "lag" of the resistance pyrometer is in many cases greater than that of the thermo-couple, the lag of the pyrometer being the time interval between the occurrence of a given temperature at a point and its indication by the recording instrument. It is evident that, considering a pyrometer which has a decided lag, immersed in an alloy which is cooling and freezing, that the temperature indicated by the recorder will not be that of the pyrometer immersed in the metal, but a higher temperature, the difference being due to the lag, this lag being a function principally of the conductivity of the protecting tube of the pyrometer.

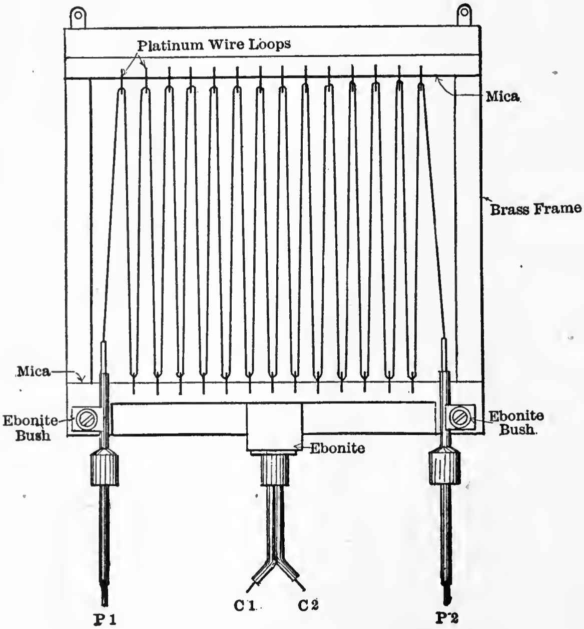

FIG. 63. — Integration frame for platinum resistance pyrometer.

When temperatures above 1200° C. are to be measured, the only two methods applicable are, first, that of the thermo-couple, and second, that of the Féry radiation pyrometer, or some form of optical pyrometer. The thermo-electric method, using the platinum-rhodium or the platinum-iridium thermo-couples, have been developed into very sensitive and accurate methods, which are widely used for scientific investigations and industrial practice. The method is readily adaptable to temperatures ranging between about 300° to 1600° C., a range within which practically all metallurgic or industrial operations fall. Certain base metals are also used for thermo-couples. The application, however, of base metal couples is rather limited, in so far as their accuracy can in no way approach that of the platinum alloys for the measurement of temperatures above 600° C. They serve very well for the indication of rather low temperatures for industrial purposes. The Féry radiation pyrometer is a very convenient instrument when temperatures are to be determined which range between 600° and upward, there being practically no upper limit, and where it is not convenient to insert a resistance of thermo-couple pyrometer into the source of heat. The application of the Féry radiation pyrometer, however, is limited by the fact that it indicates correctly only the temperature of those bodies which are under "black body" conditions, as already discussed under the description of this instrument. As these "black body" conditions are at times difficult to realize, the accuracy of the instrument of course in no way compares with that of the resistance pyrometer or of the thermo-couple. It serves, however, in many cases extremely well to readily indicate temperatures which could otherwise either be not measured at all or be measured under very great difficulties. Seger cones are used at times for the determination of approximate temperatures as described, especially in glass and pottery works.

Continuous Automatic Recorders.—Under certain conditions it is desirable to obtain a continuous record of the temperature, both in scientific laboratory work and in industrial work. It may be necessary to have a complete and continuous record of the cooling of a substance, or the continuous record of furnace temperatures to show the maximum and minimum temperatures which have occurred and the time of their occurrence. There are a number of continuous recorders that are satisfactory and which may be adapted to the thermo-couple, platinum resistance, or total radiation pyrometer.

Fig. 64 shows the thread recorder made by the Cambridge

Scientific Instrument Company.[1] The instrument is essentially a delicate recording galvanometer, so arranged as to give a series of records of the instantaneous deflections of a galvanometer pointer. The method employed for producing these records has the advantage of producing continuously visible records, while avoiding pen-friction. Fig. 65 is a diagram showing the essential parts of the recorder. A is a galvanometer pointer turning about its axis *B*, and overhanging a drum *C*. Between the pointer *A* and the drum *C* an inked thread *G* is stretched parallel to the axis of the drum, and at a short distance above its surface. A

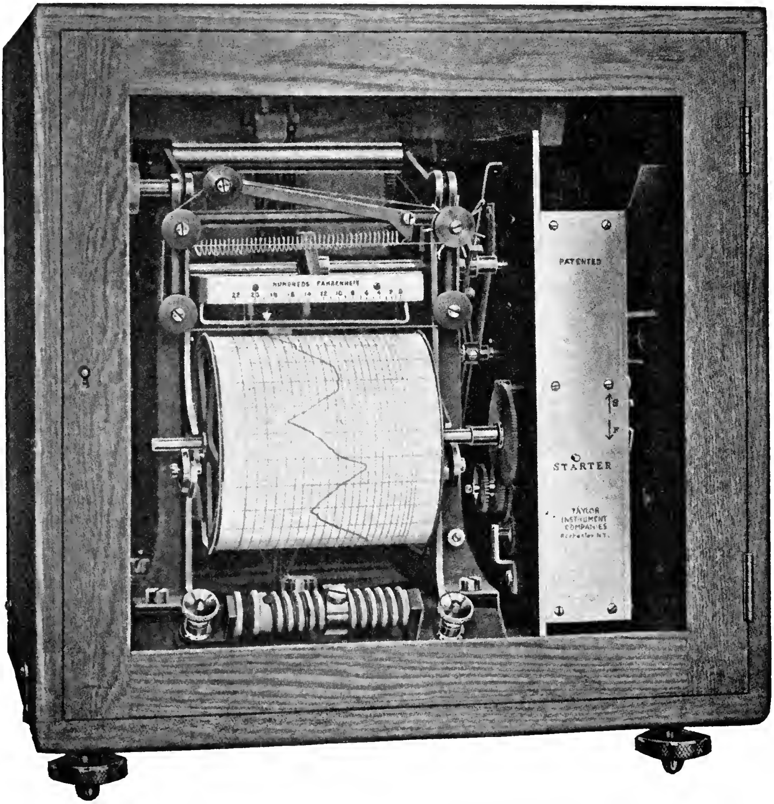

FIG. 64. — Thread recorder for a continuous record of temperature, with the thermo-couple — resistance or radiation pyrometer.

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[1] Taylor Instrument Companies, Rochester, N. Y.

presser-bar *D* is situated above the galvanometer pointer, and this bar is normally held free of the pointer by means of a cam *E*, and its follower *F*. At regular intervals the cam *E* makes a half-revolution, allowing the presser-bar *D* to fall upon the pointer *A* and then raising it again to its normal height.

As the presser-bar falls, it depresses the pointer on to the drum, nipping the inked thread between the pointer and the paper. The pointer end has an ivory knife-edge on its under side, which produces a dot upon the paper at the point of the intersection of the pointer and the thread, thus making a visible record of the instantaneous deflection of the galvanometer. The galvanometer pointer is hinged so that it can be depressed without bending the suspension. In the intervals between the production of the dots the galvanometer is, of course, free to take up its true deflection without frictional errors. As the dot is always produced where the thread and the pointer intersect, it will be obvious that by suitable arrangements of the galvanometer coefficient, paper with rectangular co-ordinates of uniform scale can be used.

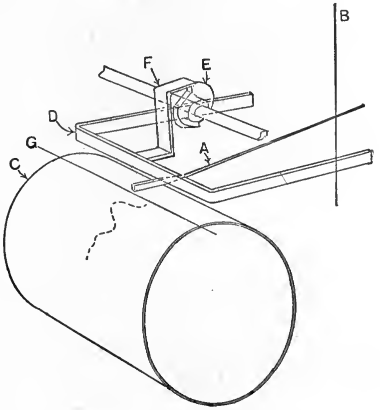

Fig. 65. — Essential parts of the thread recorder.

Fig. 66 shows the Leeds-Northrup continuous automatic recorder for use in connection with the platinum resistance pyrometer. This operates on a different principle from the thread recorder, being essentially an automatic Wheatstone bridge. As the resistance in the platinum pyrometer varies with either a rise or fall of temperature of the furnace, the balance of the bridge in the recorder is disturbed, and the unbalanced current acting on a galvanometer actuates the needle of this, which automatically adjusts resistances in the bridge to bring about again a balance. The pen which makes the record is moved by electro-magnetic means, during the time the bridge is out of balance, and is independent of the galvanometer needle for its actual motive force.

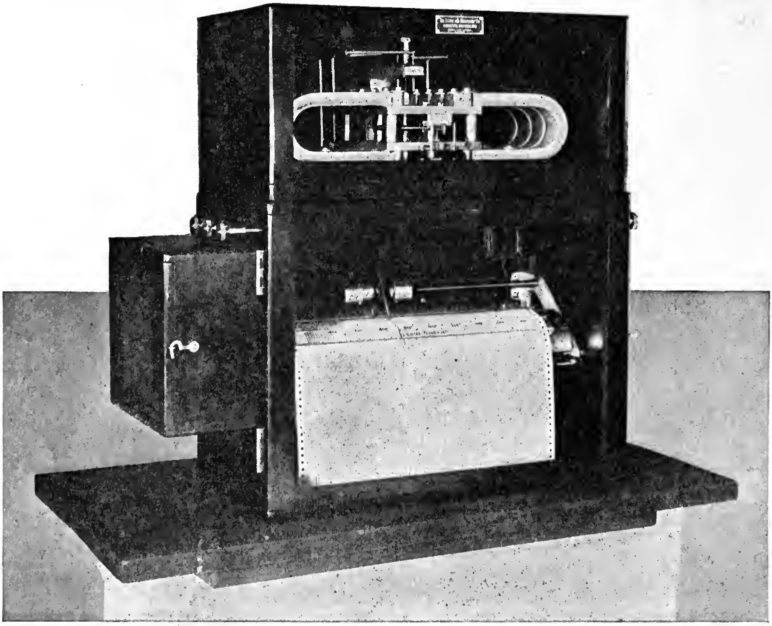

Fig. 66. — Leeds-Northrup automatic recorder.

Fig. 67 shows the Leeds-Northrup non-automatic Wheatstone bridge indicator for resistance pyrometry. It is designed for a number of pyrometer connections and the switch in the upper left-hand corner makes connections to whatever pyrometer is desired. In operating, the leads from the pyrometer are connected to the proper binding posts on the back of the instrument, and if the bridge is out of balance, the galvanometer needle, shown directly below the switch in the figure, is deflected. It is brought back to zero by turning the dial indicator to the proper position.

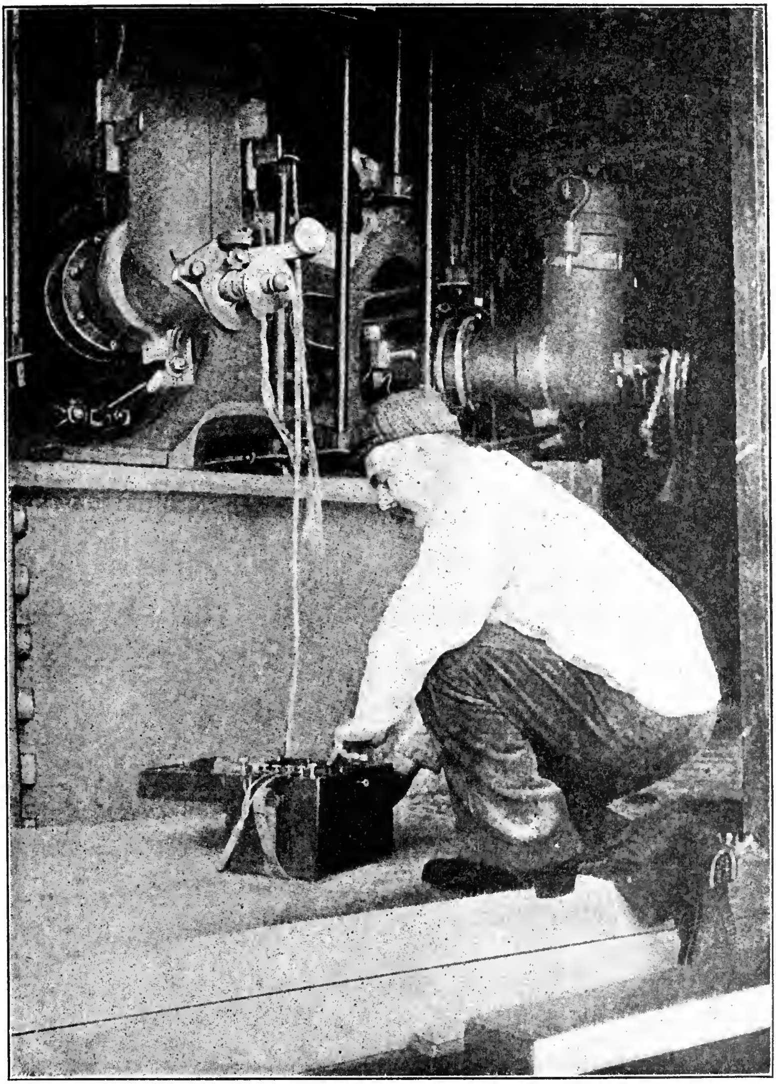

FIG. 68. — Taking the temperature of hot blast at the tuyeres of an iron blast furnace with resistance pyrometer.

The position of the indicator can be read on the circle directly in degrees, and gives the temperature indication of the pyrometer. The principles of the instrument are those of the Wheatstone bridge arrangement as shown in Fig. 67, and discussed under resistance pyrometry, the dial circle indicating resistance in terms of temperature on the gas scale. Fig. 68 illustrates a resistance pyrometer used to take hot blast temperatures in iron smelting.

Fig. 67. — Wheatstone bridge indicator for platinum resistance pyrometer.

CHAPTER VII

TYPICAL METALLURGICAL OPERATIONS

Introduction. — Metallurgy is defined as the art of extracting metals from their ores on a commercial scale. It further implies the production of a metal in such a state of purity or as an alloy with other substances in definite proportion as the requirements of the arts in which the metal is to be used may demand. These requirements are in some instances very severe. For example, steel for rails in American practice must fulfil the following specifications:[1]

For an 80 lb. to 90 lb. per yard rail —

Sulphur, not over 0.075 per cent.
Carbon, from 0.48 to 0.58 per cent.
Manganese, from 0.80 to 1.10 per cent.
Silicon, not over 0.20 per cent.
Phosphorus, not over 0.10 per cent.

It will be noted that the control of such elements as carbon, sulphur, phosphorus, and manganese, existing as they do in such small quantities, must put severe test upon the skill of the metallurgist. Not only is the chemical composition rigidly defined, but the physical constitution, as regards grain size and the mechanical treatment through which the steel must pass, are specified.

In the metallurgy of copper we have a case in which it is essential to produce a substance of great purity, particularly if the copper is to be used for electrical purposes. The following analysis of copper shows its purity as usually produced:[2]

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[1] American and Foreign Rail Specifications, A. D. Colby, T. A. I. M. E., XXXVII, 581.

[2] Peters, Principles of Copper Smelting, p. 483.

TABLE XXVII. COMPOSITION OF REFINED COPPER.

Substance	No. 1	No. 2	No. 3
	%	%	%
Lead	0.00023	0.00231	0.00054
Bismuth	—	0.0005	—
Antimony	0.00340	0.0138	0.00102
Arsenic	0.00042	0.00218	0.00034
Silver (*in oz.*)	0.31	0.54	0.43
Suboxide (Cu_2O)	0.75	0.63	0.084
Copper	99.2459	99.35121	99.9141

The case of gold is similar to that of copper. Very small quantities of such impurities as bismuth, lead, and tellurium make the gold very brittle so as to unfit it for coinage or use in the arts. Gold containing 0.05 per cent. bismuth can almost be crumbled in the fingers.[1] In fact, a large part of the metallurgical operations and cost of the same are directed to the elimination of minute quantities of deleterious substances. It is in this respect, and in the production of enormous quantities of material in the case of certain metals like iron and copper, that modern metallurgy differs from the old metallurgy.

As regards the term ore above used, it may be defined as follows: An ore is a natural mineral product which contains enough of valuable metal to warrant its extraction by metallurgical methods. It will be apparent that this definition does not cover all cases. For instance, what may be an ore in one locality, *i.e.* material of sufficient value to pay to extract the metal from, may not be so in another one where the costs are such as to preclude the treatment of the material at a profit. Under certain favorable natural conditions, very low grade ores are treated. Thus, the Alaska-Treadwell mines in Alaska successfully treat gold ore containing not more than $2.50 in gold per ton, while certain Michigan copper mines produce copper at a profit from ore containing not over 1 per cent. of copper in the metallic form. These cases, however, represent the lowest limits at the present date. The treatment of this low-grade material is the result of modern methods of mining and metallurgy. The following outlined schemes show the various metallurgical operations necessary to produce metal from the ore in the case of iron, copper, gold, and zinc. They serve to illustrate the complexity of the processes.

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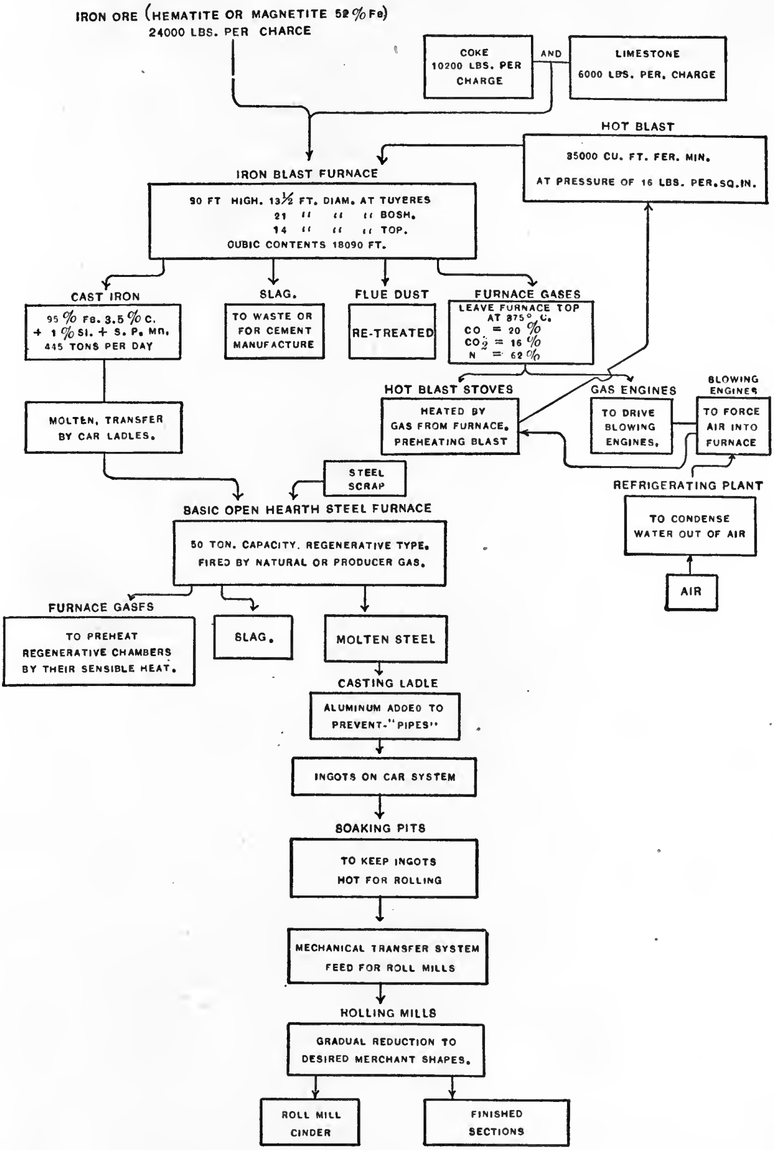
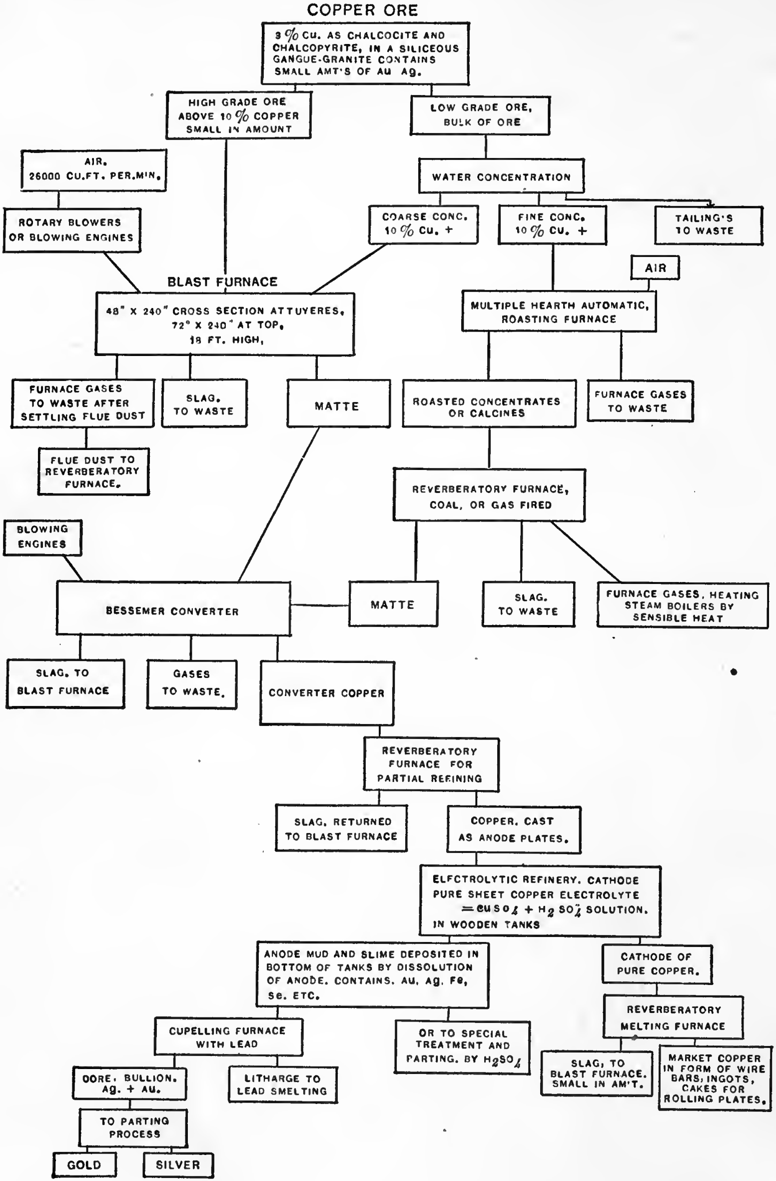
[1] Rose, Metallurgy of Gold, p. 4.

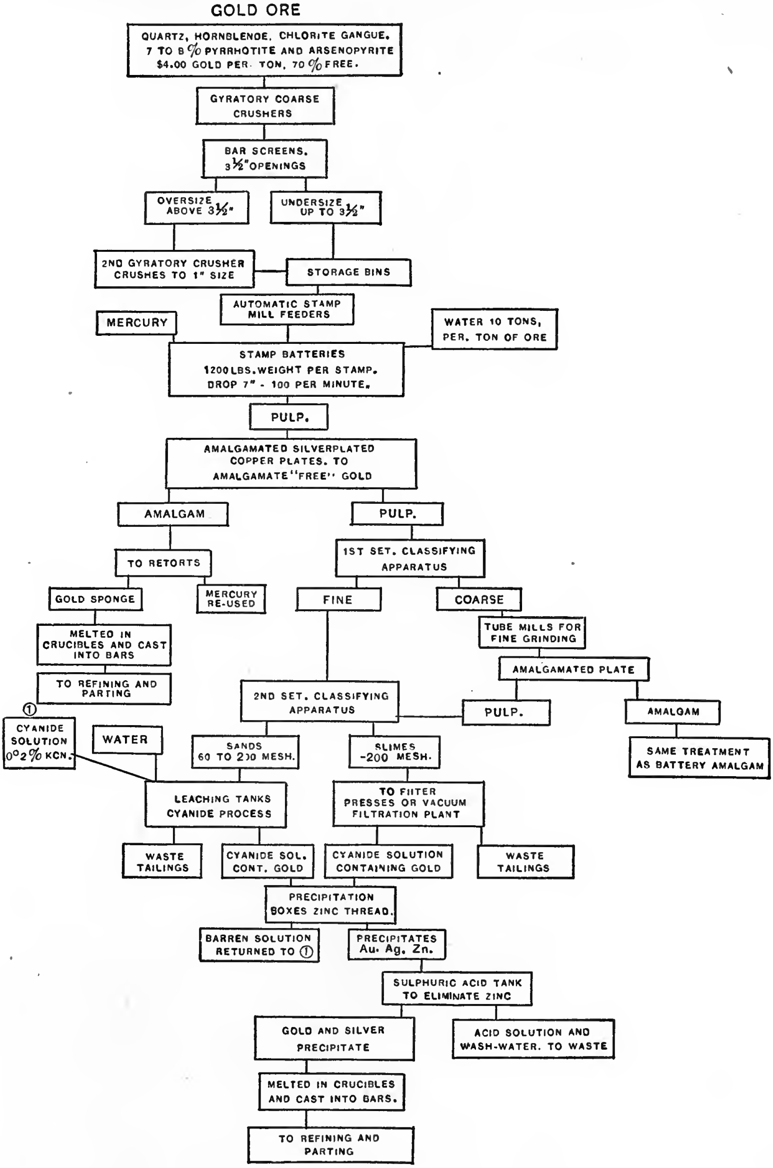
Scheme for the Production of Steel from Iron Ore.



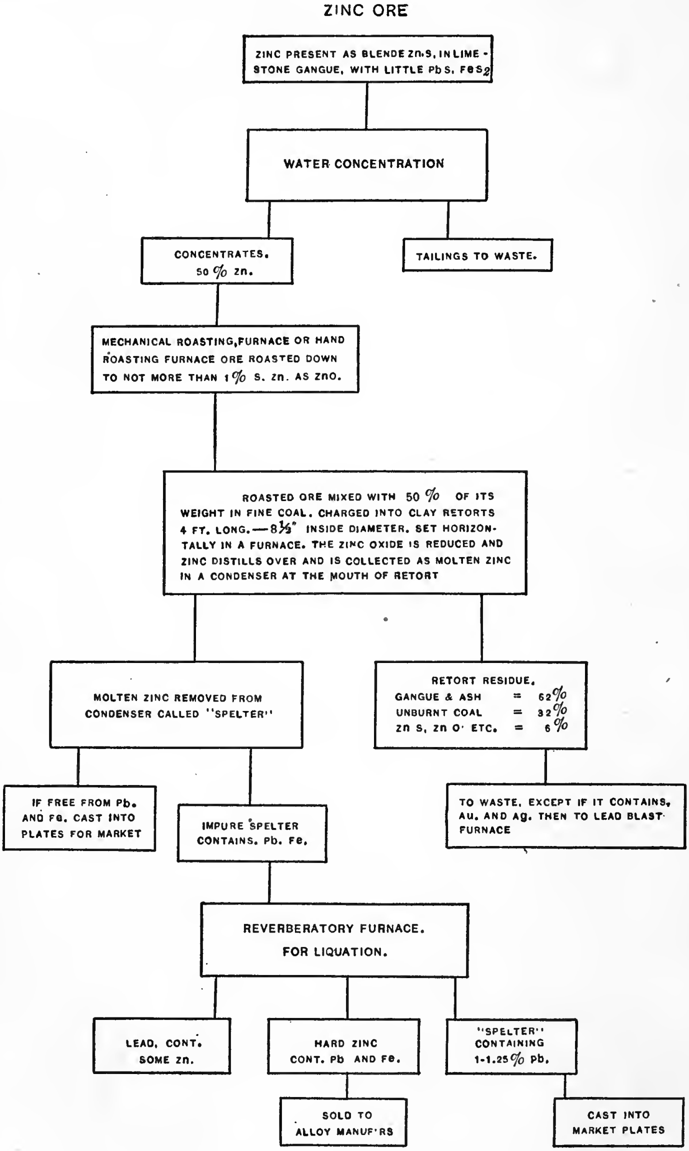
Metallurgical Scheme for the Production of Copper from its Ores.



Metallurgical Scheme for the Production of Gold from its Ores.



Metallurgical Scheme for the Production of Zinc from its Ore.



Oxidation and Reduction. — In nearly all metallurgical operations the processes of oxidation and reduction play a very important part. The significance of the terms oxidation and reduction in metallurgy is similar to that in chemistry, except that it is employed in a somewhat broader sense.

(1) OXIDATION. — This is defined as the process by means of which a metal or other element is oxidized to a compound, *i.e.* oxides, sulphates, etc., or in which a compound is raised from a low degree of oxidation to a higher one; thus — metallic iron may be oxidized to ferrous oxide (FeO) in the presence of silica and form a slag, ferrous silicate, as takes place to a limited extent when cast iron is made into wrought iron by the puddling process. Or again, when impure metallic copper, the product of the Bessemer converter, from the blowing of copper matte, is melted in a reverberatory furnace in the presence of air and steam, in order to oxidize impurities in it, such as iron, arsenic, antimony, bismuth, etc., to their oxides, so that they may be either volatilized or induced to pass into the slag, and thus be removed. During this process some of the copper is oxidized into cuprous oxide (Cu_2O) which is absorbed by the metallic copper and acts as an "oxygen carrier" to impurities present, with the formation of their oxides. The excess of Cu_2O must later on be removed by reduction. Again, copper matte, essentially an artificial sulphide of copper and iron produced in copper smelting, is converted into impure metallic copper by being placed molten into a cylindrical steel vessel lined with refractory material, called a converter, air being blown through it whereby the sulphur is oxidized to sulphurous acid gas (SO_2), which escapes, while the iron is oxidized to FeO and unites with silica, derived from the lining of the converter if this be acid, or from siliceous ore thrown into the converter if the lining is basic. The result of the reactions is metallic copper, the whole process being distinctively one of oxidation. Another important example of oxidation reactions is exemplified by the roasting of certain ores; thus pyritic ores containing copper, or copper mattes, or pyritic ores containing lead, may be heated in furnaces in the presence of air in order to convert the sulphur into SO_2 and SO_3 gas, largely eliminating it, while the iron and copper are converted into oxides and the lead into oxide and silicates. This process is termed *roasting* and serves as a preparation for the further treatment of these

ores. This type of roasting is distinctively an oxidizing reaction. There are many other examples of oxidation in the various metallurgical processes employed for the production of metal.

(2) Reduction. — A reduction reaction is one in which a metal is reduced from its compounds by means of some reducing agent. This is the distinctively metallurgical definition of reduction. Reduction in the chemical sense also implies the reduction of a compound from a high degree of oxidation to one of a lower degree of oxidation. The term reduction is used also metallurgically in this sense, *i.e.* a "reduction works" is a plant wherein some metal or metallurgical product is produced from its ore, irrespective whether this metal or product be obtained by reduction or oxidation. Thus, a metallurgical plant producing copper from a pyritic ore by pyritic smelting and Bessemerization of the matte is a "reduction works" producing copper practically solely by oxidation processes. The use of the word reduction in this sense is not to be advocated. As examples of reduction reactions, the following are quoted: In the smelting of iron ores to cast iron in the blast furnace the iron ore is reduced to metallic iron chiefly by means of carbon monoxide (CO), which is formed in the furnace by the burning of coke at the "tuyeres," or openings through which the blast is introduced, to carbon monoxide (CO), under the existing conditions. This carbon monoxide acts in the upper part of the furnace on the ferric oxide (Fe_2O_3), reducing it first to magnetic oxide (Fe_3O_4), then as this descends lower down into the furnace, where the temperature is higher, it is reduced to FeO by the carbon monoxide, and finally, as it descends still lower, to metallic iron, the reduction to metallic iron being completed at about 900° C. All this reduction takes place in the solid state, and when finally complete, the lump of material, now metallic iron plus any impurities which may be present in it, and its contained deposited carbon, is in shape and form very similar to the original piece of iron ore.

In considering reduction reactions it is to be noted that they are somewhat more complex than the ordinary chemical equations express. It has been stated that the carbon of the coke burns to carbon monoxide (CO) at the temperatures prevailing at the "tuyeres" of the furnace. This carbon monoxide suffers dissociation, as is expressed by the following equation:

$$C + CO_2 \rightleftarrows 2CO$$

in the presence of certain contact material as metallic iron or nickel or metallic oxides.[1] The reaction is a reversible one. In the system there is a state of equilibrium for any given pressure and temperature. If the pressure be held constant and the temperature be changed, there will be a change in the relative volumes of gases present until equilibrium is again established for the existing temperature. If the temperature be constant and the pressure be changed, changes in the relative volume of the gases will occur. It is evident, therefore, that under many conditions the reaction will not pass to completion. Under blast-furnace conditions the pressure may be considered practically constant at atmospheric pressure or somewhat above it, while the temperature is the variable, as the gases pass from the hearth of the furnace upward. The following table shows the relative volumes of gases present at different temperatures and at atmospheric pressure (760 mm.):

TABLE XXVIII. EQUILIBRIUM CONDITION FOR CO AND CO_2 GAS WITH TEMPERATURE

Temperature °C	%CO	%CO_2	Temperature °C	%CO	%CO_2
450	2	98	800	90	10
500	5	95	850	94	6
550	11	89	900	96.5	3.5
600	23	77	925	97	3
650	39	61	950	98.5	1.5
700	68	32	1000	99.3	0.7
750	76	24	1050	99.6	0.4

It will be noted that at a temperature of 1050° C., CO_2 can exist in the presence of carbon only to the extent of 0.4 of 1 per cent., so that carbon at that temperature burns to CO. As the temperature just above the tuyeres is about 1900° C., no CO_2 is formed. As the gases CO and N_2 rise in the furnace always in

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[1] St. Clair Deville, Comptes Rendus, LIX, 873 (1864). O. Boudouard, Ann. de Chim. et de Phys., VII, 24–25 (1901). R. Schenck und W. Heller, Ber. der Deutsch. Chem. Ges., XXXVIII, 2139 (1905). R. Schenck und E. Zimmerman, Ber. der Deutsch. Chem. Ges., XXXVI, 1232 (1903). Schenck, Physikalische Chemie der Metalle (1909).

the presence of carbon (coke), coming into the cooler zones, dissociation takes place in the presence of the spongy solid metallic iron, so that, for instance, at 750° C., equilibrium is represented by 76 per cent. CO and 24 per cent. CO_2 in a unit volume of the gases from the reaction. At 450° C., assumed here as the temperature the gases are discharged at the throat of the furnace, equilibrium is represented by 2 per cent. CO and 98 per cent. CO_2. It must be noted, however, that in the blast furnace the velocity of the rising gases is such that time for equilibrium to establish itself for any given temperature is lacking, so that the per cent. of CO will always be greater than that called for. To this reaction is due the "carbon deposition" in the furnace, viz., the deposition of finely divided carbon on the ore and walls of the furnace in its upper zone. It follows, therefore, that CO generated at the tuyeres normally dissociates, and CO_2 is present in considerable volume, before any of it is produced by the reduction of iron oxide. The gas stream which strikes the iron oxides in the upper part of the furnace is therefore a mixture of CO, CO_2, and N. In the reduction of the iron oxides by carbon monoxide, the following reactions take place:

$$Fe_3O_4 + CO \rightleftarrows 3\,FeO + CO_2$$ [1]

This is a reversible reaction with definite conditions of pressure and temperature for equilibrium. Thus, at atmospheric pressure and a temperature of 581° C., equilibrium is represented by 41.9 per cent. CO and 57.4 per cent. CO_2. If at this temperature more than 41.9 per cent. CO is present, reduction of the Fe_3O_4 to FeO will proceed; if less, FeO already formed will be oxidized back to Fe_3O_4.

In the reduction of FeO to Fe, the following table applies: (See table on next page.)

$$FeO + CO \rightleftarrows Fe + CO_2$$ [2]

This reaction takes place with the evolution of heat, viz., is exothermic, so that, once started, the temperature will automatically rise, bringing the reaction to completion from left to right. The reaction of Fe_3O_4 with CO, however, takes heat in order to proceed from left to right, viz., is endothermic, and will tend to reverse itself unless more heat is provided, as for instance, in the furnace the temperature is raised, when the charge sinks

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[1] Baur und Glaessner, Zeit. für Phys. Chem., XLIII, 354 (1903).

[2] Schenck, Physikalische Chemie der Metalle (1909).

TABLE XXIX. EQUILIBRIUM CONDITIONS FOR THE REDUCTION OF FE BY CO

Temperature °C	%CO	%CO_2
552	53.7	46.3
556	53.4	46.6
561	53.6	46.4
596	55.5	44.5
619	56.8	43.2
651	57.9	42.1
662	58.4	41.6

lower into the furnace. The reduction of iron from ore is expressed in total by the equation

$$Fe_2O_3 + 3\,CO = 2\,Fe + 3\,CO_2$$

which is exothermic, 135 calories being evolved per kg. of Fe_2O_3 at 900° C., at which temperature the reduction is practically complete. It is evident from the foregoing that in order to have the reduction of iron oxides proceed to metallic iron certain temperature conditions are necessary as well as a certain volume composition of the ascending gases. If in any zone of the furnace where reduction normally takes place by the ascending gas current, the temperature be lowered by some accident to the furnace, it is evident that reduction might cease and oxidation actually take place by the reaction being reversed. Still further it has been shown that if reduced iron be in contact with the ordinary furnace gases at temperatures below 570° C., this iron will begin to oxidize, as at this temperature the balance between iron, CO, CO_2 and carbon is such that CO is rapidly decomposed with the formation of CO_2 and FeO. The reduction of iron oxides by solid carbon is an endothermic reaction and does not set in to any extent below 900° C., when practically all the iron oxide has already been reduced by carbon monoxide. It therefore plays but a negligible part in reduction. Any water vapor in the air entering at the tuyeres is dissociated into hydrogen and oxygen, this latter uniting with carbon to carbon monoxide. The hydrogen is a reducing agent acting as follows:

$$Fe_3O_4 + 4\,H_2 \rightleftarrows 3\,Fe + 4\,H_2O$$ [1]

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[1] Preuner, Zeit. Phys. Chemie, XLVII, 416 (1904).

—a reversible reaction similar to the ones above described. At 200° C. and atmospheric pressure, 95.32 per cent. H at least must be present in order to make the reaction proceed from left to right; and at 900° C., 59.17 per cent. H., to accomplish reduction. As the usual amount of H in the ascending gas stream above the tuyeres is not more than 2 to 3 per cent., and much less than that in furnaces working on dry blast, the importance of hydrogen in blast-furnace work is negligible.

Carbon dioxide at high temperatures suffers dissociation as follows:

$$2\ CO_2 \rightleftarrows 2CO + O_2$$ [1]

At 1527° C. this dissociation, however, is but 0.507 per cent., viz., this percentage of the CO_2 is dissociated, and at the lower temperatures in the furnace at which it occurs its dissociation is practically nil.

The reduction by carbon monoxide gas of other metals than iron is similar. In lead smelting in the blast furnace the lead goes into the furnace chiefly in the form of silicate ($PbSiO_3$) and lead oxide (PbO). The lead silicate in the presence of iron oxide or lime (CaO) is reduced to metallic lead with the formation of ferrous silicate through the agency of carbon monoxide gas generated as already described for iron. In this instance the volume composition of the gases and temperature conditions are such as not to reduce the iron oxides. Many other examples of metallurgical reduction might be cited.

Reduction of Metals from Sulphides. — If sulphides of the metals be heated to a high temperature they become dissociated according to the following general reaction:

$$MeS \rightleftarrows Me + S$$

which is a reversible one, the amount of dissociation being a function of the vapor pressure of the sulphur and the temperature. Thus, under constant pressure and increasing temperature, the sulphide loses sulphur by vaporization, the remaining mass consisting of sulphide plus the metal, the amount of the sulphide constantly decreasing. The process is complicated by the fact that many of the sulphides vaporize as such and are thus in part volatilized with the sulphur, causing loss of metal. For certain of the heavy metals, as gold, the dissociation at atmospheric

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[1] Nernst und v. Wartenberg, Zeit. für Phys. Chemie, LVI, 548 (1906).

pressure is accomplished at a comparatively low temperature, but for most metals the amount of dissociation even at high temperatures is small, so that this method of obtaining metals from their sulphides is not a practical one metallurgically with the temperatures ordinarily available. In a neutral or reducing atmosphere, lead sulphide[1] (galena) vaporizes as such to the extent of 18 per cent. per hour at 860° C., and at 950° C. at the rate of 45 per cent. in one hour. In air it suffers decomposition. In a neutral atmosphere zinc sulphide (sphalerite) begins to vaporize as such at about 1000° C. and is rapidly vaporized at 1100° C.[2] Some further data on the dissociation of sulphides is given in Chapter IX.

Reduction of metals from their sulphides, based on the difference of affinity of sulphur for the various metals. An instance of this is the reduction of lead from its sulphide, galena.

$$PbS + Fe = Pb + FeS$$

This and similar reactions is based on the relative affinity of sulphur for the metals. If the degree of affinity differs widely, the reaction may be carried to practical completion. The products of the reaction are a metallic mass and a matte. If the affinity of sulphur for the metals does not differ greatly, the two metals will be found in both products, and as metals usually have at least some solvent power in the solid state for their own sulphides, both of the products will contain sulphur. Thus, the reaction

$$2\,Cu + FeS \rightleftarrows Fe + Cu_2S$$

is a reversible one, equilibrium varying with the temperature and pressure. Dealing with reactions at a constant pressure, we may consider the system at varying temperatures, in the molten state. Thus, at a temperature just above the beginning of solidification, there will be two liquids, one the heavier, essentially a metallic mass, and the other a matte. The four entities of the system will be distributed in fixed proportion in the two liquids, this proportion varying with the temperature.

If according[3] to the molecular weights of the above equation,

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[1] Doeltz und Graumann, Metallurgie, III, 441.

[2] *Ibid.*, III, 442.

[3] E. Schütz, Uber die Affinität des Schwefels zu einer Reihe von Metallen, Metallurgie, IV, 659 (1907).

126 g. of copper and 89.43 g. of iron sulphide be melted together, they react at 1195° C., and result in the two following products.

90.41 g. of metal, composition

Cu = 62.77 per cent.
Fe = 30.13
S = 5.28

124.9 g. matte, composition

Cu = 55.90 per cent.
Fe = 21.11
S = 21.74

If the reverse of the reaction be tried, *e.g.*, melting together cuprous sulphide and metallic iron, similar products result. 28.42 g. iron were melted together with 79.90 g. of cuprous sulphide and reacted with each other at 1205° C. resulting in the two products:

37.88 g. metal, composition

Cu = 50.46 per cent.
Fe = 42.33
S = 2.93

69.72 g. matte, composition

Cu = 57.15 per cent.
Fe = 18.56
S = 23.31

It is evident from the foregoing that sulphur has a greater affinity for copper than for iron, but that a separation of the metals cannot be achieved by the method. Zinc sulphide may be practically completely decomposed at 1300° C. by the reaction

$$\mathrm{Zns} + \mathrm{Fe} \rightleftarrows \mathrm{Zn} + \mathrm{FeS}$$

proceeding to completion from left to right.[1]

The relative affinity of the common metals for sulphur is expressed by the following series — manganese having the greatest affinity of the metals named—Mn, Cu, Ni, Fe, Sn, Zn, Pb.[2]

The great affinity of manganese for sulphur is made use of in the metallurgy of iron to remove sulphur from steel and cast iron. The metallic manganese in iron will unite with the greater part of the sulphur to form MnS, which can be removed by liquation, viz., from a molten bath the MnS will rise to the surface, on account of its lesser gravity, and may be removed by skimming or with the slag. Some of the sulphur, however, as iron sulphide, will remain dissolved in the iron or steel.

Critical Temperatures of the Reduction of Metals from their Oxides. — At atmospheric pressure by certain reducing agents.

Zinc oxide.[3] (*a*) When ZnO is mixed with sugar charcoal in proportion for this reaction—$\mathrm{ZnO} + \mathrm{C} = \mathrm{Zn} + \mathrm{CO}$ — under

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[1] C. A. Graumann, Metallurgie, IV, 69 (1907).

[2] Schütz, *Ibid.*

[3] F. O. Doeltz und C. A. Graumann, Metallurgie, IV, 290.

atmospheric pressure, with a removal of the gas formed, reduction begins between 900° C. and 950° C.

(*b*) When ZnO is mixed with sugar charcoal in excess, the reaction taking place is as follows — $ZnO + C = Zn + aCO_2 + bCO$ — a stream of nitrogen being used to remove the gases. Reduction begins at about 775° C. Fig. 69 shows the rate of reduction per hour at different temperatures.

(*c*) ZnO reduced by a stream of CO gas. The reaction is as follows: $ZnO + CO = CO_2 + Zn$. Reduction begins at 600° C. Fig. 69 gives the rate of reduction per hour at different temperatures. It is to be noted that the rate increases rapidly with the temperature.

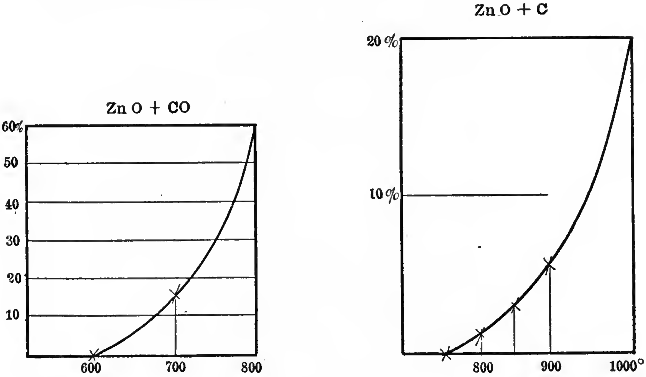

Fig. 69. — Reduction of ZnO by CO and C.

Cadmium oxide begins to be reduced at about 570° C. by solid carbon. The rate of reduction is rapid at 700° C.[1]

Lead oxide.[2] When litharge (PbO) is mixed with sugar charcoal in the proportion for the reaction—$2\,PbO + C = 2\,Pb + CO_2$ — reduction begins at 530 to 555° C., and the rate of reduction is rapid at 700° C.

Copper oxide.[2] When cupric oxide is mixed with sugar charcoal in the proportion for the reaction — $CuO + C = Cu + CO$ — reduction begins at 500 to 530° C.

Tin oxide.[2] When stannic oxide is mixed with sugar charcoal in the proportion $SnO_2 + 2\,C = Sn + 2\,CO$, reduction begins at 810° C.

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[1] Doeltz und Graumann, Metallurgie, IV, 419.

[2] *Ibid.*, Metallurgie, IV, 420.

Chromium oxide, Cr_2O_3, is reduced by solid carbon at 1185° C.; manganese dioxide at 1105° C.; uranium oxide at 1490° C.; silica at 1460° C.; zirconium oxide at 1400° C.; and thorium oxide at 1600° C.[1]

1. Roasting and Calcination. — Roasting may be defined as that metallurgical operation whereby an ore or mineral is heated in the presence of oxygen (air), which gives rise to the formation of oxides of metals or other oxidized compounds, thus resulting in the addition of an element, viz., oxygen. Calcination is that operation whereby an ore or mineral is heated, resulting in the driving out of water, both that mechanically held and that chemically combined, or the expulsion of carbonaceous matter, or of carbon dioxide. It does not result in the addition of an element. Thus, if pyrite be crushed and heated in air above a certain temperature, it is converted finally into ferric oxide. This operation is roasting. If pure limestone be heated to 812° C., the carbon dioxide (CO_2) will be completely expelled, leaving lime (CaO). This operation is calcination. The driving off of CO_2 from zinc carbonate ore is a similar operation. This begins to decompose at about 137° C., but its complete dissociation requires a continued red heat.[2] The two terms are frequently used interchangeably; not properly, however. Thus, it is very common to call sulphide ore after roasting "calcines." While roasting is usually oxidizing in its nature, it is not invariably so throughout the whole operation. There are several methods of roasting, as follows: Oxidizing roasting, reducing roasting, chloridizing roasting (with salt), roasting for especial objects, *e.g.* in preparation for magnetic concentration, etc.

Oxidation and the Dissociation Tension of Oxides. — The general equation — $M + O \rightleftarrows MO$ — representing the oxidation of a metal to its oxide is a reversible reaction. The direction in which it proceeds is a function of the temperature and partial pressure of the oxygen. The oxide has a definite dissociation tension for every temperature, and if we consider the system of a metal in contact with its oxide and oxygen or air, then if the dissociation tension of the oxide exceed in pressure that of the oxygen resting over it, there is no oxidation of the

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[1] H. C. Greenwood, Trans. Chem. Society, 93, 1484 (1908).

[2] Metallurgie, III, 443.

metal but a dissociation of the oxide already formed into metal and oxygen. Thus, suppose a metal is partially oxidized and surrounded by air at 760 mm., the partial pressure of the atmospheric oxygen is about 160 mm. of mercury. If the metal be heated it will oxidize, but if the temperature rises high enough so that the dissociation pressure of its oxide rises above 160 mm., oxidation will cease and the oxide split up into the metal and oxygen. The partial pressure of the nitrogen of the air will have no influence. In many cases complications occur, by the oxide formed being soluble in the metal, which will materially change its dissociation tension.

The heavy metals, such as silver, gold, palladium, mercury, have oxides that possess high dissociation tensions at comparatively low temperatures. The oxides of most of the common metals have very low dissociation tensions, even at comparatively high temperatures, so that oxidation at ordinary pressures proceeds rapidly, and the metals cannot be obtained from their oxides by heating, as can be done with some of the other metals named above. The following table shows the dissociation tension of certain metallic oxides at varying temperatures. It is to be noted that if these oxides be heated in air at atmospheric pressure, they will begin to dissociate when the temperature is such that their tension exceeds 160 mm., that of oxygen in air at one atmosphere pressure.

TABLE XXX. DISSOCIATION TENSION OF CERTAIN METALLIC OXIDES.

$2\,BaO_2 \rightleftarrows 2\,BaO + O_2$[1]		$2PdO \rightleftarrows 2\,Pd + O_2$[2]		$4\,CuO \rightleftarrows 2Cu_2O + O_2$	
Temp. °C.	O_2 Tension in mm.	Temp. °C.	O_2 Tension in mm.	Temp. °C.	O_2 Tension in mm.
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	—	—	—	—

[1] LeChatelier, Compt. rend., CXV, 655 (1893).
[2] L. Wöhler, Zeit. für Electrochem, XII, 784 (1906).

The following data gives the temperatures at which various metallic oxides begin to dissociate in air at atmospheric pressure:

Reaction	Temperature
$2\ Ag_2O = 2\ Ag_2 + O_2$	130° C.
$4\ CuO = 2\ Cu_2O + O_2$	1020° C.
$2\ Cu_2O = 2\ Cu_2 + O_2$	1662° C.[1]
$2\ CuO = Cu_2 + O_2$	1502° C.[1]
$2\ PbO = Pb_2 + O_2$	2075° C.[1]
$2\ NiO = 2\ Ni + O_2$	2478° C.[1]
$2\ ZnO = 2\ Zn + O_2$	3544° C.[1]
$3\ Fe_2O_3 = 2\ Fe_3O_4 + O$	1375° C.[2]

The Volatility of Metallic Oxides. — Cadmium oxide (CdO) begins to volatilize as such in air at about 700° C., and volatilization is rapid at about 1000° C.[3]

Zinc oxide (ZnO)[4] begins to volatilize in air at about 1180° C., and volatilization becomes rapid at about 1400° C. The loss at 1400° C. is 13 per cent. in two hours.

Lead oxide (PbO)[5] begins to volatilize in air at about 800° C., it melts at 882° C., and the volatilization becomes rapid at about 1000° C. The volatilization below its melting-point is very appreciable. The rate of volatilization in the case of a liquid is dependent upon the ratio of surface to mass. The greater this ratio the more rapid the volatilization.

These data have bearing on various metallurgical operations such as the roasting of zinc ores, the cupellation of lead bullion, etc.

The Operations and Chemistry of Roasting. — The roasting of ores is a preliminary step to many metallurgical operations. The usual object is to eliminate sulphur either partially or entirely so, arsenic and antimony, and other volatile constituents which may interfere with later processes, and also to convert certain metals into oxides, enabling them in smelting operations to form slag with silica, or in the subsequent treatment of ore with solutions to make it inert to attack by solvents employed for the

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[1] Calculated from Nernst's formula, and are probably high. W. Stahl, Dissoziations-Spannungen einiger Oxyde, Metallurgie, IV, 682.

[2] H. O. Hofman, T. A. I. M. E., Bi-monthly Bulletin No. 31, 621 (1909).

[3] Doeltz und Graumann, Metallurgie, III, 372 (1906).

[4] *Ibid.*, III, 212, 233 (1906).

[5] Doeltz und Graumann, Metallurgie, III, 406 (1906).

extraction of its valuable contents. Thus, in the treatment of fine sulphide mineral concentrates from concentration mills, which are smelted in reverberatory furnaces for a "matte," it is necessary to first roast the same to eliminate the greater part of the sulphur and to convert the iron sulphides largely into iron oxide, so that it may enter the slag. This material is roasted so that the final product contains an amount of sulphur, which is in definite proportion to the copper present, in order to form the proper grade of matte in the following smelting operations.

On the other hand, certain gold ores, such as telluride ores containing, aside from the small amount of tellurides of gold, a certain per cent. of pyritic minerals, are usually roasted preliminary to leaching the ore with alkaline cyanide solutions for the extraction of the gold. The object of the roasting is to separate the gold from its combination with tellurium, this being in small part volatilized, the balance forming probably tellurate of iron, which remains in the ore, leaving the gold "free," or in the metallic form. During the roasting the pyritic minerals roast in part to sulphates, unless the temperature is finally brought to such a point as to insure their decomposition. These sulphates are readily acted on by the cyanide solutions in the subsequent treatment, causing a heavy loss of the solvent, so that it is essential to remove them. The roasting of this kind of ore requires, therefore, the almost complete removal of the sulphur. Such a roast is called a "dead" or a "sweet" roast.

Roasting operations on a large scale are carried out either in furnaces of the reverberatory type (see Chapter XIII) on finely crushed ore, the fineness depending on certain conditions, or in kilns, stalls or heaps, on lump ore consisting chiefly of solid sulphides, so as to be self-burning. This latter form of roasting is only permissible when the sulphur dioxide and other gases formed are not objectionable to the community. The ores to be roasted consist of the various gangue minerals — quartz, calcite, rhodonite, rhodochrosite, etc., the rock in which the ore occurs, which may be of many different kinds, mixed with a varying percentage of sulphide minerals, arsenic, antimony bearing minerals, as pyrite, marcasite, pyrrhotite, chalcopyrite, bornite, galena, zinc blende, stibnite, arsenopyrite, etc. The percentage of sulphides may be small, 4 to 7 per cent., as in certain gold ores, or very much higher, as in the case of copper, zinc, and lead ores. The different sulphide minerals present may be many or few. In order to understand the chemistry of the roasting operations, we will consider the crushed ore as spread in a layer from one to several inches thick on the enclosed hearth of a reverberatory furnace, overlain by air, with which are mingled certain gases as CO_2 from the fuel and SO_2, SO_3, etc., from the roasting. This atmosphere is constantly being removed through the stack and fresh air brought in through the furnace doors. The heat is supplied by burning fuel on grates in fire boxes adjoining the hearth of the furnace. The products of combustion of this fuel, CO_2 in large part and some CO, may form part of the furnace atmosphere, or in the muffle type of furnaces may pass around the hearth, and not come into contact with the roasting ore. Ores consisting largely of sulphides furnish the heat for the roasting by their own combustion after the sulphides are once ignited. The ore is usually charged at the cool end of the furnace away from the fire boxes and is worked forward toward the hot end, either by hand labor, with a tool called a "rabble," or by automatic mechanically actuated plows and rabbles. This procedure stirs the ore and constantly exposes fresh surfaces to the influence of the furnace atmosphere. The length of time of passage of the ore through the furnace depends upon its nature, the principle involved being that the ore shall be sufficiently roasted when it arrives at the fire-box end to be discharged. The raw ore is constantly charged at the cool end of the furnace.

The Chemistry of the Roasting of Sulphides. — When sulphides such as pyrite, pyrrhotite, chalcopyrite, are heated in air at the normal pressure — 760 mm. — to their ignition-point they begin to burn according to the following reaction:

$$2MeS + 3O_2 = 2MeO + 2SO_2$$

or, expressed for pyrite,

$$2FeS_2 + 11O = Fe_2O_3 + 4SO_2.$$

The air above the ignited sulphide becomes charged with SO_2 gas, and the atmosphere in which roasting takes place consists of nitrogen, oxygen, and sulphur dioxide. In the presence of contact substances such as silica, or ferric oxide, the following reaction takes place between the SO_2 and the O_2:

$$SO_2 + O \rightleftarrows SO_3$$

This is a reversible reaction and the formation of SO_3 or its dissociation if formed varies with the temperature, the pressure in this case being considered constant. The atmosphere above the roasting sulphides is hence composed of N_2, O_2, SO_2, and SO_3, in varying proportions. The total pressure, in millimeters of mercury, of this atmosphere is that essentially of the outside atmosphere, and is made up of the partial pressures of the different gases present. These partial pressures are dependent upon the relative quantity of each gas present. Thus, in 100 volumes of air there are 21 volumes of oxygen and 79 volumes of nitrogen, and the partial pressure of the oxygen will be $\frac{21}{100} \times 760 = 159.6$ mm., while that of the nitrogen will be $\frac{79}{100} \times 760 = 600.4$ mm. If to these 100 volumes of air be added 10 volumes of SO_3 gas, and 25 volumes of SO_2 gas, there will be a total of 135 volumes of gas at 760 mm. pressure, and the partial pressure of the gases are as follows: SO_3, $\frac{10}{135} \times 760 = 56.3$ mm.; SO_2, 140.2 mm.; N_2, 444.5 mm.; and O_2, 119 mm. It will be noted that the partial pressure of oxygen is reduced, as well as that of nitrogen, and it may readily be seen that with no rapid removal of the furnace gases the oxygen in the furnace atmosphere might be so reduced and that of SO_2 so increased, as to stop further roasting. This point is reached when the gases contain about 9 per cent. of SO_2 by volume.

The presence of SO_3 in the gases and its amount, and the existing temperature, determine the formation of the sulphates of the metals. The following reactions express this:

$$1.\quad \begin{cases} 2FeS_2 + 11O = Fe_2O_3 + 4SO_2 \\ Fe_2O_3 + 3SO_3 \rightleftarrows Fe_2(SO_4)_3 \end{cases}$$

$$2.\quad \begin{cases} Cu_2S + 4O = 2CuO + SO_2 \\ 2CuO + 2SO_3 \rightleftarrows 2CuSO_4 \end{cases}$$

$$3.\quad \begin{cases} ZnS + 3O = ZnO + SO_2 \\ ZnO + SO_3 \rightleftarrows ZnSO_4 \end{cases}$$

The formation of sulphate from oxide and sulphur trioxide is a reversible reaction dependent upon the temperature and the partial pressure of the sulphur trioxide. The following table gives the equilibrium conditions for temperature and pressure of SO_3 (or the dissociation tension) of several sulphates:[1]

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[1] SO_3 Tension der Sulfate, L. Wöhler, Plüddemann und P. Wöhler, Ber. der Deutch. Chem. Ges., XLI, 703 (1908). Keppeler, Zeits. f. Angew. Chemie, XXI, 532 (1908).

TABLE XXXI. EQUILIBRIUM CONDITIONS FOR SULPHATES.

$Fe_2(SO_4)_3 \rightleftarrows$ $Fe_2O_3 + SO_3$		$Al_2(SO_4)_3 \rightleftarrows$ $Al_2O_3 + SO_3$		$2CuSO_4 \rightleftarrows$ $2CuO + SO_3$		$2CuOSO_3 \rightleftarrows$ $2CuO + SO_3$		$ZnSO_4 \rightarrow$ $ZnO + SO_3$	
Temp.	Tension in mm.	Temp.	Tension in mm.	Temp.	Tension in mm.	Temp.	Tension in mm.	Temp.	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	—	—	—	—	—	—	—	—

Taking as an example the basic copper sulphate in column 4: At a temperature of 600° C., the dissociation tension is 62 mm. If the partial pressure of SO_3 in the atmosphere above the sulphate is less than 62 mm., the sulphate will dissociate into CuO and SO_3, $(SO_2 + O)$; if it be greater, there will be no dissociation at that temperature. If the temperature be raised and the partial pressure of the SO_3 in the furnace atmosphere remain the same, the sulphate will rapidly dissociate.

Whether sulphates or oxides form originally in the furnace is dependent upon the amount of SO_3 (partial pressure) present in the furnace atmosphere. The following table[1] gives the necessary partial pressures of SO_3 which indicate the dividing line between the formation of the oxide or the sulphate of the metal. If the partial pressure of the SO_3 in the furnace atmosphere exceed the figures given, sulphates will form; if it be less, then oxides will form. The table includes some partial pressures at temperatures at which some of the sulphates cannot exist. (See table on next page.)

Keeping in view what has gone before, the roasting of an ore mixture containing considerable pyrite, pyrrhotite, and chalcopyrite with some silver will proceed as follows: The ore at the cooler end of the furnace takes fire at about 325° C., and the

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[1] R. Schenck, Phys. Chem. der Metalle, 1909.

TABLE XXXII. PARTIAL PRESSURE OF SO_3 NECESSARY FOR THE FORMATION OF SULPHATES.

Temperature °C.	Partial Pressure of SO_3 in mm.			
	$Fe_2(SO_4)_3 : Fe_2O_3$	$CuSO_4 : (CuO)_2SO_3$	$(CuO)_2SO_3 : CuO$	$ZnSO_4 : ZnO$
550	12	27	—	—
600	22.5	29	29	—
650	61.5	40	33	—
700	244.0	99	35	1
750	—	—	52	8.7
800	—	—	104	28.5

outside of the particles become coated with ferric oxide, the furnace atmosphere sweeping over the ore from the other parts of the furnace is charged with SO_2 and SO_3, and as the temperature is below 600° C. and the partial tension of the SO_3 considerable, some $Fe_2(SO_4)_3$ forms from the ferric oxide. The local rise in temperature is, however, very rapid, due to the heat evolved by the burning sulphur, and the temperature conditions for the existence of $Fe_2(SO_4)_3$ are exceeded, so that a large part of the iron sulphides pass directly to Fe_2O_3. This Fe_2O_3 aids in the formation of SO_3 as already mentioned. The copper sulphate having a rather high dissociation temperature at the existing partial pressure of the SO_3 in the furnace gases, forms from part of the CuO which has been produced by oxidation of the copper sulphide, and if the temperature at this stage does not exceed about 700° C., nearly all of the copper may be converted into basic sulphate. As the ore is moved forward into the hotter parts of the furnace, the temperature at which copper sulphates can exist at the partial pressure of the SO_3 prevailing, is exceeded, and the sulphate decomposes into CuO and SO_3, this latter aiding in sulphatizing of copper oxide in the cooler parts of the furnace as described. Any silver minerals in the furnace are in a similar manner converted into sulphate, except that it is metallic silver or silver sulphide which is sulphatized, as the oxide of silver cannot exist at the furnace temperatures prevailing. The silver sulphate begins to be decomposed into metallic silver and SO_3 at 870° C. under the prevailing conditions. Silver sulphate melts at 655° C. It is thus seen that as the ore is forwarded in the furnace, the rise in temperature causes the dissociation of sulphates; the final product of the roast if carried to completion will be ferric oxide (Fe_2O_3), cupric oxide (CuO), and metallic silver. If the temperature rises above 1020° C., dissociation of the CuO into Cu_2O and O_2 may begin, and if above 1350° C., $3\,Fe_2O_3$ into $2\,Fe_3O_4 + O$. The presence in the furnace atmosphere of reducing gases may also give rise to Cu_2O and Fe_3O_4.

It is to be noted that as the ore is in grains of somewhat varying size, which may be of complex composition, and as it is forwarded by the rabbles, it will be at the surface exposed to the furnace atmosphere at one moment, while again it is submerged amongst other ore particles where the local atmosphere immediately surrounding the grain may even be reducing or neutral, due to the presence of sulphur vapor, or much SO_2. A grain may therefore be composed of several constituents at the same time; thus, it may have a surface of sulphate, and a core of oxide and undecomposed sulphide. In fact, many grains may reach the end of the roast, with cores of sulphide, unaltered except through a loss of part of their sulphur by distillation. Neither is the furnace atmosphere uniform throughout, but just above the roasting ore it contains much more SO_2 and SO_3 than higher up, while at the cool end of the furnace the concentration of these gases is also greater than at the hot end of the furnace. If it is desirable to roast to sulphates of the metals, as sulphate of copper, or silver sulphate, to be later leached out by hot water as in the Ziervogel process, and precipitated by means of metallic copper, the temperature must be closely controlled, so as to first form and later decompose iron and copper sulphates to aid the formation of silver sulphate, but not high enough a temperature to decompose this latter.[1] It is also desirable during the sulphatizing stages of the process to keep the temperature well below the decomposition points and permit as much accumulation of SO_3 in the furnace atmosphere as possible by a slow removal of furnace gases.

On the other hand, if the ore is tobe roasted only for the purpose of eliminating sulphur, the temperature control is not important, except that it should not rise high enough to unduly sinter and frit the ore, thus preventing roasting of the interior of the ore particles. In this case the furnace gases should be removed

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[1] R. H. Bradford, T. A. I. M. E., XXXIII, 68 (1903).

as rapidly as possible and no accumulation of SO_2 and SO_3 permitted. The usual percentages by volume of SO_2 in furnace gases at the flue is from 2 to 5 per cent., preferably not more than 2.5 per cent.[1] Under certain conditions magnetic oxide of iron will form from the ferric oxide, as at certain stages it will be reduced by SO_2 gas as when an ore particle becomes submerged. Thus, $3\ Fe_2O_3 + SO_2 = 2\ Fe_3O_4 + SO_3$, and when the relative partial pressure of oxygen is low. During heavy firing on the grate, the furnace gases are temporarily charged with hydrocarbon gases or carbon monoxide, then $3\ Fe_2O_3 + CO = 2\ Fe_3O_4 + CO_2$. The magnetic oxide may readily be detected in the roasted product by its black color, as against the red of the ferric oxide, and also by its magnetic properties. The maximum temperature attained by self-roasting ore (34 per cent. S.), in the McDougal roaster is 960° C., and the gases are discharged at about 315° C.[2] The composition of the escaping gases is:

Gas	Per cent. by Weight	Per cent. by Volume
SO_2	4.95	2.25
SO_3	1.46	0.53
O	19.60	18.45
N	74.00	78.77

Thirty-two pounds of air are needed per pound of sulphur, and the air supply depends upon the number of pounds of sulphur burnt per minute in the furnace, and may be readily calculated for any furnace whose constants are known.

In the roasting of galena ores (lead sulphide), preliminary to smelting in the blast furnace, we have to do with mineral mixtures consisting of galena (PbS), pyrite (FeS_2), or other iron sulphides, some sphalerite (ZnS) mixed with gangue minerals, chief among which is quartz (SiO_2). Usually the percentage of galena will be high. During roasting, lead sulphate ($PbSO_4$) will form, under similar conditions as described, but as it is stable at high temperatures, it would not decompose except for the presence of silica, and certain complicated reactions between PbS and $PbSO_4$ and between PbS and PbO. The melting-point of $PbSO_4$ is about 950° C.

[1] L. S. Austin, Washoe plant, T. A. I. M. E., XXXVII, 466 (1906).

[2] L. S. Austin, Washoe Plant, T. A. I. M. E., XXXVII, 466 (1906).

The reaction between $PbSO_4$ and SiO_2 is as follows:

$$2\ PbSO_4 + SiO_2 = 2\ PbO.SiO_2 + 2\ SO_3\ (SO_2 + O)$$

The reaction between lead sulphate and silica takes place probably at nearly the same temperature as that between PbO and SiO_2, viz., between 700° and 800° C., depending on the ratio of the two substances. Litharge and silica combine in practically all proportions to form solid solutions,[1] so that the final product of the roast as regards the lead is a silicate. In roasting lead ore not less than 12 to 15 per cent. SiO_2 should be present. The reactions

$$(1)\quad PbS + PbSO_4 \rightleftarrows 2\ Pb + 2\ SO_2$$

$$(2)\quad PbS + 2\ PbO \rightleftarrows 3\ Pb + SO_2$$

are reversible reactions of the nature already described, dependent upon the temperature and the partial pressure of the SO_2 gas. No. 1, under ordinary conditions, begins to proceed from left to right at 550° C., and No. 2 at 650° C., with the production of metallic lead. This is very undesirable, as the presence of metallic lead during the further progress of the roast causes high losses in lead by volatilization, as well as losses later on in the upper part of the blast furnace. Under the high partial tensions of the SO_2 present in the furnaces, the temperatures at which the reactions proceed from left to right are raised, probably nearly into the zone of the lead silicate formation, thus preventing the reactions producing metallic lead. This reaction may, however, take place in roasting if much lead sulphide be still present in the furnace, when the above temperatures are reached or if too little silica be present. At this point, however, comparatively little lead sulphide will remain, unless the temperature at the beginning has been too high, so as to sinter and agglomerate the sulphides hindering the penetration of air to the individual particles, preventing the formation of sulphate and oxide. The reactions are, however, important[2] for certain metallurgical processes for lead, called the "roast-reaction" processes, carried out in reverberatory furnaces, or on hearths. They were formerly of more importance than at present. The reactions are then

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[1] W. Mostowitsch, Metallurgie, IV, 647 (1907). S. Hilpert, Metallurgie, V, 535–539.

[2] For a complete discussion of these complicated reactions from the viewpoint of physical chemistry, see R. Schenck and W. Razbach, Metallurgie, IV, 455 (1907).

carried out for the production of metallic lead. In roasting lead ores a source of loss may be the volatility of lead sulphide and that of lead oxide, already referred to.

Arsenic or antimony may be present in ore to be roasted, often in the form of sulphides, or as arsenides or antimonides of other metals and sometimes in very complex mineral form. The sulphides of arsenic As_2S_2 (realgar) and As_2S_3 (orpiment) are readily volatile, and Sb_2S_3 (stibnite) is also volatile, but not to the same extent as the arsenic sulphides. Some of the arsenic and antimony is eliminated in the early stages of the roasting by the formation of these sulphides, aided by the distillation of sulphur from the pyrites present.[1] The lower oxides of these elements form As_2O_3 which is readily volatile at 218° C., and Sb_2O_3 which is volatile only at a low red heat. Considerable of the arsenic and antimony may be eliminated in this way. Further oxidation, however, changes these oxides into the higher oxides, As_2O_5 and Sb_2O_5, which when present alone are again readily dissociated at a full red heat, but in the presence of certain base metal oxides, such as iron and copper, are converted into very stable arseniates and antimoniates of these metals, which will persist as such in the roasted material. In the process of roasting, the ore particles, as already mentioned, are alternately on the surface of the ore bed subject to an oxidizing atmosphere, and submerged among partially roasted particles from which sulphur is distilling. This sulphur vapor and SO_2 gas will reduce arseniates and antimoniates and again cause the volatilization of sulphides of arsenic and antimony, and their lower oxides. The arsenic and antimony are therefore most readily eliminated by alternate oxidation and reduction. A roasting furnace may be specially operated in this way, by methods of firing, when much arsenic or antimony is present.

In the roasting of zinc blende (ZnS) to ZnO for the succeeding distillation process, zinc sulphate forms under similar conditions as already described. Zinc sulphate begins to decompose into possibly basic sulphates at 525° C., and with no partial pressure of SO_3 gas, completely decomposes into ZnO and SO_3 at 739° C.[2]

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[1] H. M. Howe, Copper Smelting, Bulletin No. 26, p. 12, U. S. G. S. (1885).

[2] H. O. Hofman, T. A. I. M. E., XXXV, 811 (1905). F. O. Doeltz und C. A. Graumann, Metallurgie, III, 445 (1906).

Within the last years the "blast roasting" processes for galena ores, invented by Huntington and Heberlein, Savelsberg, and Carmichael-Bradford, have been extensively applied both to lead and copper sulphide ores. In the first mentioned process the galena concentrates are roasted in mechanical reverberatory furnaces, reducing the sulphur contents to 11 to 12 per cent. from 20 to 22 per cent. This partially roasted ore is then fed to "converters"[1] which are hemispherical pots of cast iron 9 ft. in diameter at the top and about 4 ft. deep. They are provided with a circular cast-iron grate 6 ft. in diameter and 0.75 in. thick, set and secured horizontally in the pot. The grate is perforated with holes 0.75 in. in diameter, 2 in. apart. The pot is made 2.5 in. thick at the bottom and 1.5 in. at the rim. It is supported by trunnions, so that the pot may be readily revolved and emptied of its charge. The blast pipe through which the air is blown into the converter, for the oxidation of the ore, enters the bottom of the pot and is 6 in. in diameter. Into a pot previously heated by a wood fire, some hot calcines are thrown and then filled with the partially roasted calcines mixed with limestone in the approximate proportion of 4 to 1. The calcines almost invariably contain silica. If air be blown through the charge, lead sulphide is oxidized to PbO, and $PbSO_4$, finally forming silicate of lead as already described. The limestone is decomposed into CO_2 and CaO, which latter in part prevents the massive agglomeration and fusion of the whole charge and permits the penetration of the blast. The temperature locally developed in spots may be high. If ferric oxide be present, as may readily be the case from iron sulphides in the ore, this will unite at least in part with the lime as follows, forming calcium ferrite:[2]

$$CaO + Fe_2O_3 = CaO \cdot Fe_2O_3$$

The calcium ferrite begins to form at about 1200° C., and melts at 1230° C., and aids in agglomerating the charge. The contents of the converter are thoroughly agglomerated and sintered together (except for a small proportion of fines which are retreated), and make the best kind of material for blast-furnace smelting. The sulphur contents of the roasted material is usually from 3 to 5 per cent.

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[1] W. R. Ingalls, T. A. I. M. E., XXXVII, 636 (1906).

[2] H. O. Hofman, T. A. I. M. E., XXXIX, 645 (1908).

Formerly, the roasting of silver ores containing silver in the form of argentite (Ag_2S), and in complex mineral form associated with arsenic and antimony, with salt ($NaCl$), to convert the silver into the form of chloride, was much practised. This is called "chloridizing roasting."[1] The present importance of this method is diminished. Silver in the form of chloride is readily amalgamable, and soluble in sodium hyposulphite, and alkaline cyanide solutions, and the ore is roasted preliminary to treatment by either amalgamation or leaching with "hypo"-solution; much more rarely in preparation for cyanidation. The ore is roasted at comparatively low temperatures, not much above 800° to 900° C., in reverberatory types of roasting furnaces. It is essential to have some sulphides present, particularly pyrite or chalcopyrite, etc., as the roasting of these to sulphates, which reacting with the salt furnish the chlorine, in the main chloridizes the silver. Galena, zinc blende and arsenopyrite are rather harmful.

$$
\begin{aligned}
FeSO_4 + 2\,NaCl &= Na_2SO_4 + FeCl_2 \\
4\,FeCl_2 + 3\,O &= 2\,Fe_2O_3 + 4\,Cl_2 \\
Ag_2S + O_2 + Cl_2 &= 2\,AgCl + SO_2
\end{aligned}
$$

The reactions express in a general way the chloridization of the silver. The reactions on the whole may be very complicated; some of the base metal chlorides are volatilized as such, and arsenic and antimony are volatilized in part as chlorides. The amount of salt added varies from about 3 to 20 per cent., dependent largely on the amount of sulphides present. Usually it is under 10 per cent. Silver chloride melts at 460° C., and is said to be volatile at a white heat;[2] there is, however, an appreciable loss of silver in the chloridizing roast which increases with the temperature. Gold ores[3] were also formerly subjected to chloridizing roasting, in preparation for the chlorination process. At the present day gold ores are roasted with a simple oxidizing roast, the reactions for which have already been discussed.

In the metallurgy of antimony the ores treated are chiefly the sulphide, stibnite (Sb_2S_3), and sometimes the oxides, senarmontite and kermesite. The ore is roasted, usually for the purpose of forming either the higher oxide Sb_2O_5, which is non-volatile,

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[1] Ottakar Hoffman, "The Hydro-Metallurgy of Silver" (1907), p. 3, etc.

[2] Roscoe and Schorlemmer, II, 462 (1907).

[3] S. B. Christy, T. A. I. M. E., XVII, 3 (1888).

or, in the later processes, the volatile lower oxide Sb_2O_3, which is volatilized and sublimed. The method of roasting for the production of the volatile oxide is known as "volatilizing roasting." When stibnite is heated in air to a few degrees above 350° C. the following reaction takes place:

$$Sb_2S_3 + 9\,O = Sb_2O_3 + 3\,SO_2,$$

and, in the presence of more oxygen,

$$Sb_2O_3 + O_2 = Sb_2O_5.$$

The two oxides present then react with each other in part as follows:

$$Sb_2O_5 + Sb_2O_3 = 2\,Sb_2O_4.$$

If in the mixture there be present sulphides of other metals, such as galena, pyrite, chalcopyrite, etc., or the corresponding oxides, permanent and stable antimoniates are formed. If the ore be roasted in the presence of carbon, in the form of coal or coke, at a higher temperature and in the presence of insufficient air for complete oxidation, the antimony passes practically entirely to the volatile oxide Sb_2O_3, which may be sublimed by suitable methods and then reduced to metal and refined.[1]

Roasting of certain ores in preparation for magnetic separation.—In the treatment of complex zinc, lead, iron sulphide ores, magnetic separation plays an important part. The zinc sulphide, sphalerite, may be separated from pyrite and marcasite if the ores are first roasted in a proper manner. The object of the roasting in this instance is to convert the pyrite or marcasite into either the magnetic sulphide of iron, pyrrhotite, or into the still more magnetic oxide, magnetite. When properly crushed and sized, ore, containing pyrite and marcasite, is roasted with air, sulphur is driven off as SO_2 and the non-magnetic pyrite is changed superficially to pyrrhotite. If the sulphur is driven off completely magnetic oxide of iron results, Fe_3O_4. If the roasting is carried still further, the iron passes to the very feebly magnetic oxide, Fe_2O_3. Pyrite and marcasite begin to lose sulphur and change over into the magnetic sulphide at 370° C. At 600° C. the zinc sulphide begins to ignite and lose sulphur. Therefore, the roasting must be carried on between these two temperatures. Below 400° to 460° C., pyrite will not become thoroughly magnetic, so

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[1] Wang, Antimony, Its Chemistry and Metallurgy, p. 7 (1909).

that the actual temperature of the roast must be very close to 600° C. One of the objects of roasting for the purpose of magnetic separation is to get material of uniform permeability, viz., of uniform magnetism, so that a clean separation may be effected. It is desirable for this reason to roast sized material only, since the roasting and magnetization take place from the surface inward, and in a mass of material containing a large range of coarse and fine particles the finer sizes will be over roasted while the coarser ones will be insufficiently so. If, during the roast, much of the iron has been converted into Fe_2O_3, it may be turned back into the magnetic oxide, Fe_3O_4, by working the furnace reducing. The magnetic oxide is black, while the non-magnetic oxide is red.[1]

2. SMELTING. — Smelting is that metallurgical operation whereby ores or furnace products are reduced to the molten condition with or without the addition of fluxes. During the operation complicated reactions may take place with the resultant production of a metallic alloy or metal, matte, speise, and slag. The general nature of the reactions during smelting may be either reducing, oxidizing or neutral; when no reactions of any significance take place the operation may be termed "melting." In order to produce fluid products in the furnace it is frequently necessary to add material to the ore or furnace products which by their combination with the same produce fluid compounds. Such material is known by the general name of flux. Thus, in iron smelting in the blast furnace, the common flux is limestone which, furnishing lime to unite with the silica and alumina existing as impurities in the iron ore, forms a fluid slag. In lead smelting this same material must frequently be added, as well as iron oxide, either in the form of barren iron ore or valuable ores carrying iron oxides in excess. In the melting and refining of gold and silver bullion, borax is used as a flux which, uniting with the oxides of the base metals formed during the operation, produces a fluid slag. Fluorspar is sometimes used as a flux in certain metallurgical operations, as after once molten it is very thinly fluid and capable of holding in fluid suspension considerable amounts of non-fusible oxides. Almost any substance added for the purpose of producing fluidity in a smelting operation may be termed a flux. In smelting copper-bearing iron sulphides into

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[1] Electro-Magnetic Ore Separation, C. Godfrey Gunther, p. 116 (1909).

matte by the pyritic process, it is necessary to add silica in the form of quartz which may then be termed a flux. The products of the smelting operation are:

a. Slag, usually a waste product and in most instances composed essentially of the silicates of various metallic bases as FeO, CaO, Al_2O_3, MnO, MgO, etc. Slags, however, may also be silicate phosphates or oxides. In the case of lead, copper, and iron-blast furnace smelting, they are silicates. In the case of steel making by the basic open hearth and basic Bessemer processes they may be silicate-phosphates. In the cupellation of lead bullion for its contained silver and gold it will be chiefly a mixture of oxides in which lead oxide predominates. Slags are fully discussed in Chapter VIII.

b. Matte. A matte is an artificial sulphide usually of copper and iron or of copper, iron, and lead, the first being a concentration product in copper smelting and the second a between product in smelting lead ores to lead bullion. It is an intermediate metallurgical product which is further treated by other processes. Aside from its value due to contents in copper, or lead and copper, it serves frequently as a collector of gold and silver in certain forms of smelting; *e.g.*, in a furnace charge in which matte only is produced and not a metal or bullion, the gold and silver in the charge will be collected in the matte. The subject of mattes is fully treated in Chapter IX.

c. Metal or Bullion. This is the metallic product of smelting, produced in certain instances. Thus, in iron smelting by the blast furnace, the valuable product is cast iron, an alloy of iron and carbon containing also certain other substances in smaller amount, such as silicon, manganese, phosphorus, and sulphur. In lead smelting the valuable product is metallic lead containing small quantities of copper, etc., and if there be gold and silver in the ore, practically the whole of these metals. It is known as lead bullion. In smelting oxidized ores of copper or rich copper slags in the blast furnace, the product is an impure metallic copper called black copper, containing about 95 per cent. copper, with the rest as iron, sulphur, arsenic, etc. In bessemerizing copper mattes the product is converter copper, an impure copper containing from 98 to 99 per cent. copper, which undergoes further treatment for purification.

d. Speise. Speise is an artificial arsenide, usually an arsenide of iron containing smaller amounts of other metals. In constitution it is similar to a matte except that arsenic replaces sulphur. It is produced as an unwelcome by-product in lead and copper smelting under certain conditions, also in lead-refining operations, in the smelting of "softening" furnace skimmings. Its treatment is usually difficult. It is further discussed in Chapter IX.

e. Furnace Gases. Furnace gases are produced in great quantities by most types of furnaces and are the products of combustion of the burning of coke or other fuel, and in part decomposition products of constituents in the ore charge. In iron smelting they contain a large percentage of carbon monoxide and are used for fuel in hot-blast stoves to preheat the air going to the blast furnace, and also for power in gas motors driving the blowing engines for the production of blast. The furnace gases from most other smelting operations are without value, except that in pyritic smelting, as in Tennessee, where market conditions warrant it, they may be used in the manufacture of sulphuric acid. The following table gives composition of furnace gases, as taken from the top of the furnace without dilution by air.

TABLE XXXIII. COMPOSITION OF FURNACE GASES.

Gases. Per cent. by Volume	Iron Blast-Furnace			Copper Smelting[1] Pyritic Process			Lead Blast-Furnace[2] Smelting			
	1	2	3	1	2	3	1	2	3	4
Nitrogen	59	60	54.5	84.5	87.0	85.80	74.1	68.6	75.5	75.20
Carbon dioxide	12	15	10	5.42	5.08	5.93	15.2	21.6	18.2	17.20
Carbon monoxide	25	22	27.5	0.02	0.16	0.02	9.7	10.8	5.9	5.40
Sulphur dioxide	—	—	—	8.92	6.64	7.88	—	—	—	—
Oxygen	—	—	—	0.70	0.84	0.35	1.0	0.40	0.40	—
Hydrogen	2	—	3.0	—	—	—	—	—	—	1.50
Methane	2	—	—	—	—	—	—	—	—	0.70

f. Flue Dust. In blast-furnace smelting the air is introduced into the furnace under pressure, causing the furnace gas to escape at the top with considerable velocity which varies in different cases. For this reason it carries off considerable por-

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[1] Sticht, Metallurgie, III, 386 (1906).

[2] Hofman, Metallurgy of Lead, p. 309.

tions of fine furnace charge which is collected in specially provided settling chambers and flues. This material is known as "flue" dust. Its composition usually is similar to that of the furnace charge, although the finer constituents of the charge are represented to a greater degree. Flue dust is produced also by reverberatory smelting and roasting furnaces through the draft. Flue dust is re-treated in various ways, usually by either sintering or briquetting and then smelting.

g. Fume. Under certain conditions of smelting, portions of the charge may be volatilized either in the form of metal, oxides, sulphides, sulphates or chlorides of metal which escape with the furnace gases and flue dust. Thus, in lead smelting a certain portion of the lead and a small portion of the silver suffer volatilization and escape as fume. The lead is volatilized as lead sulphide and oxide, and in part as metallic lead which is converted to oxide by the air. In the bessemerizing of copper-lead-iron mattes in basic lined converters, the lead is volatilized, probably as oxide, and escapes with the gases rich in SO_2 gas from the converter. This fume is sublimed in specially built chambers and flues and bag houses and the lead recovered, largely in the form of sulphate.

Types of Smelting.—*A. Reducing Smelting.* This is a smelting process in which the metal in the ore is reduced to the metallic state by means of a reducing agent which is usually either carbon monoxide or solid carbon in the form of coal or coke. Examples of reducing smelting in the blast or shaft furnace are furnished by iron smelting and lead smelting. The furnace for iron smelting is a shaft from 60 to 100 ft. high, formed of two truncated cones of unequal length which join some distance below the middle of the total height. It is about 12 ft. in diameter at the bottom or hearth, and about 22 ft. at the junction of the cones. It is constructed of refractory fire brick and tiling to resist the high temperatures developed. The charge of the furnace consists of iron ore, limestone (to flux the impurities of the ore), and coke, to furnish the heat. These materials are charged in horizontal layers at the top, as the charge below melts away. Air is blown in near the bottom of the furnace through a number of openings or "tuyeres," so that essentially there is a slowly descending column of charge of solid material and a rapidly ascending column of gases produced by the oxygen of the air acting on the hot coke just above the tuyeres. The oxygen unites with the carbon to form carbon monoxide, since at the temperature at the tuyeres (about 1900° C.), no carbon dioxide can exist. The gases, therefore, immediately above the tuyeres consist practically solely of carbon monoxide and the inert nitrogen of the air plus some hydrogen from the decomposition of water vapor in the air. These rapidly ascending gases passing up the furnace shaft in the upper zones come into contact with the iron ore and reduce the same to metallic iron as already described under *reduction.* The gases usually escape at a temperature of between 250° and 350° C. In the upper portion of the furnace this temperature serves to drive out moisture from the ore, drying the same.

As the charge slowly descends into the lower and hotter parts of the furnace, the melting temperature of the iron carbon mixture is reached at about 1100° to 1200° C., and this then commences to drip over the mass of solid incandescent coke below it into the hearth of the furnace, where it collects. Somewhat further down, where a temperature of 1400° to 1500° C. exists, the earthy bases and silica unite, forming slag, which also drips down through the interstices of the incandescent solid coke below it and collects above the iron in the crucible of the furnace. From time to time the iron and slag are tapped from the hearth of the furnace. The operation is thus a continuous one; ore, fluxes, and fuel being added at the top, while iron and slag are drawn off from the lower part of the furnace.

In lead smelting the general reactions are similar. The furnace is from 18 to 20 ft. high and of rectangular cross-section, 42 to 48 in. wide at the tuyere zone and 12 to 16 ft. long. The amount of fuel used is very much less and the intensity of the reactions is modified in so far as lead is an easily reducible metal, and it is undesirable to reduce iron from its oxides which enter the furnace. Most of the lead in the ore going into the furnace is in the form of silicate, produced by roasting, although some is in the form of the sulphide, or galena. When this latter is present it is reduced by means of the addition of small quantities of metallic iron in the shape of pieces of old castings, etc., or scrap. The reaction taking place is as follows:

$$\mathrm{PbS} + \mathrm{Fe} = \mathrm{Pb} + \mathrm{FeS}$$

the FeS entering into the matte which is formed. In smelting lead ores it is found that some copper is almost always present and it is desirable that this copper should not enter into the reduced lead and alloy with it. Therefore, the furnace is operated to produce a certain amount of matte, or artificial sulphide, since, due to the great affinity of copper for sulphur, any copper present will enter the matte almost completely. The iron sulphide will enter the matte as well as some lead sulphide, but the result is that the lead bullion produced is practically free from copper. The addition of metallic iron as a reducing agent also has the tendency to decrease the amount of lead in this matte.

The products of the furnace are metallic lead or lead bullion, containing 85 to 95 per cent. of the lead and about 96 per cent. of the silver which have been in the ore, a lead-copper-iron matte which contains nearly all the copper in the ore, and slag, the waste product. The furnace gases are permitted to escape after passing through flues and chambers to settle flue dust, and through bag houses to collect the fume.

B. Oxidizing Smelting. — Oxidizing smelting may be carried on in a shaft or blast furnace, as for example, pyritic smelting of copper ores, or in special forms of furnace apparatus such as the bessemer converter for steel and the converter for copper matte, or in any furnace of the reverberatory type wherein the fuel is burned upon a grate separate from the hearth or smelting portion of the furnace. Essentially, the difference between reducing and oxidizing smelting is that in reducing smelting we produce a metal by means of reducing the same from its compounds by carbon monoxide and incandescent solid carbon, while in oxidizing smelting we use the heat generated by the burning of the fuel, whatever that may be, to attain a high enough temperature so that the oxygen of the air may react with the furnace charge to produce the metallurgical result which we desire. In the pyritic smelting of copper-bearing pyrites in the blast furnace, but very small amounts of carbonaceous fuel are used, 1 to 3 per cent. of the furnace charge. The fuel is essentially the iron and part of the sulphur of the pyrites. The furnace is similar to the lead furnace described and the general operations are also similar. Instead of having, as in lead smelting, a mass of incandescent solid coke from the tuyeres upward to a certain height, in this instance, we have a mass of incandescent silica or quartz lying above the tuyeres. The iron sulphide trickling down through the interstices of this mass in an inert ascending atmosphere of sulphurous acid gas and nitrogen reaches a point where the oxygen from the tuyeres strikes it, with the result of the rapid combustion of the liquid sulphide in the presence of silica into ferrous silicate and SO_2 gas, a small amount of iron sulphide carrying the copper sulphide escaping oxidation and sinking into the hearth of the furnace to form the matte.

Another example of oxidizing smelting is that of smelting copper-bearing iron sulphide concentrates partially roasted, with the proper fluxes to form a fluid slag, in the reverberatory furnace. The reverberatory furnace consists of a covered-in hearth upon which the ore charge is placed, and a fire box containing the grate upon which the fuel is burned. The ordinary fuel is bituminous coal placed in such thickness upon the fire grate that combustible gas is produced, which is carried over into the hearth of the furnace where it burns with the air admitted through doors. The heat acts from above downward to melt the charge. A sufficient excess of air is admitted to furnish oxygen for the reactions, which, briefly, are as follows:

The roasted "calcines" contain ferric oxide, iron sulphide (FeS), cuprous sulphide (Cu_2S), cuprous and cupric oxides (Cu_2O, CuO), some metallic copper, certain earthy bases and silica.

$$3\,Fe_2O_3 + FeS = 7\,FeO + SO_2$$

$$Cu_2O + FeS = FeO + Cu_2S$$

$FeO + SiO_2 = 2\,FeO{\cdot}SiO_2$ (slag) unites with other silicates.

If any copper passes to the silicate it is reduced again to sulphide as follows:

$$Cu_2O + SiO_2 = Cu_2O \cdot SiO_2$$

$$Cu_2O{\cdot}SiO_2 + FeS = Cu_2S + FeO \cdot SiO_2$$

Metallic copper in the presence of air is changed to sulphide.

$$2\,Cu + O + FeS = Cu_2S + FeO$$

The iron sulphide in excess of the above reactions, and that not oxidized during the smelting, unites with the cuprous sulphide to form matte. It is evident that the further these reactions are carried on by prolonging the time of smelting the more FeS will be oxidized and the more slag formed and the less matte, but this of higher grade in copper. The matte produced in this way is further treated in the copper converter.

A further example of oxidizing smelting is the process of cupellation. The cupellation of lead containing gold and silver for the recovery of these latter metals is carried out in a cupeling furnace, which essentially is a small reverberatory furnace with a removable hearth, the fuel, usually wood or coal, being burned as before upon a separate grate and the flame therefrom admitted to the hearth or *test*, so called. The lead bullion is placed upon the "test" and the fire urged so as to melt the same. When molten, the temperature is raised to approximately 950° to 1000° C., and an air blast turned on the surface of the molten lead. The molten lead oxidizes to litharge on the surface. This litharge in turn carries oxygen to any other base metals which may be in the lead in smaller quantities, such as copper, etc., oxidizing the same. The litharge and the other oxides form a molten oxide slag which is allowed to flow from the surface of the lead and collected in pots. A comparatively small part of the litharge volatilizes. Eventually all of the lead is oxidized to litharge, leaving buttons of metallic silver and gold alloy on the hearth, these metals not oxidizing under the conditions the work is carried on.

Another form of oxidizing smelting is that known as the bessemerization of copper matte in a type of bessemer converter.[1] The converter is named after Sir Henry Bessemer, who invented this type of furnace for the production of steel. It was later adapted to the production of copper from mattes by John Halloway, and first with success by M. Manhes in France. The converter for copper mattes in its present form consists of a horizontal cylindrical steel shell supported on roller bearings to permit of its partial revolution about its longitudinal axis. It is thickly lined with either a siliceous refractory material such as gannister or a quartzose ore, or with magnesite brick, a basic refractory material. It is provided near the bottom with several tuyeres through which air is forced under pressure. Taking as an example the siliceous lined converter, the operation is briefly as follows: It is thoroughly preheated by burning wood within it, cleaned of ashes, then revolved to such a position that the

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[1] James Douglas, Trans. Inst. Min. and Met., Vol. VIII, p. 2. C. Offerhaus, Engineering and Mining Journal, LXXXVI, 747.

tuyere openings will be free from the charge of molten matte poured into it from a ladle. After it has received its charge of molten matte the blast is turned on with a pressure of from 3 to 10 lb. per square inch and the converter revolved back so as to submerge the tuyeres. The air is forced through the molten matte and the following reactions take place:

$$xCuFeS + O = FeO + SO_2 + yCuFeS.$$

This proceeds until all of the iron sulphide is converted into FeO, the FeO uniting as fast as formed with the silica of the lining as follows:

$$2\,FeO + SiO_2 = 2\,FeO{\cdot}SiO_2$$

It must be understood that as long as any iron sulphide remains, copper is practically protected from oxidation by the reactions quoted under "reverberatory oxidizing smelting." When the iron is about converted into silicate, the slag is poured and the "blow" continued, when this reaction takes place:

$$2\,Cu_2S + 3\,O_2 = 2\,Cu_2O + 2SO_2$$
$$Cu_2S + 2\,Cu_2O = 6\,Cu + SO_2$$

This reaction begins at about 450° C.[1] with no partial pressure of SO_2 and is very rapid at the temperature prevailing in the converter at this stage, viz., from 1150° to 1200° C. When it begins there is a large mass of Cu_2S from which the oxide forms, and it is essential that the speed of the reaction be high, since if Cu_2O accumulates it will pass into the slag. Metallic copper is thus produced by oxidation. This metallic copper, as soon as formed, sinks through the molten matte charge and collects in the bottom of the converter below the level of the tuyeres, so that it is not chilled by being struck by the cold blast entering the converter. When all of the matte is converted into copper and slag, the converter is revolved to clear the tuyeres and the blast stopped, the second slag poured, and the copper cast into ingots. The heat for carrying on the operation is furnished by the combustion of the iron and sulphur.

C. Electric Smelting. — The development of the electric furnace for smelting operations has been rapid within recent years. The most prominent example of electric smelting is that by means of which aluminium is produced in large quantities. The fur-

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[1] F. O. Doeltz und C. A. Graumann, Metallurgie, IV, 421 (1907).

nace[1] for the reduction of aluminium consists essentially of an iron casting which is thickly lined with carbon in which is shaped a bed to hold the fused electrolyte and the reduced aluminium. The electrolyte consists of the mineral cryolite, a fluoride of sodium and aluminium (Na_3AlF_6) to which some aluminium fluoride is added. The melting-point of this cryolite is 1000° C., and becomes lowered on the additon of purified bauxite (Al_2O_3), the aluminium ore. At about 950° C., cryolite will dissolve 20 to 25 per cent. of its weight of Al_2O_3. Into this molten bath dip 48 heavy carbon rods 3 in. in diameter and 15 in. long, which serve as the positive electrodes for the electric current, while the lining serves as the negative electrode. The passage of the current, which is a very heavy one at low voltage (each rod carries 200 amperes, the total voltage being 5.5 volts), reduces the alumina dissolved in the bath to aluminium, which sinks to the bottom and is tapped from the furnace, while the oxygen passes to the positive electrodes or anodes, uniting with these to form carbon monoxide, which escapes. The anodes have to be frequently renewed. The proper composition of the electrolyte is important. The refined alumina is added from time to time to the electrolyte as aluminium is reduced from the bath. The bauxite ore must first pass through a refining process before it can be made into aluminium. The refining process consists of mixing the calcined bauxite with enough carbon to reduce the impurities contained therein, such as iron and silicon. The reduction and purification is effected in a carbon and bauxite lined electric furnace, with a carbon block for the bottom, which serves as one of the electrodes. The current is adjusted to give a working temperature of 3000° to 3500° C., so that only the impurities are reduced, which collect in the bottom of the furnace as a melted alloy of iron, silicon, and titanium, leaving a pure fused alumina suitable for the manufacture of aluminium. It will be noted that this type of electric smelting is essentially an electrolysis, the reduction of aluminium from its compounds being accomplished by the electric current without the intervention of carbon as a reducing agent. In other electric furnaces, however, the electric current may be used solely for the generation of heat to carry on the process, the actual reduction taking place by means of carbon. In general, all metallurgical reactions which require very high temperatures,

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[1] J. W. Richards, Mineral Industry, XIV, 13 (1905).

such as the production of ferro-silicon, ferro-manganese, ferro-tungsten alloys, etc., are made in the electric furnace. Electric furnaces have recently been successfully applied in steel making.

3. Refining and Parting. — Refining is that metallurgical operation whereby crude metals or alloys are separated from impurities, and pure metals or alloys of definite composition produced. Refining is usually an oxidation operation if it be carried on by smelting, but it may also be an electrolytic process carried on by means of aqueous solution electrolytes or by fused electrolytes. The following cases of refining illustrate the process: Reasonably pure copper not containing gold and silver may be refined into pure copper in the reverberatory furnace by an oxidizing smelting. The molten copper in the furnace is rabbled, *i.e.* is stirred and worked by means of long iron tools so as to facilitate the formation of cuprous oxide, Cu_2O. This cuprous oxide diffuses through the molten copper and part of it gives up its oxygen to impurities such as arsenic, antimony, iron, bismuth, etc., which are converted into their oxides and pass completely to the slag, as iron, or in part to the slag and in part to the volatile state, as arsenic and antimony. When this operation has proceeded for a sufficient length of time and the mass of copper becomes more or less saturated with cuprous oxide, the "fining" slag is skimmed and the copper is "poled." This poling consists of working through the molten copper with long poplar wood poles, the gases produced thereby again reducing the cuprous oxide in the copper to a small amount. When the operation is completed, which is usually determined by taking sample bars and examining their appearance and fracture, the copper is cast into market shapes. In the case of copper which contains gold and silver, the refining takes place by electrolysis. The copper is cast into "anode" plates which are hung in rectangular wooden tanks alternating with thin sheets of pure copper called the "cathodes." The tank is filled with a solution of copper sulphate acidulated with sulphuric acid. The copper anodes are connected with the positive pole, all of the connections within the tank being usually in parallel. The anode is decomposed and under the conditions of composition of electrolyte and current prevailing, deposited practically pure on the cathode, while all the impurities of the anode, including the gold and silver, sink to the bottom of the tank in the form of

"anode mud," which is later removed and further refined into gold, silver, etc. The cathodes, when fully grown, are removed and melted down in a reverberatory furnace and cast into market shapes.

Gold bullion containing some silver and impurities, such as copper, lead, bismuth, etc., may be refined by melting in clay crucibles and passing through the same a stream of chlorine gas. The chlorine converts the silver and other constituents into chlorides which rise to the top and collect as a fused mass, which is removed. This carries some gold with it and is further treated by melting with a certain percentage of sodium bicarbonate, which will precipitate a rich gold-silver alloy. Silver is recovered from the chlorides. The refined gold is poured into molds and is sufficiently fine for coinage. Gold may be refined also in a similar way by blowing air through it in the molten state and adding borax at the top to take up the oxides of the base metals produced, forming borate slag. Silver cannot be removed in this way.[1]

"Parting" is a refining process applied to the separation of gold from silver. Several processes are in use. In the sulphuric acid process the bullion, which should contain at least 2 parts of silver to 1 of gold, is granulated and boiled in cast-iron pots with concentrated sulphuric acid, the operation being repeated several times. This converts the silver into sulphate and leaves the gold as finely divided metallic gold. The latter is thoroughly washed with acid and finally with distilled water and melted into bars, while the silver sulphate is reduced by one of several methods and melted and cast into pure silver bars. Electrolytic parting processes for gold and silver bullion are also in use.

4. DISTILLATION AND SUBLIMATION.— Distillation is a metallurgical process whereby a metal is converted into its vapor which is conducted to another part of the furnace, where it is "condensed" if it collects into the liquid form, or "sublimed" if it passes directly from the vapor into the solid form without going through the intervening liquid condition. In the general sense, "distillation" embodies both the vaporization from the liquid state and subsequent condensation of the metal again to liquid, while sublimation embodies the vaporization from the solid state

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[1] T. K. Rose, Trans. Inst. Min. and Met., XIV, 378, 1905, "Refining Gold Bullion and Cyanide Precipitates with Oxygen Gas."

and the subsequent sublimation to the solid state again. Reference to the physical laws which govern distillation and sublimation have been made in the chapter on physical properties of metals, under "Vapor Tension." Examples of distillation in metallurgy are the recovery of mercury from its ores whereby the ore, which is usually cinnabar (HgS), is heated in retorts or furnaces with free access of air, distilling the mercury as vapor, which is cooled to its condensing point and then caught as liquid mercury in suitable receivers. Zinc is also obtained by distillation, and reference to the process has been made in earlier parts of this chapter.

In some smelting operations, one of the products is "fume." Thus, in lead smelting in the blast furnace a portion of the lead, 3 to 10 per cent., is volatilized in the furnace in the form of lead oxide and lead sulphide, with arsenic and antimony, as As_2O_3 and Sb_2O_3, bismuth, etc. These vaporized compounds of the metals pass with the furnace gases through the flues and dust chambers and thence out through the stacks. In the flues and chambers, when the temperature is low enough, they sublime into finely divided solid material called "fume." This fume, however, is in many cases so exceedingly finely divided that instead of completely settling out of the furnace gases and collecting in the flues and chambers, it is carried out of the stack with the gases. To prevent this it is necessary to filter the gases through long cylindrical cotton or woolen bags, sufficient suction being induced by draft fans, the cloth filtering out all fume and permitting practically only gases to escape into the atmosphere. This fume is then resmelted in a manner dependent on its composition. Fume condensation of this type plays important parts in the metallurgy of lead and zinc.

5. Solution and Leaching. — In the metallurgy of copper, and more particularly in that of gold and silver, there are processes in which the metals are recovered by dissolving them from their ores by means of aqueous solutions. Thus, in the extraction of gold from certain of its ores by means of the cyanide process, crushed ore is submitted to the action of dilute cyanide solutions (from 0.05 to 0.5 per cent. of KCN or $NaCN$), which acts on the gold and silver, causing these metals to pass into solution as potassium auro-cyanide ($KAu(CN)_2$) and potassium silver cyanide ($KAg(CN)_2$) or the corresponding sodium salts,

while other substances in the ore are but slightly acted upon by the cyanide solution under the existing conditions. The solution contains also a small percentage of lime and caustic alkalies which protects the alkaline cyanide from destruction by certain acid salts in the ore, the decomposition products of sulphides, such as pyrrhotite, etc. Usually, the solution is passed continuously through the ore in tanks, this filtering process being called "leaching." Before solution of the gold and silver can be effected it is necessary that the ore be crushed to such size that the gold or gold and silver minerals be liberated from the enclosing gangue of the ore so as to be readily attacked by the solutions. If the ore contain any substances such as clay or other hydrated minerals which during this crushing operation may become very finely comminuted and form impervious hydrogels with water, it will become impossible to filter or leach solution through the crushed ore, owing to the presence of these finely divided hydrated minerals or slimes which clog filtration. It is therefore necessary to separate the granular, hard portions of the ore, or sands, from the very finely divided hydrated mineral portions or "slimes," and treat the two products separately. The sands are treated as before by leaching in tanks, while the slimes are treated by means of vacuum filtration or filter pressing.

It is to be noted that for effective solution the solvent must be carefully chosen to be one that does not indiscriminately attack all the constituents of the ore but only those which it is desired to extract. Thus, the effect of potassium cyanide solution on most of the ordinary minerals present in gold and silver ores is negligible, especially if a certain amount of lime or caustic alkaline salts be in the solution at the same time.

Certain copper ores are treated by a hydro-metallurgic process, the oxidized copper minerals therein being dissolved out by means of dilute sulphuric acid. In order to have this process applicable it is essential that minerals which are attacked by sulphuric acid be absent, or else that they be converted into non-soluble form by some operation as roasting. At Rio Tinto, Spain, pyritous ores containing copper as chalcocite (Cu_2S) are permitted to oxidize in heaps, converting the copper into sulphate, which is then leached out by pumping hot acidulated liquors from previous similar operations over the heap.

6. Precipitation. — Precipitation is the recovery from solution of the valuable metal contained therein by means of some chemical agent. Thus, in the cyanide process, the gold in solution is precipitated by means of zinc thread or zinc dust, the zinc in part going into solution to replace the gold precipitated. Copper from sulphuric acid solutions is precipitated by passing them over a large amount of scrap iron, the copper precipitating in the metallic form, while the iron goes into solution as sulphate.[1]

In the extraction of gold from roasted ore by means of chlorine solution, the gold is dissolved as chloride and is precipitated from solution by means of either sulphurous acid gas (SO_2), hydrogen sulphide or ferrous sulphate, the operation being carried on in specially designed apparatus. One principle to be noted in the precipitation of metals on a large scale metallurgically is that the precipitant must be cheap and in a manner act selectively only on the metal or metals to be precipitated, so that the precipitate may be as pure as possible.

7. Liquation. — Liquation[2] is that operation whereby certain alloys or furnace products are melted in a furnace at carefully regulated temperature, causing them to separate into two or more distinct layers of different composition, due to their relative non-solubility in each other at the prevailing temperature, and their difference in specific gravity, thus affording means of their separation. All the layers may be molten, or one may be solid, in the form of a "dross." Thus, in "drossing" lead bullion in preparation for desilverization,the lead is melted and kept at a comparatively low temperature; the small amount of copper contained therein rises to the surface probably as sulphide (Cu_2S) with the nickel and cobalt and some iron and a little arsenic, mixed mechanically with lead and lead oxide. This scum or dross is skimmed off, leaving the main bulk of the lead relatively pure. Liquation also takes place in certain alloys or furnace products in cooling through the freezing range. The principles of this subject are thoroughly covered by the chapters on physical mixtures and on alloys. As an example, if to lead containing silver a comparatively small amount of zinc be added in the molten state and thoroughly stirred in, the silver will combine with the zinc to

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[1] C. H. Jones, Wet Methods of Extracting Copper at Rio Tinto, Spain, T. A. I. M. E., XXXV, 3 (1905).

[2] K. Friedrich, Einiges über das Saigern, Metallurgie, III, 13 (1906).

form an intermetallic compound, thus abstracting it from its lead alloy. If the mass of metal be now cooled to somewhat above the melting-point of lead, the solid zinc-silver alloy being lighter than the lead, will rise to the surface by liquation and can be skimmed from the lead. The method affords a ready, means of separating silver from lead, the small amount of silver diffused through a great quantity of lead being taken up by a small amount of zinc and very highly concentrated. The products of this operation are, however, by no means pure lead or a pure zinc-silver alloy, since some of the zinc will be retained by the lead in solution and considerable lead be found in the zinc-silver alloy.

Another case of liquation is that afforded by the Pattinson process. If lead containing from 0.5 to 1.0 per cent. silver per ton be melted in large iron kettles and then cooled to between 327° C., the melting-point of lead, and 304° C., the melting-point of the eutectic between lead and silver, which occurs at lead 96½ per cent. and silver 3½ per cent., then during this cooling practically pure lead will freeze out, the silver concentrating in the liquid mother metal. When a certain temperature is reached, about 310° to 312° C., the still liquid mother metal is tapped from the kettle. The maximum enrichment possible by this process of liquation is 3½ per cent., and in practice about 2½ per cent. The operation must be carried on between the temperatures above mentioned. By referring to page 101, and Fig. 34, to the lead-silver series, it will be seen that the process is a case of the freezing out of excess metal, viz., pure lead, the silver passing into the mother metal which concentrates towards eutectic composition. In the actual carrying out of the process the frozen lead crystals are removed and again liquated, the same being done to the mother metal. The silver in the enriched silver-lead alloy is recovered finally by cupellation.

8. Amalgamation. — Amalgamation is that process whereby metallic gold, metallic silver, or chlorides and certain other silver minerals, are brought into contact with liquid mercury and converted into amalgams which can readily be separated from the excess mercury by filtration.[1] Thus, in the metallurgy of gold the ore is finally crushed with water in stamp batteries or other suitable crushing machinery and the resultant pulp induced to flow in a thin sheet over slightly inclined amalgamated copper

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[1] T. T. Read, T. A. I. M. E., XXXVII, 56 (1906).

plates, *i.e.* copper or silver-plated copper plates covered with a sheet of copper or silver amalgam and a film of mercury. Mercury may also be added into the battery with the ore so that any fine particles of metallic gold are immediately brought into contact with it and form amalgam which later collects on the outside plates above mentioned. At certain intervals the accumulated amalgam on these plates is scraped off and squeezed through chamois or canvas which removes the excess mercury and leaves the gold amalgam as a hard, silvery white alloy. This amalgam is further treated, the mercury being distilled therefrom, leaving gold sponge, which is melted into bars. Silver ore containing metallic silver or silver in the form of chloride (AgCl) either as a natural mineral or produced by roasting the ore with salt is ground with mercury in amalgamating pans, the silver forming amalgam which is treated in the same manner as described for gold. Amalgamation is essentially a mechanical process and is based on the formation of definite alloys between gold and silver and mercury, which can be readily recovered from the excess mercury.

9. Flotation Processes. — Certain sulphide minerals in complex ores are subject to heavy losses in ordinary water concentration operations on account of their fine state of division and their tendency to float away in the waste water. This type of loss is called a loss by "sliming." Within recent years the so-called flotation processes have been developed whereby this finely divided mineral may be saved from the "tailings" or waste product of the concentration apparatus. A flotation process[1] is one in which the metallic or sulphide constituent of an ore is caused to float on the surface of a liquid as a scum by means of one of three agents — oil, or a similar substance, bubbles of gas, and surface tension, or by a combination of two or all three of them. If tailings containing finely divided sulphides are treated in vats with dilute sulphuric acid or acid sodium sulphate (saltcake) solution, the fine sulphide minerals will rise and float as a scum on the surface of the liquid while the gangue minerals remain at the bottom of the vat. The essentails of the process are that the acid be hot, about 60° C., and that among the gangue minerals be manganese and iron carbonate to furnish the carbonic acid gas bubbles which attach themselves to the sulphides

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[1] Mining Magazine, London, I, 61 (1909).

and cause them to rise to form the scum. It is stated that carbonates, such as calcite, acted on in the cold, will not answer the purpose. The reason that the gas bubbles attach themselves to the sulphides and not to the gangue minerals is a question of surface tension, such minerals as quartz, etc., being entirely wetted by the solution, affording no place for attachment of gas bubbles, while the sulphides, on the other hand, are practically but little wetted, affording places for the attachment of gas bubbles which cause them to rise to the surface. In the Elmore oil concentration process, crushed ore is brought into contact with a layer of oil on water in a mixing drum, the whole then allowed to flow into a settling box, in which the oil carrying the sulphides is separated from the water and gangue. The oil and sulphides are then separated in a centrifugal machine.

10. MAGNETIC SEPARATION. — Certain metallic minerals may be separated from gangue minerals by means of the action of the magnetic field. The ordinary magnetic minerals, magnetite and pyrrhotite, are readily separated from their gangue minerals by ordinary magnetic concentration. It is found, however, that many other minerals possess magnetic permeability to a slighter but variable degree, so that in very strong magnetic fields separation of minerals may be brought about which are ordinarily not acted upon by the magnet.

CHAPTER VIII

SLAGS

A SLAG is one of the products resulting from the fusion, under either oxidizing, neutral, or reducing conditions, of various kinds of ore, or certain intermediate metallurgic products with or without fluxes, and is usually either: first, a silicate of earthy and other bases; second, a phosphate, or a mixed phosphate and silicate; third, oxides of various bases, or mixed oxides and silicates; fourth, or any of the above with an admixture of fluorides. The slag is usually the waste product of the furnace and is separated from the valuable product such as the metal, alloy or bullion, matte (artificial sulphides of certain metals), etc., in a hot fluid, or semifluid condition by means of specific gravity separation. Slags from certain operations, viz., those obtained by cupellation of lead bullion, etc., are not free from valuable metallic contents and are retreated, and are thus classified as an intermediate metallurgic product. Slags from certain metallurgic operations are valuable intrinsically for other purposes, as certain iron-blast furnace slags, from which Portland cement may be manufactured, or those obtained from the basic Bessemer steel process, and at times from the basic open-hearth steel process, which are valuable for fertilizing purposes, owing to their phosphoric acid contents. In certain districts where crushed rock is costly, broken slag has also been used for concrete construction and railroad ballast, and granulated slag has been used for the latter purpose, but with doubtful results owing to its non-packing properties. Slag has also been cast into paving blocks and used for paving purposes. The best slags for the purpose are the more basic stony slags, as the more siliceous slags splinter readily and break into sharp chips. The silicate slags are by far the most important and are most fully treated in this chapter.

THE MINERALOGICAL NATURE OF SLAGS.—The occurrence of artificial crystallized minerals in *slags* has been long familiar to metallurgists,[1] but more particularly to mineralogists, and the older literature contains many examples of the description and in not a few cases the identification of the artificial minerals with natural species. It is due, however, to J. H. L. Vogt, in the main, that practically all slags have been identified with mineral species. Broadly, it may be stated that the formation of minerals in silicate magmas at ordinary pressures, as is the case in metallurgic work, is determined by the *chemical constitution* of that magma. The minerals are formed by the action of chemical equilibria of the chief constituents, viz., by the law of "mass action." Such factors as time of cooling, temperature to which the molten mass is heated, etc., play practically no part in the formation of the minerals.

There is a large number of hypothetical hydrates of silica which are possible of existence, and a considerable number of the silicate minerals are probably salts of these hypothetic acids, but of most importance by far are the two silicic acids which have been isolated, namely, ortho-silicic acid, H_4SiO_4 or $2\,H_2O{\cdot}SiO_2$, and the meta-silicic acid, H_2SiO_3 or $H_2O{\cdot}SiO_2$. Practically all of the minerals found in slags are salts of these two silicic acids. Only one mineral in slags is known which corresponds to the hypothetic silicic acid — H_6SiO_5 or $3\,H_2O{\cdot}SiO_2$, a sub-silicate, and only one which corresponds to the hypothetic acid — $H_8Si_3O_{10}$ or $4\,H_2O{\cdot}3SiO_2$, a sesqui-silicate. The following table shows the nomenclature adopted for the classification of the slags and minerals found in slags.

TABLE XXXIV. CLASSIFICATION OF SILICATES.

Ratio $\frac{0 \text{ in Acid}}{0 \text{ in Base}}$	Formula		Metallurgic Nomenclature	Chemical Nomenclature
	RO Base	R_2O_3 base		
$\frac{2}{3}$	R_3SiO_5	R_2SiO_5	Sub-silicate[2]	
1	R_2SiO_4	$R_4Si_3O_{12}$	Singulo-silicate Mono-silicate	Ortho-silicate
1.5	$R_4Si_3O_{10}$	$R_8Si_9O_{30}$	Sesqui-silicate	—
2	$RSiO_3$	$R_2Si_3O_9$	Bi-silicate	Meta-silicate
3	$R_2Si_3O_8$	$R_4Si_9O_{24}$	Tri-silicate	—
4	—	—	Quadri-silicate	—

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[1] See a bibliography of the subject, "Grundzüge der Sideralogie," H. F. v. Jüptner, I (1900), p. 304.

[2] There may be many other "sub-silicates."

The classification is based on the relative amounts of oxygen in the acid and base radical of the salt. Thus in the silicate $MgO \cdot SiO_2$ or $MgSiO_3$, the oxygen in the base, MgO, is to the oxygen in the acid, SiO_2, as 1 is to 2. The mineral is therefore a bi-silicate or a meta-silicate. In the mineral $2MgO \cdot SiO_2$ or Mg_2SiO_4, the oxygen in the base, MgO, is to the oxygen in the acid, SiO_2, as 1 is to 1. The mineral is therefore a mono-silicate or an ortho-silicate. The sesqui-silicate, ratio $\frac{\text{O in acid}}{\text{O in base}} = \frac{1.5}{1.0}$, is probably a mixture of mono-silicate and bi-silicate, as follows: $(R_2SiO_4) + 2\ (RSiO_3) = R_4Si_3O_{10}$. The sub-silicate in the above table is but one of many possible. Any slag will be termed a sub-silicate when the above ratio falls below one. In the example above, the ratio is $\frac{2}{3}$.

From the analysis of a given slag the oxygen ratio can be readily computed. This may coincide with the exact figures above stated, but usually will give a ratio between two types; thus we may get a ratio of 1.3 which will lie between a mono- and a bi-silicate, then this slag will be a mixture of *definite minerals* and the minerals present will be mono- and bi-silicates. The kind is dependent upon the bases present; in other words the mineral *entities* present in the slag are definite mono- or ortho-silicates and bi-silicates or meta-silicates, or possibly a sequi-silicate.

Vogt[1] gives the following as the chief minerals found in slags and states that practically *all* slags of metallurgy are definite mineral compounds or mixtures of minerals, the mineral or minerals found being solely a function of the chemical composition of the siliceous magma produced in the furnace. (See table on page 248.)

Other silicates found, but not very important, are: leucite, $(KNa)\ AlSi_2O_6$; nepheline, $(NaK)\ AlSiO_4$; sillimanite, Al_2SiO_5; cordierite, $(MgFe)Al_4Si_5O_{16}$; tridymite, SiO_2; garnet; hauynite; sodalite; etc.

Of oxides, aluminates, and ferrates, the following are found:

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[1] J. H. L. Vogt, "Studier over Slagger" Bih till K. Svenska Vet. Akad. Handlingar, 1884. "Beiträge zur Kenntniss der Gesetze der Mineralbildung in Schmelzmassen u. s. w." "Archiv. für Mathematik og Naturvidenskab, Christiana, Vols. XIII, XIV, 1888–90." Die Silicatschmelzlösungen, I. Uber die Mineralbildung in Silicatschmelzlösungen; II. Über die Schmelz-punkt-Erniedrigung der Silicatschmelzlösungen, Christiana, 1903–04.

TABLE XXXV. MINERALS FOUND IN SLAGS

Silicate Degree	General	Name of Mineral	Composition
Mono or Ortho-Silicates	Members of the *Olivine* or *Chrysolite* series Orthorhombic R_2SiO_4	Forsterite	Mg_2SiO_4
		Fayalite	Fe_2SiO_4
		Knebelite	$(Fe,Mn)_2SiO_4$
		Tephroite	Mn_2SiO_4
		Iron monticellite	$FeCaSiO_4$
		Monticellite	$MgCaSiO_4$
		Glaukochroite	$MnCaSiO_4$
		Iron-lime Olivine	$(CaFe)_2SiO_4$
		Olivine	$(MgFe)_2SiO_4$
		Zinc-bearing Olivine	$(RZn)_2SiO_4$
	Willemite series	Willemite	Zn_2SiO_4, $(ZnFe)_2SiO_4$
Meta or Bi-Silicates	Members of *Pyroxene* series. $RSiO_3$	Enstatite (orthorhombic)	$MgSiO_3$
		Hypersthene (orthorhombic)	$(FeMg)SiO_3$
	Monoclinic	Augite (aluminous pyroxene)	$Ca(MgFe)(SiO_3)_2 + (MgFe)(AlFe)_2SiO_6$
		Wollastonite?	$CaSiO_3$
	Triclinic	Rhodonite	$MnSiO_3$
		Babingtonite	$(CaFeMn)SiO_3, Fe_2(SiO_3)_3$
	Members of a new artificial series. Hexagonal. (Tetragonal?)	Mineral corresponding to Wollastonite	$CaSiO_3$ also $(CaZnSrBaPb)SiO_3$
	Members of a new artificial series (*Monoclinic?*)	Biotite	$MgSiO_3$, $FeSiO_3$ $(KNa)_2(MgFeCa)_2Al_2Si_3O_{12}$
Sesqui-Silicates and Sub-Silicates	Members of the *Melilite series* (Tetragonal)	Melilite	$(CaMgNa_2)_6(AlFe)_2Si_5O_{19}$
		Ackermanite	$Ca_4Si_3O_{10}$
		Gehlenite	$(CaMgFeMn)_4Si_3O_{10}$ $Ca_3Al_2Si_2O_{10}$
	Feldspar series (Ca in anorthite may be replaced by Sr, Ba, Pb.)	Anorthite = An	$Ca_2Al_4Si_4O_{16}$
		Albite[1] = Ab	$Na_2Al_2Si_6O_{16}$
		Labradorite	Ab_1An_1 to Ab_1An_3
		Oligoclase	Ab_6An_1 to Ab_3An_1

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[1] Not found, put in here to show its constitution, as it enters into labradorite and oligoclase.

corundum, Al_2O_3; hematite, Fe_2O_3; magnetite, Fe_3O_4: members of the *magnetite-spinel* series (RO,R_2O_3) where R = Mg, Fe, Mn, Zn, Ca; and $R_2 = Fe_2, Al_2, Cr_2, Mn_2$.

Of sulphides, members of the oldhamite-zinc blende troilite (FeS) series, RS, where R = Cr, Mn, Zn, Fe.

Of phosphate-silicates, new artificial phosphates from slags, as: $3Ca_3P_2O_8 \cdot Ca_3SiO_5$; $4Ca_3P_2O_8 \cdot Ca_3SiO_5$; which crystallize in the hexagonal system, and $4Ca_2P_2O_8 \cdot 3Ca_3SiO_5$, monoclinic, and $Ca_4P_2O_5$, orthorhombic.

The minerals commonly found in silicate slags are limited to a much smaller number than given in the table and may be summarized thus: hexagonal calcium meta-silicate,[1] ackermanite, melilite, gehlenite, augite, rhodonite, enstatite, hypersthene, the olivine group, anorthite. Other minerals, not silicates, are spinels and sulphides, and in certain slags from steel-making processes — phosphate-silicates. When the silicate degree of a slag goes beyond that of a bi-silicate, it does not form definite mineral compounds in cooling, but congeals largely to *a glass* (solid solution). In some of these higher silicate slags spherulites (incipient crystals), have been observed, but their mineral identity is not established. *Glass* may also be present in slags of lower silicate degree than the above under certain conditions (such as very rapid cooling or when *under cooling* takes place), but is more rare.

Some General Considerations.—It is essential to state here, that while a crystallized mineral may be a definite *chemical compound,* it is by no means necessarily so, and in most cases is not, but that the mineral species may be considered a *mixed crystal* of indefinite composition, varying within certain limits. This mixed crystal may belong to an *isomorphous series,* or to a *morphotropic series,* which series have been discussed in Chapter II. Taking for instance the olivine group of minerals, in the ortho-silicates, we may consider the matter in this form. The bases concerned in this group are MgO, FeO, MnO, CaO, and possibly ZnO. The chemical compounds to be considered are therefore Mg_2SiO_4, Fe_2SiO_4, Mn_2SiO_4, Ca_2SiO_4 (not found in nature and not stable by itself), and Zn_2SiO_4. These, or most all, are isomorphous, and in a crystal are capable of replacing each

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[1] The monoclinic calcium meta-silicate ($CaSiO_3$) or wollastonite is probably not found in slags.

other indefinitely or within certain limits. Starting thus with *pure* Mg_2SiO_4, or perfect forsterite, and with pure Fe_2SiO_4 or perfect fayalite, we have a system as shown in Fig 70.[1]

In this series occur three definite mineral species, viz., forsterite, which may contain a certain amount of Fe_2SiO_4, then olivine which is always composed of Mg_2SiO_4 and Fe_2SiO_4 in varying amounts, and finally fayalite, chiefly or all Fe_2SiO_4, but which may contain certain amounts of Mg_2SiO_4. Further than this, *small amounts* of Mn_2SiO_4, Ca_2SiO_4, or Zn_2SiO_4 may enter into the constitution and *not* change the mineral entity. When, however, these latter bases exceed certain amounts the mineral form is changed. There is a sub-group in this series — the *monticellite group* — in which the molecular ratio of CaO to other bases present is as 1:1, thus $MgCaSiO_4$, a so-called double salt. In this group there is an artificial iron monticellite, $CaFeSiO_4$. In true monticellite, viz., $MgCaSiO_4$, small amounts of Fe and other bases are usually present. An iron-lime olivine, viz., a *mixed crystal*, but not a double salt, in which the relation of CaO to FeO is indefinite, is also found. This explanation will give an idea of the nature of the silicate minerals in slags and brings out the fact that a given mineral species may vary rather widely in composition.

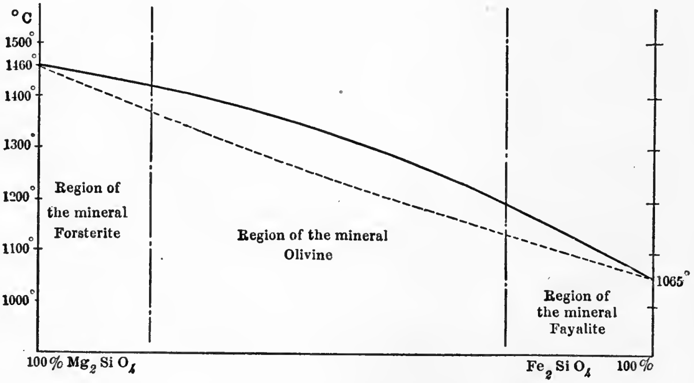

FIG. 70. — The Forsterite-Fayalite series of minerals.

As already stated, the mineral or minerals crystallizing out of

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[1] Vogt, *Ibid.*, I, p. 151.

a molten slag magma will depend on the chemical composition of the magma; if this corresponds closely to that of any in the given list of minerals, *that* mineral alone will result; if it does not correspond, two minerals may form and in some cases three or more minerals may crystallize out during solidification. In Figs. 71 and 72 is shown the relationship between *mineral composition* and *chemical composition* as regards both the degree of acidity and the bases present. That mineral crystallizing out *first* is mentioned, though it may be subordinate in amount, and be followed by another mineral in much larger amount.

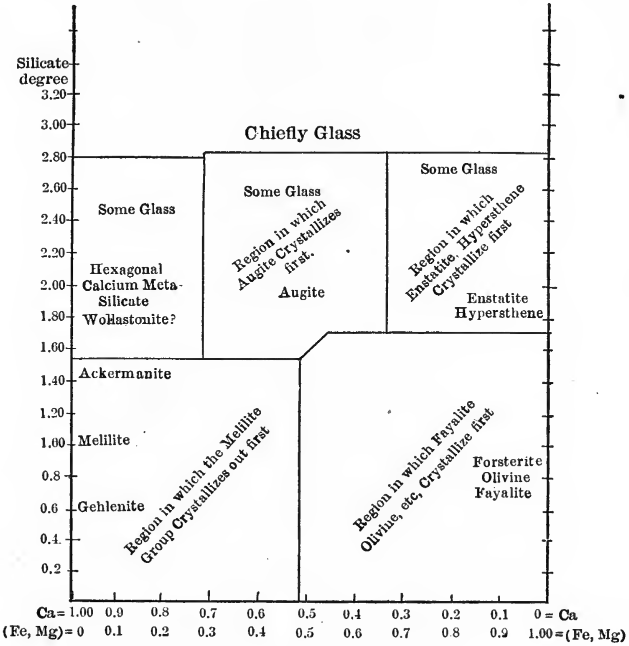

FIG. 71. — Diagram relating the mineral and chemical composition of the Ca, Mg, Fe silicates in slags.

Ortho- and Meta-Silicate. — *The individualization limits, as regards silicate degree, determining the first crystallization of ortho- and meta-silicates respectively.* From a large number of observations (microscopic examinations), this is placed as ranging from 1.55 to 1.70. In the presence of some Al_2O_3 the lower figure, in its absence the higher figure, is to be taken. Thus, if we have a silicate magma above 1.7 in silicate degree, the first mineral to crystallize out will be a meta-silicate, if below this figure the first mineral to crystallize out will be an ortho-silicate.

Which particular ortho- or meta-silicate mineral crystallizes depends upon the bases present. In general, in the ortho- and meta-silicates, Ca acts as one against (Mg, Fe) and also Mn to some extent. Thus the relative amounts of Ca and (Mg, Fe, Mn) determine which particular ortho- or meta-silicate forms; further, the particular base which predominates in the group (Mg, Fe, Mn) determines which particular mineral forms. As regards bases present the silicate magmas may be divided into three groups:

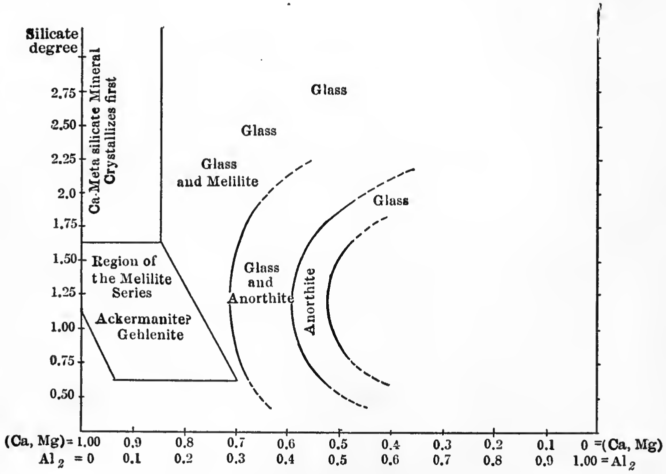

Fig. 72. — Diagram relating the mineral and chemical composition of the (CaMg)-Al_2 silicates in slags.

First. — That in which the bases are Ca as opposed to (Mg, Fe, Mn), with Al_2O_3 from 0.5 to not exceeding 10 per cent.

Second. — That in which the bases are Ca, Mg, Fe, as one group opposed to more than 10 per cent. Al_2O_3.

Third. — That in which conditions exist which cause the crystallization of aluminates, viz., spinel, etc.

The Meta-Silicate Minerals as Determined by the Bases Present. — The limiting conditions in regard to the influence of the various bases in determining the mineral species of this group are depicted graphically in Fig. 73.

A. The base Ca as against (Mg, Fe).

The upper bar shows the ranges of composition within which the particularly named meta-silicates will crystallize out first. The lower bar shows the range in composition possible within the mineral species.

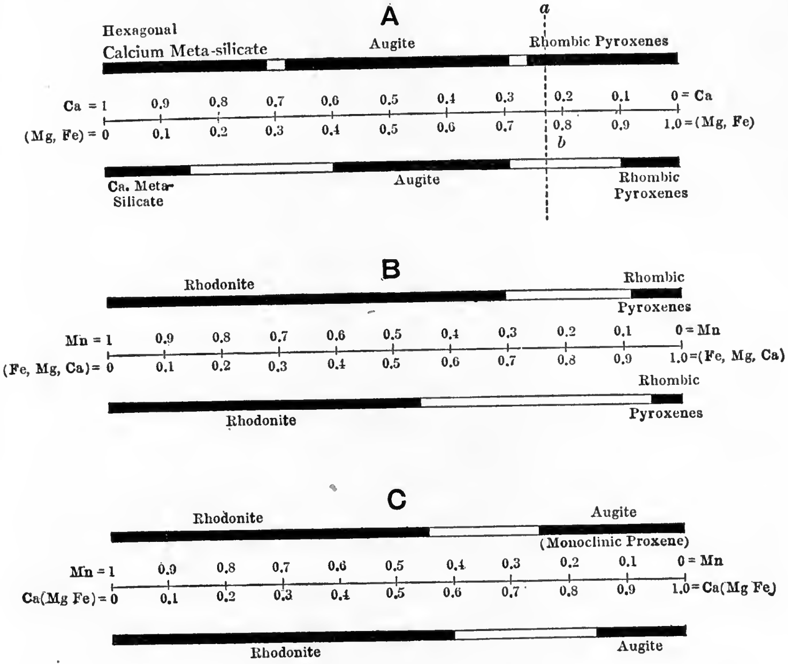

FIG. 73. — The Meta-silicate minerals in slags. Influence of bases in determining mineral species.

Thus, taking the composition indicated by the line — *ab* — .78 (MgFe) and .22 Ca, the first mineral to crystallize out will be a *rhombic pyroxene* (which one, depends on the relative amounts of Fe to Mg) followed by *augite*.

B. The bases (FeMg) with little Ca as opposed to Mn.

The interpretation is the same as for "A."

C. The base Ca with little (MgFe), up to .05 part, as opposed to Mn.

The Ortho-Silicate Minerals as Determined by the Bases Present. — The limiting conditions in regard to the influence of the various bases in determining the mineral species of this group are depicted graphically in Fig. 74.

A. The bases (Fe, Mg, Mn) against Zn.

In this connection it is worthy of note that Zn is usually present in comparatively small quantities in slag and will enter the mineral form of willemite only when iron is practically absent. The only mineral of the *olivine group* capable of taking up zinc in any quantity (see Fig. 74) is fayalite, iron ortho-silicate. As will be seen further on, the presence of appreciable zinc with Al_2O_3 is conducive to the formation of spinel, particularly when some magnesia is present.

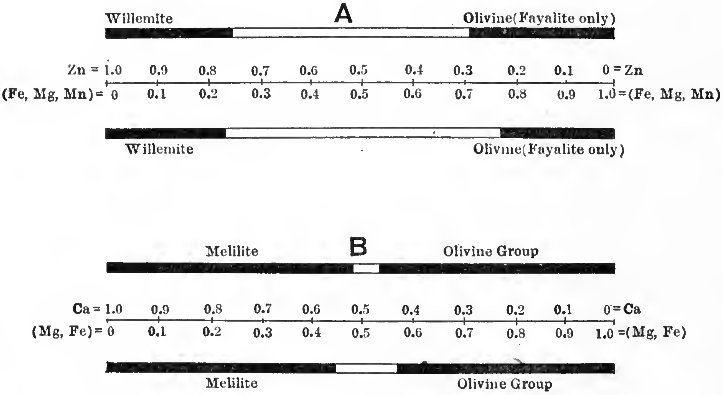

FIG. 74. — The ortho-silicate minerals in slags. Influence of bases in determining mineral species.

B. The base Ca against (Fe,Mg,Mn).

In the presence of little Al_2O_3 (up to 8 per cent.), Fig. 74 graphically depicts the limiting conditions.

The melilite group of minerals consists of *ackermanite, melilite,* and *gehlenite.* Ackermanite is $(CaR)_4Si_3O_{10}$, in which R = Mg, Fe. Gehlenite is $(CaR)_3(Al_2Fe_2)\ Si_2O_{10}$ and melilite is a *mixed crystal* composed of ackermanite and gehlenite in varying proportions, the minerals being isomorphous.

It is thus seen that gehlenite is the mineral into which the alumina enters as a necessary constituent part, and in this way enters into the constitution of *melilite.* When the Al_2O_3 exceeds

8 per cent., the limiting composition between the olivine group and the melilite group shifts to the left, as the presence of Al_2O_3 facilitates the formation of melilite, even though the CaO be decreased.

Melilite is thus not a definite degree silicate, but may range between the silicate degree of ackermanite — 1.5, to that of gehlenite — .66. The melilites identified have a silicate degree ranging from 0.79 to 1.15.

The Melilite Group of Minerals and Anorthite. — The limiting conditions regarding chemical composition for the formation of the *melilite group of minerals and anorthite.*

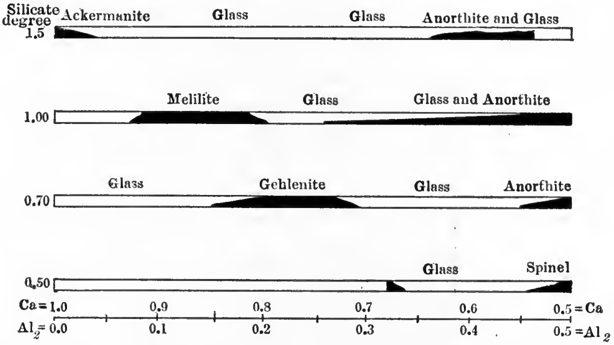

FIG. 75. — The lime-alumina minerals in slags. Influence of bases and silicate degree in determining mineral species. The height in the black areas indicates the relative amounts of crystallized mineral and glass present. The black areas indicate the range of occurrence of crystallized minerals.

The melilite minerals have a greater ratio of $\frac{CaO}{Al_2O_3}$ than anorthite. The accompanying illustration, Fig. 75, shows the limits.

The following is the composition of the minerals:

Ackermanite, $(CaR)_4Si_3O_{10}$, can contain no Al_2O_3; silicate degree 1.5.

Melilite (normal), $(CaR)_7Al_2Si_5O_{20}$, equivalent to 1 ackermanite plus 1 gehlenite. The ratio of ackermanite to gehlenite may vary much from the above figures. Silicate degree = 1.

Gehlenite, $(CaR)_3(Al_2Fe_2)Si_2O_{10}$. Silicate degree = 0.67.

Anorthite, $Ca_2Al_4Si_4O_{16}$. Silicate degree = 1.

In the absence of the R bases, viz. Mg,Fe,Mn), the limiting conditions as regards the individualization of *melilite* or *anorthite* is found in the ratio 0.8 Ca to 0.2 Al_2. In the presence of R bases (Mg,Fe,Mn) up to 11 per cent., the ratio is .49 Ca to .51 Al_2. Thus the presence of R bases aids in the formation of melilite as against anorthite.

In this series the *silicate degree* has great bearing since anorthite is an ortho silicate, while melilite is not a definite degree silicate as above noted, so that anorthite is chiefly formed, the condition of Al_2 to Ca being right, when the silicate degree is 1. When it is less or more than this, gehlenite and melilite form, as is seen from the following tabular statement giving the relation of Ca to Al_2:

TABLE XXXVI. INFLUENCE OF THE SILICATE DEGREE ON THE FORMATION OF MELILITE, GEHLENITE, AND ANORTHITE.

Silicate Degree	Name of Mineral	Ratio of Ca to Al_2
1.5	Ackermanite	1 Ca to 0 Al_2
1.0	Melilite	7 Ca to 1 Al_2
0.67	Gehlenite	3 Ca to 1 Al_2
1.00	Anorthite	1 Ca to 1 Al_2

In silicate magmas of such composition as above, viz., from which the melilite group and anorthite crystallize, certain compositions congeal to *glass* (solid solution), as may be seen by referring to Fig. 75. This is due to a very decided lowering of the melting-point in the neighborhood of the eutectic composition between anorthite and the respective mineral of the melilite group, accompanied by *great viscosity*, preventing the final crystallization of the eutectic mixture, the mass passing to the solid form without crystallization.

On the Conditions Determining the Individualization of Spinel and Corundum in Slags. — Spinel ($RO \cdot R_2O_3$), chiefly an aluminate, *i.e.* a salt in which alumina acts as an acid, forms in those magmas which contain Al_2O_3 above that amount which can enter into the *silicate minerals* that will form, as determined by the total chemical constitution of the magma. The formation of spinels also requires the presence of Mg or Zn. The last particularly is conducive to the formation of spinel.

The Al_2O_3 in such a mixture as the above will be distributed between the silicate mineral and the spinel.

Spinel will crystallize out first, and always at a high temperature.[1] This is a feature which makes the crystallization of spinel in a slag undesirable.

In this connection it is well to point out that in the *meta-silicates*, neither the new meta-silicate group, such as $CaSiO_3$, etc., nor the orthorhombic pyroxenes can contain more than a very small amount of Al_2O_3, but that augite is capable of absorbing a very considerable proportion up to 20 per cent.; the Al_2O_3 therefore goes into the augite molecule, and the more augite that can form, the more Al_2O_3 will be taken up. In the ortho-silicates, and in lower silicate degrees, melilite, through its contained gehlenite constituent, takes up Al_2O_3, as do also gehlenite proper, and anorthite, while ackermanite and the olivine group of minerals take up but very small amounts.

Nature of the Spinel in Slags. — The general formula for spinel is $RO{\cdot}R_2O_3$, in which the R_2O_3 may be Al_2O_3, Fe_2O_3, Mn_2O_3, or Cr_2O_3. We have in slags chiefly the true spinels, $MgO{\cdot}Al_2O_3$, and $(MgCa)O{\cdot}Al_2O_3$ and also $(ZnFe)(Al_2Fe_2)O_4$.

In the following tables are given some analyses of slags in which spinel was formed.

TABLE XXXVII. SLAGS FROM WHICH SPINEL CRYSTALLIZED

Composition	No. 1		2		3		4		5		6		7	
	B	A	B	A	B	A	B	A	B	A	B	A	B	A
	%	%	%	%	%	%	%	%	%	%	%	%	%	%
SiO_2	28.74	36.9	24.92	31.3	27.01	31.3	27.64	30.9	26.46	29.9	30.08	34.3	27.53	30.3
Al_2O_3	25.63	17.5	23.47	14.6	20.13	15.1	22.93	18.4	23.44	19.8	15.13	12.0	22.23	19.6
CaO	27.40	33.1	35.32	42.6	38.93	43.2	35.06	39.1	33.50	37.8	35.46	40.5	34.30	37.7
MgO	13.75	12.5	13.23	11.5	11.09	10.4	12.95	11.6	13.34	12.5	12.33	12.0	13.00	12.4
MnO	—	—	—	—	—	—	—	—	—	—	0.59	0.7	—	—
FeO	—	—	—	—	—	—	—	—	—	—	0.47	0.5	—	—
CaS	2.00	—	2.00	—	2.00	—	2.00	—	2.00	—	5.72	—	2.00	—
per cent. Spinel	17.68	—	17.40	—	10.82	—	9.04	—	8.18	—	6.50	—	6.07	—

NOTE. — Column A gives the composition of the slag before the crystallization of spinel, and column B the composition of the slag after the crystallization of the spinel.

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[1] The crystallization of spinel and sulphides from silicate magmas at high temperatures is due to the decrease of solubility of these substances due to the presence of a "common ion," since silicate magmas are electrolytes, and are ionized to a considerable degree. Vogt, II, *ibid.*, p. 151.

TABLE XXXVIII. IRON-ZINC-SLAGS FROM WHICH SPINEL CRYSTALLIZED

Composition	No. 1	No. 2	No. 3	Remarks
	%	%	%	
SiO_2	20 to 30	35	20 to 25	Slags also contain some PbO, BaO, alkali and some sulphide.
Al_2O_3	1.3–4.3	4–7	8–12	
Fe_2O_3	0.25–0.30	0–0.6	0.6–1.0	
FeO	40 to 50	40–45	37–45	
ZnO	10–18	5–8	8–12	
MgO	8–1.5	a little	a little	
CaO	3–4	"	"	
Per cent Zn spinel	0.5	1.7–1.8	3.5–3.7	

NOTE. — In these slags the formation of spinel is due largely to the presence of Zn, and some Mg.

The following table gives analyses of slags which approach the composition for the crystallization of spinel, but from which it did not crystallize.

TABLE XXXIX. COMPOSITION OF SLAGS APPROACHING CONDITIONS FAVORABLE FOR THE CRYSTALLIZATION OF SPINEL.

Composition	Melilite First, Followed by Augite or by Olivine					Olivine First, Followed by Augite or by Melilite				Glass plus Melilite and Anorthite	
	1	2	3	4	5	6	7	8	9	10	1
Silicate degree	1.46	1.36	1.32	1.03	0.95	1.53	1.33	1.21	1.18	1.05	0.98
Per cent. SiO_2	46.90	46,50	43.90	35.50	36.70	48.90	44.40	42.90	43.80	43.40	39.70
Al_2O_3	6.90	12.90	8.30	9.10	11.80	10.00	8.90	10.00	9.90	29.30	24.10
CaO	33.40	32.10	35.00	34.10	33.50	22.70	24.40	26.40	27.70	15.50	30.30
MgO	9.70	6.80	7.80	5.40	10.10	15.20	11.40	12.30	18.00	8.30	3.20
(FeMn)O	2.00	8.20	3.30	10.50	7.20	2.30	9.60	8.10	0.60	2.90	0.50

On the Calculation[1] of the Amounts of the Various Silicate Minerals Present in a Silicate Magma. — These calculations are approximate only and determine the amount of ortho-, meta- or sub-silicate present. They serve to determine how near any silicate mixture is to a eutectic composition discussed in the following section.

The oxygen ratio of acid to base, viz., $\frac{O_2 \text{ in acid } (SiO_2)}{O_2 \text{ in base } (CaO, Al_3O_3, FeO, \text{etc.})}$ must be first determined. In

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[1] Hans Freiherr v. Jüptner, Grundzüge der Sideralogie, p. 260 (1900).

making this calculation subtract from the O in the base one half the sulphur contents (equivalent to its combining power with oxygen).

Name of Acid or Base		Per Cent of O_2
SiO_2	Silica	53.3
Al_2O_3	Alumina	47.0
CaO	Lime	28.6
MgO	Magnesia	40.0
FeO	Ferrous oxide	22.2
MnO	Manganous oxide	22.2

Let the O in the acid be designated by A (expressed in per cent.).

Let the O in the base be designated by B (expressed in per cent.).

Case I. The silicate degree is above 2.

Then the slag consists of $x(RO{\cdot}SiO_2) + y(2RO{\cdot}3SiO_2)$ and

$$2x + 6y = A \qquad x + 2y = B$$

$$y = \frac{A}{2} - B \quad \text{and} \quad x = 3B - A$$

x and y designating the relative amounts of bi-silicate and tri-silicate in the slag.

Case II. The silicate degree is between 1 and 2.

Then the slag consists of $x(RO{\cdot}SiO_2) + y(2RO{\cdot}SiO_2)$ and

$$2x + 2y = A \qquad x + 2y = B$$

$$x = A - B \quad \text{and} \quad y = B - \frac{A}{2}$$

x and y designating the relative amounts of mono-silicate and bi-silicate present in slag.

Case III. The silicate degree is between 1 and 0.5.

Sub-case 1. In which the ratio of CaO to (MgO + FeO + MnO) is not less than 1: 0.70.

Then the slag consists of $x(3RO{\cdot}SiO_2) + y(2RO{\cdot}SiO_2)$ and

$$2x + 2y = A \qquad 3x + 2y = B$$

$$x = B - \mathrm{A} \quad \text{and} \quad y = \frac{3}{2}A - B.$$

If y is negative, then instead of $2RO{\cdot}SiO_2$, *spinel* is present.

Sub-case 2. In which $\dfrac{\text{CaO}}{(\text{MgO} + \text{FeO} + \text{MnO})}$ is less than $\dfrac{1}{0.70}$.

Then the slag consists of $x(2RO{\cdot}SiO_2) + y(RO{\cdot}Al_2O_3)$, (spinel)

and $\quad 2x = A \qquad\qquad 2x + 4y = B$

and $\quad x = \frac{A}{2}$ and $y = \frac{B - A}{4}$.

Example under Case II.

Slag No. 27 in Table XL. Composition; $SiO_2 = 34.30$; $Al_2O_3 = 0.78$; $CaO = 33.72$; $MgO = 4.68$; $MnO = 0.68$; $FeO = 25.64\%$. Contains Acid—

Oxygen in $SiO_2 = 0.343 \times 53.3 = \qquad 18.28 = A$.

Bases—

Oxygen in $Al_2O_3 = .0078 \times 47.0 = 0.366$
" " $CaO = .3372 \times 28.6 = 9.644$
" " $MgO = .0468 \times 40.0 = 1.870$
" " $MnO = .0068 \times 22.2 = 0.150$
" " $FeO = .2564 \times 22.22 = 5.697 \qquad = 17.727 = B$.

$$\text{Silicate degree} = \frac{\text{O in acid } (SiO_2)}{\text{O in bases } (CaO,\ Al_2O_3,\ \text{etc.})} = \frac{18.28}{17.727} = 1.03.$$

Composition of slag $= x(RO{\cdot}SiO_2) + y(2RO{\cdot}SiO_2)$

$$x = A - B = 18.28 - 17.727 = 0.553$$

$$y = B - \frac{A}{2} = 17.727 - 9.140 = 8.587$$

or $\quad 0.553\ (RO{\cdot}SiO_2) + 8.587(2RO{\cdot}SiO_2)$

or $\quad$ 6 per cent. $(RO{\cdot}SiO_2)$ + 94 per cent. $(2RO{\cdot}SiO_2.)$.

The actual composition of this slag as determined by microscopic examination is 85 per cent. monticellite (olivine) plus some little melilite and a little magnetite. No bi-silicate is present, but the melilite is in this case over 1 in silicate degree, and probably closer to ackermanite than normal melilite. This shows that the calculations can be approximate only, although it is quite close. After the relative amounts of the silicates present have been calculated, the exact mineral present in any group is determined by the relation of the various bases, as has been discussed. It will also be noted that in a number of the slags in table XL *considerable* glass is present, the quantity of which cannot be solved by the calculations outlined. This glass has usually the same composition as the last crystallized mineral, or of the

TABLE XL. SLAGS SHOWING THE RELATION BETWEEN COMPOSITION AND MINERAL NATURE

Silicate Degree	Composition									Minerals Found		
	SiO_2	Al_2O_3	CaO	MgO	MnO	FeO	ZnO	Fe_2O_3	CaS	1st Crystal	2d Crystal	3d Crystal
2.08	55.7	10.95	27.25	2.27	0.42	1.90	—	—	—	Hexag. $CaSiO_3$	—	—
1.73	50.64	3.83	38.10	6.82	0.18	0.17	—	—	0.33	Hexag. $CaSiO_3$	—	—
1.64	48.20	8.41	37.67	0.74	2.23	0.97	—	—	0.83	Hexag. $CaSiO_3$	—	—
2.46	59.24	1.66	20.49	14.25	1.13	1.57	—	—	—	Augite	—	—
2.00	55.60	5.86	24.90	11.07	1.09	1.30	—	—	—	Augite	Rhodonite	—
2.42	58.60	3.70	25.30	7.00	2.60	2.60	—	—	—	Augite	Spherulites	—
1.91	55.20	10.20	15.15	7.20	10.35	0.40	—	—	—	Augite		—
1.56	47.70	5.80	30.71	8.87	5.67	0.54	—	—	0.50	—	—	—
1.92	56.77	5.30	12.20	22.75	1.63	1.66	—	—	—	Enstatite	—	—
1.57	52.30	16.68	6.60	13.26	—	1.06	—	9.42	—	Olivine, Magnetite	Augite, Enstatite	—
1.70	44.72	2.45	1.89	—	25.00	28.00	—	—	—	50% Rhodonite	Fayalite 10% cont. Mn	40% glass
1.50	41.23	2.29	1.19	—	37.00	22.00	—	—	—	30 to 35% Fayalite	50 to 55% Rhodonite	Little glass
1.75	45.61	2.58	2.41	4.65	17.07	27.93	—	—	—	70% Rhodonite		Glass
1.48	46.32	4.57	34.05	10.25	2.68	0.52	—	—	0.76	60% Ackermanite	2% Augite	38% glass
1.42	45.92	6.50	31.85	7.82	5.31	2.85	—	—	—	60% Ackermanite	10% Augite	36% glass
1.39	45.45	4.64	35.25	10.32	3.25	0.73	—	—	0.38	60% Ackermanite	10% Augite	Glass
1.36	46.50	12.90	32.07	6.75	0.58	0.90	—	—	—	Melilite		
0.95	36.71	11.81	33.46	10.12	6.60	0.57	—	—	MnS 3.21	50 to 70% Melilite	2 to 8% Olivine	Glass
1.03	38.34	21.22	29.20	2.44	—	1.98	—	—	0.04	Melilite		
0.79	35.10	27.35	28.14	7.04	0.24	0.75	—	—	—	Spinel	50 to 70% Gehlenite	2 to 8% Olivine
1.05	43.37	29.31	15.48	8.25	2.38	0.50	—	—	—	Melilite	Anorthite	Glass
0.86	32.00	8.30	36.70	2.80	—	18.70		—	—	60–65% Melilite	5% Magnetite	Fayalite
0.86	31.8	8.30	32.70	2.90	—	22.60	—	Na_2OK_2O	—	Melilite	Magnetite	Fayalite
0.98	36.48	7.81	37.26	11.27	2.74	2.00		some	2.40	90% Melilite	Biotite	
1.68	53.20	7.15	17.40	20.39	0.49	0.82	—	—	—	2% Olivine	40–50% Augite	45% glass
1.47	48.50	3.40	20.14	23.79	0.85	2.60	—	—	—	15% Olivine	40% Augite	Glass
1.03	34.30	0.78	33.72	4.68	0.68	25.64	—	—	—	80–85% Monticellite	Magnetite	Melilite
0.92	31.80	5.33	24.59	5.57	29.86	—	—	—	MnS 3.72	Monticellite, Melilite		
—	26 to 35	some	some	some	—	40 to 60	—	71%	—	Fayalite	Magnetite	Glass
—	20 to 30	1.3 to 4.3	3 to 4	.8 to 1.5	—	40 to 50	10 to 18	0.25 0.30	ZnS some	Zinc spinel	Zn bearing Fayalite	
—	35	4 to 7	some	some	—	40 to 45	5 to 8	0.6	ZnS some	Zinc spinel	Zn bearing Fayalite	

eutectic between the two minerals. The calculations serve only as an approximation and should be elucidated and corrected by the data on mineral formation outlined in the previous pages.

Example under Case III.

Slag No. 22 in Table XL. Composition $SiO_2 = 32$ per cent.; $Al_2O_3 = 8.3$ per cent.; $CaO = 36.7$ per cent.; $MgO = 2.8$ per cent.; $FeO = 18.7$ per cent.

Contains Acid —

Oxygen in $SiO_2 = 0.32 \times 53.3 = 17.05 = A.$

Base —

Oxygen in $Al_2O_3 = 0.033 \times 47.0 = 3.901$
" " $CaO = 0.367 \times 28.6 = 10.496$
" " $MgO = 0.028 \times 40.0 = 1.120$
" " $FeO = 0.187 \times 22.2 = 4.15 = 19.66 = B.$

$$\text{Silicate degree} = \frac{\text{O in acid } (SiO_2)}{\text{O in bases } (Al_2O_3,\ CaO,\ \text{etc.})} = \frac{17.05}{19.66} = 0.86.$$

Composition of slag $= x\,(3RO{\cdot}SiO_2) + y\,(2RO{\cdot}SiO_2)$

and $x = B - A$ or $x = 19.66 - 17.05 = 2.61$

and $y = \frac{3}{2}A - B$ or $y = 25.57 - 19.66 = 5.61$

or $2.61\,(3RO{\cdot}SiO_2) + 5.61\,(2RO{\cdot}SiO_2)$

or 32 per cent. $(3RO{\cdot}SiO_2)$ + 68 per cent. $(2RO{\cdot}SiO_2)$.

The actual composition of this slag is, as determined by microscopic examination, 60 to 65 per cent. melilite and most of the balance olivine (fayalite), with some little magnetite. This does not correspond to the calculated mineral composition, which would be 32 per cent. of the $(3RO{\cdot}SiO_2)$ silicate = gehlenite, and 68 per cent. of the $2RO{\cdot}SiO_2$ silicate = olivine group. It must be borne in mind in this connection that melilite which forms is not of a definite *silicate* degree, but ranges between about 0.8 to 1.25 in silicate degree, being a mixed crystal composed of gehlenite and ackermanite. In view of the fact that we can put no formula in place of the gehlenite ($\frac{2}{3}$ silicate), only the above approximate calculation can be made in this instance.

THE SLAGS FROM THE STANDPOINT OF PHYSICAL MIXTURES. It has been shown by Vogt and others that in any molten silicate magma, those *mineral entities* are in solution which crystallize out from it on cooling. Thus if we have a solidified slag consisting of two definite minerals, say augite and one of the olivine group, these two minerals are to be considered as having been in solution in the molten condition of the slag and on cooling to have crystallized therefrom according to the laws of solution, as applying to physical mixtures as fully discussed in Chapter II, to which reference is made for further explanation of what follows.

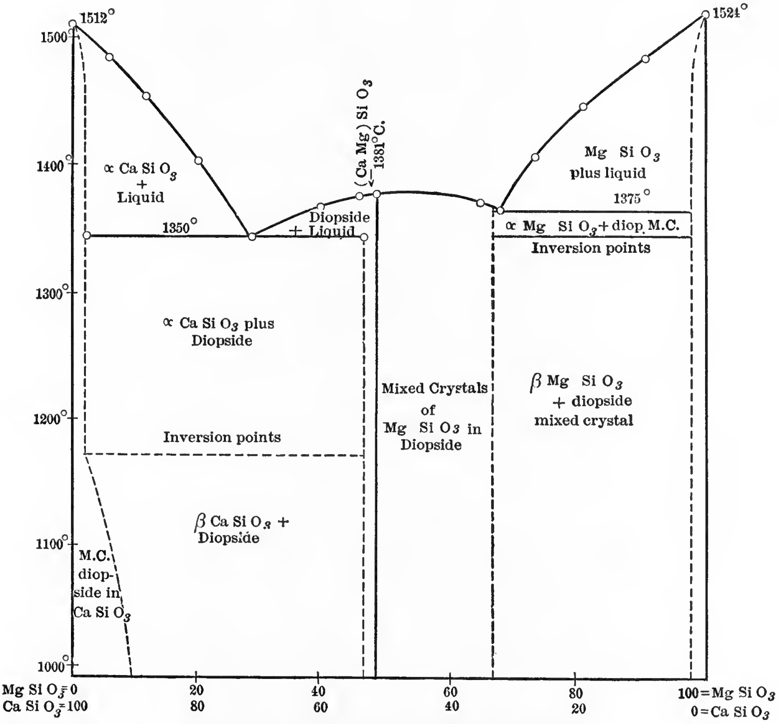

Fig. 76. — The System $CaSiO_3$–$MgSiO_3$.

Two cases may be cited here, which have been fully worked out, viz., that of the system $CaSiO_3 - MgSiO_3$ [1] and that of $CaAl_2Si_2O_8 - NaAlSi_3O_8$,[2] viz., anorthite-albite. In Fig. 76 is shown the melting-point curve of $CaSiO_3$ and $MgSiO_3$. It belongs to type IIA and shows a maximum at 47 per cent.

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[1] E. T. Allen and W. P. White; Diopside and its Relation to $CaSiO_3$ and $MgSiO_3$, Amer. Jour. of Science, Jan., 1909.

[2] The Isomorphism and Thermal Pioperties of the Feldspars, A. L. Day and E. T. Allen, Amer. Journ of Science, IV series, vol. XIX, p. 93 (1905).

$MgSiO_3$ and 53 per cent. $CaSiO_3$, which corresponds to the compound, $CaMg(SiO_3)_2$, the mineral diopside. Two eutectics are present, one at 28 per cent. $MgSiO_3$ and 72 per cent. $CaSiO_3$, the entities in which are a mixed crystal of $CaSiO_3$ dissolving 10 per cent. diopside, and a mixed crystal of diopside dissolving a small amount of $CaSiO_3$. The melting-point of the eutectic is 1350° C., while the end members of the series, $CaSiO_3$ and $MgSiO_3$, have for their melting-points 1512° and 1524° C., respectively. This refers to the pure, synthetically prepared silicates. The natural minerals corresponding to these end members, viz., wollastonite and enstatite, have lower melting-points, as they invariably contain some impurities which appreciably lower the melting-point.

The second eutectic occurs at a composition of 68 per cent. $MgSiO_3$ and 32 per cent. $CaSiO_3$, with a melting-point of 1375° C. It is composed of these entities — 95.5 per cent. of a mixed crystal of $MgSiO_3$ in diopside and 4.5 per cent. of a mixed crystal, consisting of $MgSiO_3$ dissolving 3.7 per cent. diopside. Both $CaSiO_3$ and $MgSiO_3$ have inversion points, viz., they are dimorphic, the crystallization changing when passing a certain temperature. In the case of $CaSiO_3$, the change is from the hexagonal to the monoclinic system on cooling, if this be very slow.

Fig. 77 shows the melting-point curve of the anorthite-albite series of feldspars. It belongs to type IAa discussed in Chapter II, *i.e.* it is a continuous series of mixed crystals of the isomorphous type.

On the Freezing and Solidification of Slags. — It is evident from the foregoing that slags may be classed as physical mixtures, of the nature of alloys, and are to be interpreted according to the same laws. We may have, therefore, and do have, eutectic mixtures in slags, and the freezing of a silicate magma follows that rule as exemplified by the type to which it belongs. See Chapter II. *The individualization limits* between various silicate degrees, and between the different minerals of the ortho-silicates and meta-silicates, and between certain meta-silicates and ortho-silicates discussed in the foregoing section of this chapter, correspond to the eutectic composition between the two minerals, viz., that proportion of the two minerals which will have the lowest melting-point. Thus between augite (hedenbergite) and iron hypersthene, ($CaFeSi_2O_6$, and $Fe_2Si_2O_6$), the eutectic occurs at 60 per cent. $Fe_2Si_2O_6$ and 40 per cent. $CaFeSi_2O_6$. The ratio is Ca: Fe = 0.2: 0.8. This ratio will also represent the "individualization limits" between the two minerals, viz., with more than 0.2 Ca to 0.8 Fe, hedenbergite crystallizes first; with less, hypersthene crystallizes first. This first crystallization of the mineral enriches the mother liquid in one constituent so that it finally reaches eutectic composition and freezes as the *eutectic.* This method of freezing is identical with that discussed for alloys, but the problem in the slags is complicated by the fact that *undercooling* is very common, which has the tendency to modify the microscopic structure. The typical eutectic structure most common in alloys consists of *interstratified platelets,* or other forms, of the constituents of the eutectic. This is often depended upon to prove the existence of a eutectic in conjunction with the observance of its solidification or melting-point in the thermal analysis. In the case of silicate magmas, however, there is usually a very decided viscosity of the mass manifested as it cools, which, retarding the mobility of the molecules, prevents crystallization (solidification) at the normal temperature in the case of *rapid cooling,* such as we usually have in slags. We have thus a condition similar to the following:

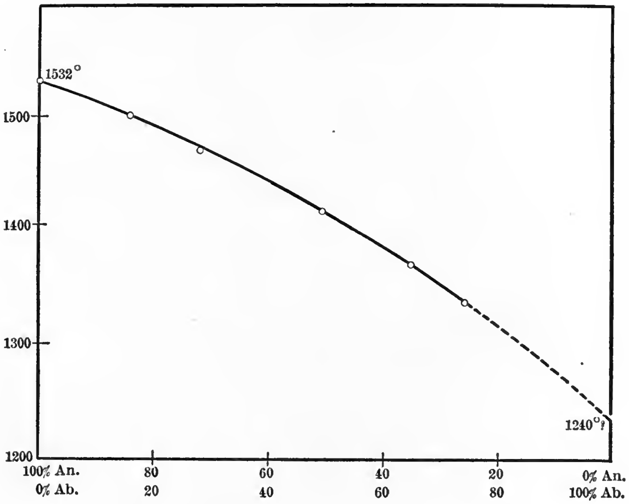

Fig. 77.—Melting-point curve $CaAl_2Si_3O_8$–$Na_2Al_2Si_6O_{16}$
Day and Allen, Am. Jour. Sci. IV, Ser. XIX, 93 (1905).

Two minerals "a" and "b" form a series in which occurs a eutectic. If a concentration be considered in which the mineral "a" is the "excess substance," some of this will crystallize first, thus concentrating the liquid magma in "b" toward eutectic composition; but now with falling temperature, increasing viscosity manifests itself and undercooling takes place, thus enriching the liquid magma in "a" and supersaturating it with this constituent for the existing temperature. When this supersaturation has reached a certain point, "a" will again begin to crystallize out, and again stop. If now a point near the eutectic composition has been reached, and the undercooling goes on below the eutectic freezing-point, and "a" again crystallizes, it will happen that when the crystallization of "a" stops, the mother liquid has become enriched in the mineral "b" beyond the composition called for by the eutectic, and this supersaturation in "b" will cause crystallization of "b" alone, instead of eutectic a + b, the viscosity increasing meanwhile to such an extent that the balance of the mother liquid passes to a glass without crystallization.[1] This method of freezing of a slag magma accounts readily for the microscopic structure found, viz., the practical absence of any typical eutectic structure.

The presence of glass in slags is accounted for by this undercooling with increasing viscosity as the temperature falls. Some silicates exhibit this phenomenon to a marked degree, viz., the higher degree silicates and some like albite,[2] orthoclase, etc., which pass gradually from the molten state to a solid non-crystalline glass exhibiting no *definite freezing-point*, and in freezing or melting are unaccompanied by any internal evolution or absorption of heat. Borax exhibits a similar phenomenon, but on cooling it can be induced to pass into the crystalline state by repeated shocks. The glass residual in slags may thus have the chemical composition of the mineral entity which has crystallized out, or it may have the composition near the eutectic between the minerals, if these belong to a series in which one occurs. Thus in the series $CaAl_2Si_3O_8$–$Na_2Al_2Si_2O_{16}$, shown in Fig. 77, the members near the anorthite end on cooling slowly pass practically entirely to the crystalline state, but as members of the series are taken toward the albite end the amount of glass rapidly increases, this glass

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[1] Vogt, Mineralbildung in Silicatschmelzölsungen, 101, 133.

[2] A. L. Day and E. T. Allen, *ibid.*

being of identically the same composition as the crystals. In this case the series belongs to type IAa, Chapter II, in which the solid and liquid phases are practically identical.

In considering the cooling curves in Fig. 78, it is necessary to explain that the cooling curves of slags, *e.g.* silicate magmas, present different features from those of the metals and alloys, due to the great *viscosity* and relatively low conduction of heat of the magmas. From the accompanying figure in which the *heating* curves of silver and some of the feldspars are given it will be seen that while that of the metal shows the melting-point by a sharp, practically horizontal jog, that of the silicates is entirely different, and in Ab_1An_2 the melting "point," so called, must be defined as lying in that region where the rise of temperature in a given time interval is a minimum, or that *point* on the curve where the tangent to the curve has the greatest inclination.

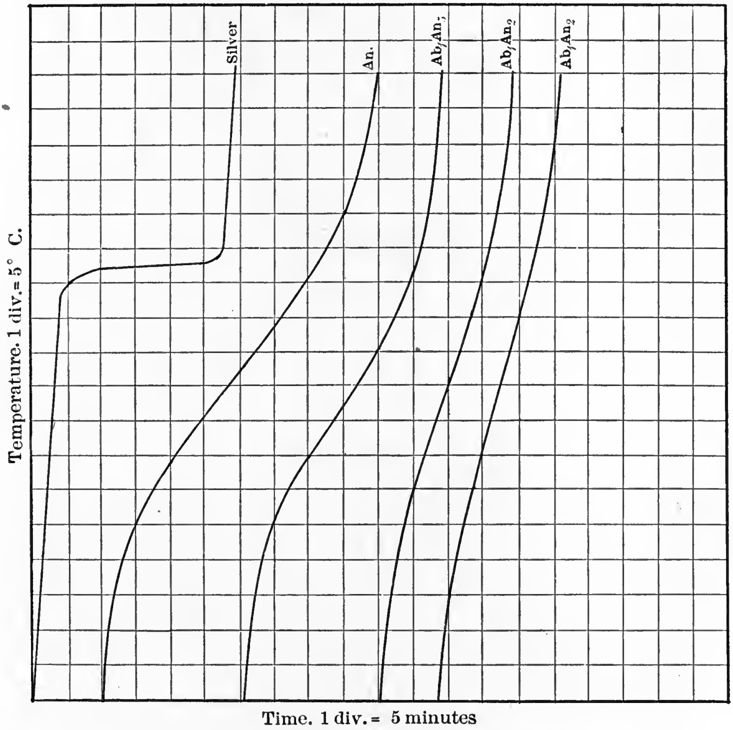

FIG. 78. — Cooling curves of silver and silicates.

In Fig. 79, let *A* be a mass of cooling slag in a crucible in the air and *B* a thermo-couple, and let the slag be liquid at first. Then, when freezing commences, a crust *a* will form on the top and then the concentric layer *b* will freeze, and so on until finally the sphere *d* around the thermo-couple congeals. While the whole slag is liquid, the cooling curve will be convex, but when the outer layers crystallize, the latent heat given out will effect the rate of radiation from the liquid center, the temperature of which the thermo-couple is recording, and the

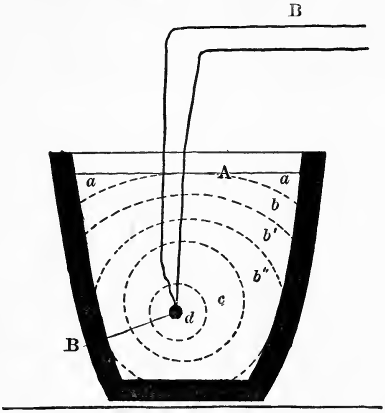

Fig. 79. — Method of freezing of a slag.

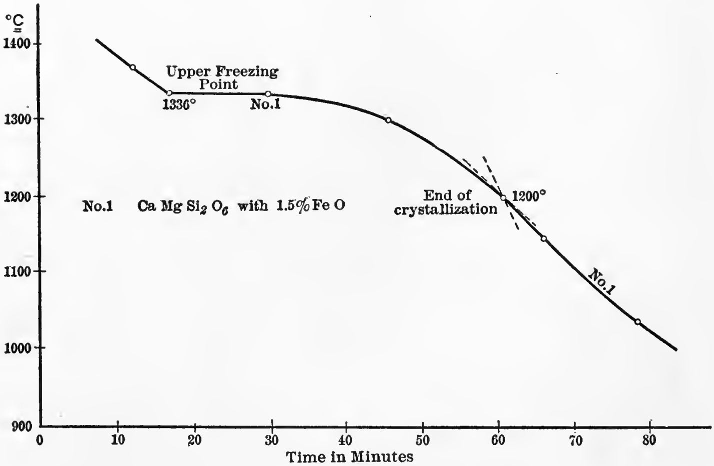

Fig. 80. — Cooling curve of a slag.

cooling curve will change its direction. Now in a metal the conduction is so rapid that this effect is instantly transmitted to the thermo-couple and the change of direction is very marked, viz., it approaches the horizontal, while in a silicate magma the conduction of heat is slow, not considering the effect of *undercooling* due to viscosity at all. Thus the effect is but slowly transmitted to the thermo-couple, and the change of direction is much more gradual. The mass of material which must be considered is, therefore, that immediately surrounding the thermo-couple, and when this finally is frozen, all latent heat having been given up, another change of direction in the curve takes place. This change of direction marks the *freezing* or crystallization point. (See Figs. 80 and 81.)

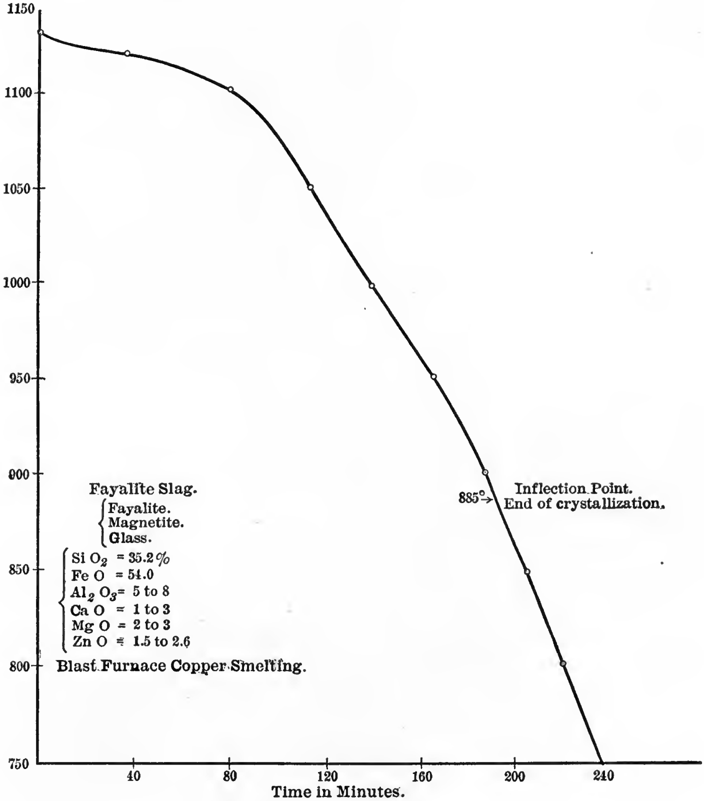

FIG. 81. — Cooling curve of a slag.

It is also to be noted that when the slags contain minerals which fall into a series of type IB, etc., we have distinct upper and lower freezing-points, except at the eutectic composition, and in this case the upper freezing-point is the only one of technical interest.

The Nature of Metallurgical Slags.—It is now necessary to consider the relation of all these data to metallurgic slags as far as this can be done in the present meager state of positive data at hand. Taking the slags of copper, lead, and iron smelting as comprising by far the greatest number of interest, we find that the following minerals comprise practically all that are found in them:

1. *Meta-silicates.* The hexagonal $(CaR)SiO_3$; augite; hypersthene (viz., that in which Fe predominates over Mg); rhodonite.
2. *Ortho-silicates,* including the sesqui-silicate ackermanite. Olivine group (olivine; fayalite; knebelite; tephroite; iron-lime olivine, and the double salts (meta-stable) of the monticellite group); and ackermanite; melilite; anorthite.
3. *Two-thirds silicate.* Gehlenite.
4. Spinels and magnetite.

Given a silicate magma of certain composition, we may consider that this in a state of fusion consists of a solution of certain of the above minerals, dependent upon composition. For simplicity's sake we will consider slags only, in which not more than two minerals are in solution, *e.g.* most *slags* crystallize to two minerals, some to three. These two minerals are then to be considered as end members of a definite series of a certain type as described in Chapter II. It has been found by Vogt that the commonest types, as far as investigations go, are types IAa; ICb, and IAc. The type of most interest technically is IAa and ICb, and those others in which definite eutectics occur, since here there are certain compositions which have low melting-points and hence low "total heats of smelting," attractive to the metallurgist, from the standpoint of low fuel consumption, and also if viscosity permits it, for fast driving of furnaces. Figs. 76 and 77 show two such series which have been completely worked out. In these the pure empirical minerals form the basis of the work. In considering slags we have to deal with a more complex case in so far as a number of extra bases enter into consideration, and fixing our attention upon Fig. 76, for instance, we will have present beside $CaSiO_3$ and $MgSiO_3$, some $Al_2O_3 \cdot 3\ SiO_2$ and $FeSiO_3$. The effect of this is that the $Al_2O_3 \cdot 3\ SiO_2$ entering into the diopside molecule (augite) lowers its melting-point and the $FeSiO_3$ entering into the enstatite molecule lowers its melting-point, so that in effect the melting-point of the whole series is lowered, and the eutectic point changed not only in melting-point, but somewhat in composition. When these other bases are present in such proportion that new mineral entities are formed, a new series of course takes the place of the old one. The presence of certain bases, on the other hand, may in a like manner raise the melting-points of the members of the series.

Below follows some data on series of minerals which have an especial bearing on common slags.

Note to Table. — In the last column, in which are given the bases expressed in ratio, Mg stands in reality for (Mg, Fe, Mn, Zn), though the data was determined for slags in which (Fe, Mn, Zn) played *subordinate parts* except where otherwise stated. The melting-points of end members and eutectics are not for the pure

TABLE XLI. MINERAL SERIES ENTERING INTO SLAGS.

Series	Silicate Degree	Type	Melting-Point of End Members of Series	Eutectic Composition and Melting-Point	Eutectic Composition Expressed as Base Ratio
Augite (Hedenbergite) $CaFeSi_2O_6$ and Hypersthene $Fe_2Si_2O_6$	2.0	ICb	Hedenbergite 1110° C. Hypersthene 1050°	60 per cent. $Fe_2Si_2O_6$ 40 per cent. $CaFeSi_2O_6$ at 1000° C.	0.8Fe: 0.2Ca
Augite ($CaMgSi_2O_6$) and Olivine $(MgR)_2SiO_4$	1.5 to 1.65	ICb	Diopside 1225° Olivine 1400°	70 per cent. Augite (Diopside) 30 per cent. Olivine at 1100° - 1125° C.	0.5Ca: 0.5Mg Mg = (MgFe,ZnMn)
Olivine $(MgR)_2SiO_4$ and Melilite [1]	1.0	ICb	Olivine 1400° Melilite 1130°	24 per cent. Olivine 76 per cent. Melilite mixture contains 10 per cent. Al_2O_3 at 1030° C.	0.55Ca: 0.45Mg
Melilite [1] and Anorthite	1.0	ICb	Melilite 1130° Anorthite 1230°	65 per cent. Melilite 35 per cent. Anorthite at 1020° C.	0.75Ca: $0.25Al_2$
Augite ($CaMgSi_2O_6$) and Ackermanite [2]	1.56	ICb	Augite 1225° Ackermanite 1200°	60 per cent. Ackermanite 40 per cent Augite at 1100° C.	0.73Ca: 0.27Mg
Rhodonite ($Mn_2Si_2O_6$) and Hypersthene ($Fe_2Si_2O_6$)	2.0	ICb	Rhodonite 1180° Hypersthene 1050°	78 per cent. Hypersthene 22 per cent. Rhodonite at 970° C.	0.78Fe: 0.22Mn

[1] $(0.5\ R_4Si_3O_{10} + 0.50\ R_3Al_2Si_2O_{10})$ R = Ca, Mg – Ca : Mg = 6:1 [2] $(0.75\ R_4Si_3O_{10} + 0.25\ R_3Al_2Si_2O_{10})$ R = Ca, Mg – Ca : Mg = 2:1

silicate, but for silicates containing certain amounts of foreign base; thus olivine is given as Mg_2SiO_4, but the data given is for $(MgR)_2SiO_4$, in which R is Fe, Mn, Zn in certain amounts. Olivine is here used to designate a group, and for instance may be anything between Mg_2SiO_4 and Fe_2SiO_4. Thus in No. 3 in the series, olivine-melilite, reference is made to olivine practically free from iron, and applies to certain *iron blast-furnace slags.* If the olivine in this case becomes or approaches Fe_2SiO_4, viz., fayalite, we have the group to which practically *all lead slags belong.* Applying the same remarks to the olivine in No. 2, we have this referring to certain lead slags, and find that practically all *copper slags* fall into this group 2 and group 1, and between the two.

Groups 3, 4, 5 represent iron blast-furnace slags, and groups 1 and 6 slags from acid steel processes.

It must be conceded that the data on which to base exact practical metallurgical calculations is very meager, especially for lead and copper slags, but the author has treated the subject from this new point of view in the hopes that it may induce study and research of the subject by scientific metallurgists, from the metallurgists' standpoint, and thus lead to directly practical results.

THE PHYSICAL CONSTANTS OF SLAGS. **Formation Temperatures of Slags.** — In the previous sections the slags have been considered as having already been formed, *i.e.* are in the condition of molten silicate magmas, which, on cooling, form certain mineral entities. In actual furnace operations the question must be looked at from a somewhat different viewpoint. The furnace charge will consist of, not the *formed silicates,* though some of these may be present as silicate minerals in the ore, but rather as the individual bases, such as CaO and MgO in the form of limestone, FeO in the form of Fe_2O_3 and Fe_3O_4 in oxidized or roasted ores, or as FeS_2, Fe_7S_8, etc., in sulphide ores. These bases, with the quartz, SiO_2, of the ores, form a mechanical mixture, and are so proportioned by calculation that they smelt together into the slag eventually discharged from the furnace. It is a well-known fact that the temperature necessary to cause these various bases and the silica to unite into the slag is different from the melting or solidification temperature of the formed slag. The temperature necessary to cause the various ingredients of the final slag to unite chemically and go into solution is known as the "formation temperature" of the slag. This formation temperature, for any given mechanical mixture, is a function of the size of particles comprising the mixture and of time. This fact may be readily demonstrated by the ordinary Seger cones, used for the determination of temperature. (See page 186.)

It has been shown by Hofman [1] and Gredt,[2] that in determining the *formation temperatures* of mechanical mixtures of a series, a curve results, and this has been shown by Vogt to be roughly parallel to the freezing-point curve of the series formed by the mineral entities to be expected from the chemical composition of the mechanical mixtures. It may thus be stated that the formation point curve of a series of mechanical mixtures of silica and bases is parallel to the freezing-point curve of the corresponding formed slags, but lies at a higher level.[3] The formation temperature may be very appreciably higher than the freezing temperature of the corresponding slag, depending on the factors mentioned; in some cases from 200° to 300° higher than the freezing-point. It is this formation temperature which is of most interest to the metallurgist, but since it is really not a definite temperature, but varies with certain factors and is better represented by a range or interval of temperature, the freezing-point furnishes the most definite information upon which the formation temperature data may be based.

It has been shown by Doelter[4] that in any complex mixture of bases and silica subjected to such a temperature as to cause fusion, certain silicates, viz., mineral entities will *form first, e.g.* those which have the lowest formation point, and that this mineral will absorb the rest of the mixture gradually as the temperature rises until the whole is in combination or solution. This fact has been frequently observed by the author in heating up charges of various mixtures in crucibles, heating to certain definite temperatures and examining the contents, and then if certain constituents were still present in the original state, reheating to higher temperatures until the mass had become entirely homo-

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[1] Hofman, T. A. I. M. E., Vol. XXIX, p. 682. The Temperature at which certain Ferrous and Calcic Silicates are formed, etc.

[2] P. Gredt. Stahl und Eisen, 1889, II, Vol. IX, p. 756.

[3] Vogt, *ibid*, Vol. II, p. 92.

[4] Doelter, C. Die Silicatsschmelzen, Sitz. Ber. der Akad. der Wiss. Wien. Mathemat. Naturwesen, Kl. B. CXIII., Abt. 1, April, 1904.

geneous and fluid, and showed itself to be such on solidifying. The formation temperature of any given mechanical mixture may be appreciably lowered by adding to it a certain percentage of formed slag of the same chemical composition, thus not changing the composition of the whole, for from what has been stated above, the "slag" will have a lower melting-point than the corresponding mechanical mixture, and the added slag melting first will aid materially in the rapid solution and combination of the ingredients of the mixture. It is a well-known fact of furnace practice in lead and copper smelting that the charge should contain a certain amount of slag as such, not only because this slag in some cases needs to be resmelted for its contained values in valuable metals, but also because it greatly aids in the operation of the furnace, probably for the reason above stated. Figs. 82, 83, and 84 show the formation temperatures of certain ferrous-calcic silicate slags,[1] chiefly those of lead and copper smelting. These formation temperatures were determined by mixing the ingredients of the slag mixture, viz., SiO_2, FeO (from ferrous oxalate), CaO, MgO, etc., in the form of powder, moistening with a 10 per cent. dextrine solution and forming the same in the shape of small Seger cones and heating slowly in a gas furnace. The temperatures were determined by Seger cones. The temperatures are from the nature of the work rather approximate but fully within the range of metallurgical requirements.

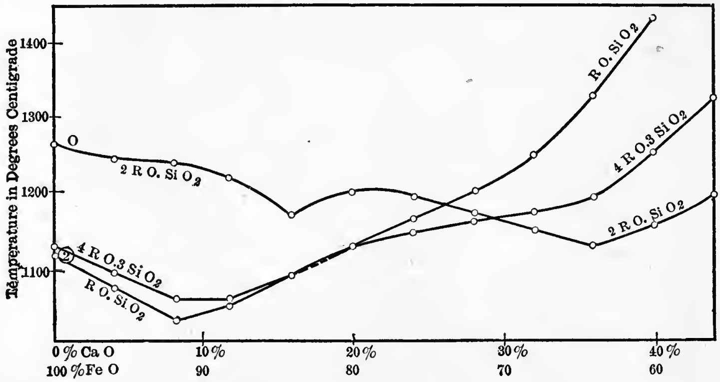

FIG. 82. — Formation temperatures of the ortho-, sesqui-, and bi-silicates of iron and lime, with varying percentages of the two constituents.

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[1] H. O. Hofman, T. A. I. M. E., Vol. XXIX, p. 682.

Fig. 82 shows the formation temperatures of ortho-, sesqui- and bi-silicates of iron and lime with the varying percentages of iron and lime in the range of copper and lead slags. Fig. 83 shows the formation temperature of an ortho-silicate of FeO and CaO in which the lime is replaced partially by the bases, ZnO, BaO, and MgO, in equivalent combining amount. Fig. 84 shows the

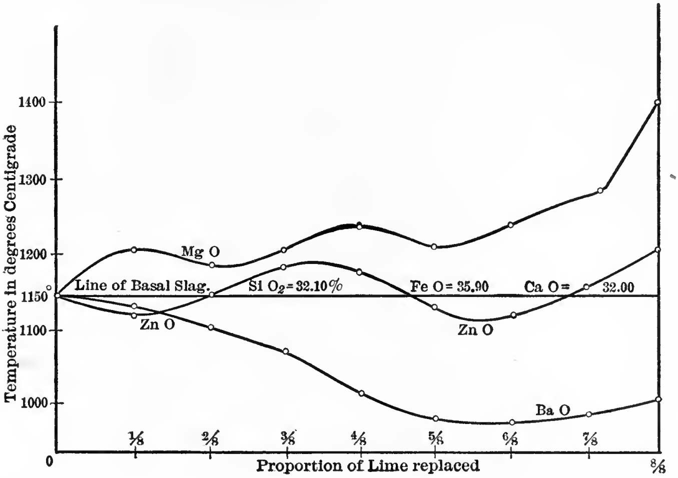

Fig. 83. — Formation temperatures of a Ca–Fe silicate in which lime is replaced gradually by MgO, ZnO, BaO in equivalent combining amounts.

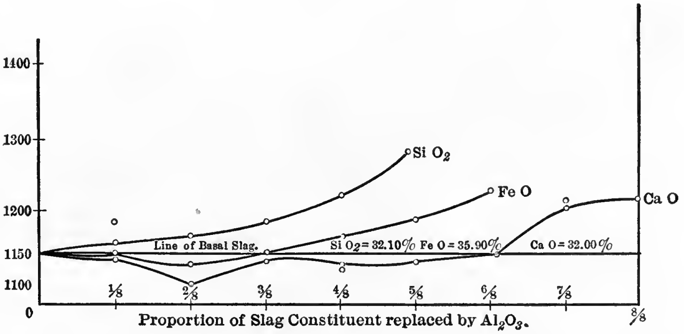

Fig. 84. — Formation temperatures of a Ca–Fe silicate in which the slag constituents are gradually replaced by Al_2O_3 in equivalent combining amounts.

formation temperatures of the same ortho-silicate when its constituents, SiO_2, CaO, and FeO are partially replaced by an equivalent combining amount of Al_2O_3.

Fig. 85 shows the formation temperatures of the ortho-silicate of lime and alumina,[1] with varying amounts of these bases. The data for the curve was determined in a similar manner to that described for the ferrous-calcic silicates.

In considering these formation temperatures, the remarks previously made as to how the silicates form during heating should be taken into consideration. It is possible that in heating a mixture of slag ingredients in the form of cones, that bending and fusion, by means of which temperature is judged, seeming complete combination will take place, without certain amounts of the ingredients being completely absorbed into combination. Also the fact that "formation temperature" is a rather indefinite term and depends on several factors, already mentioned.[2]

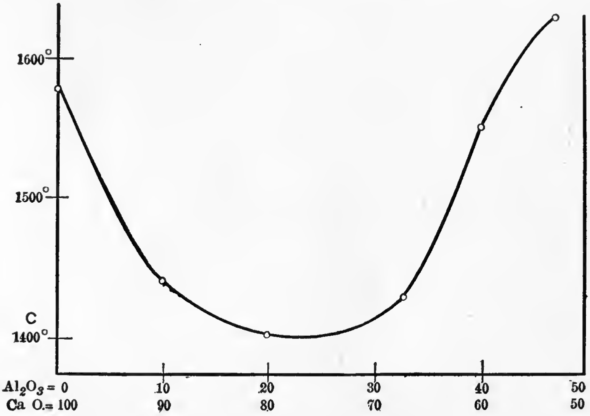

FIG. 85.—Curve of formation temperature of the ortho-silicate of lime and alumina, viz., melilite and anorthite, after Gredt.

Total Heat Required to Form Slags. — The total quantity of heat required to form slags is of vital importance metallurgically. The question of "*total smelting heat*" has been extensively

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[1] Gredt, Die Bildungstemperaturen der Hochofen-Schlacken. Stahl und Eisen, 1889, II.

[2] Consult also, remarks on formation temperature of slags, H. T. Hofman, Min. Ind. XVII, 597 (1908).

investigated by Ackerman[1] and Vogt,[2] for certain slags. The *total smelting heat* is defined as that amount of heat necessary to just bring into the fused state a unit weight of slag from zero degrees C. Its value is expressed by the following equation:

$W = t \times c_{(t-o)} + R + (t' - t)\, c_{(t'-t)}$, in which

W = total smelting heat in gram calories.

R = latent heat of fusion in gram calories.

t = melting-point of the slag in degrees C. from zero.

t' = temperature to which slag has been heated to make it fluid, *i.e.* a temperature above t.

$c_{(t-o)}$ = specific heat (mean) between o and t.

$c_{(t'-t)}$ = specific heat (mean) between t and t'.

Table XLIV gives the total heats of smelting of Ca, Mg, and Ca, Al silicates as determined by Ackerman. Ackerman's figures are all experimental data from calorimeter determinations. In cases where the slags or part thereof solidify to glass, the figures do not represent the "*total smelting heat*," since the heat of fusion or crystallization of that part represented by glass has *not been liberated*, so that some of the figures are considerably lower than the actual "total smelting heat." In order to make the calorimeter experiments the slag must be superheated to some extent, *e.g.* 20° to 50° above its crystallization or solidification point. This correction is included in the equation, but has not been subtracted from the figures in the table.

It is to be noted that these figures apply to the formed slag, and represent the total heat in a unit weight of slag at a certain small temperature above its melting-point.

It is of interest to compare with this data the total heat required to *form* a slag from the original mechanical mixture of its constituents.

For this calculation a simple case is taken, for which all data is at hand, viz., the calcium meta-silicate $CaSiO_3$. In order to form 100 grams of $CaSiO_3$, 48.3 grams of CaO and 51.7 grams of SiO_2 are necessary. The melting-point of $CaSiO_3$ with small amounts of impurities is given by Vogt as 1250° C. Assuming such physical conditions of the CaO and the SiO_2 that a *forma-*

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[1] R. Ackerman, "Die zum Schmelzen von Schlacken erforderliche Wärmemengen" Jernkontorets Annaler, 1886, and Stahl und Eisen,-1886.

[2] *Ibid.*

tion temperature of 1450° C. is required, we have the total heat absorbed by these two constituents in heating from zero to 1450° C. as follows:

$$51.7 \times 1450° \times (0.1833 + \{.000077 \times 1450\}) = 22489.5 \text{ cal.}^1$$

$$48.3 \times 1450° \times (0.1743 + \{.00007 \times 1450\}) = \underline{19024.0} \text{ “}$$

$$\text{Total, } 41513.5 \text{ “}$$

or per gram of $CaSiO_3$, 415.13 calories.

At the formation point, CaO and SiO_2 unite with evolution of heat.

$$CaO + SiO_2 = CaSiO_3$$

$$+ 131500 + 180000 + 329350$$

$$= 17850$$

$$\text{or} \quad \text{per gram } CaSiO_3 = \frac{17850}{116} = 154 \text{ calories.}$$

The latent heat of fusion of $CaSiO_3$ is given by Vogt as very nearly 100 calories, therefore out of the 154 calories generated by combination of the CaO and SiO_2, 100 calories are absorbed by the mass as latent heat in passing into the liquid state, and 54 calories are available under the conditions assumed, to raise the temperature of the formed silicate still higher. The specific heat of the molten silicate is about 0.40 according to Vogt, so that since $C = mtc$[2] we have

$$54 = 1 \times t \times 0.4 \quad \text{or } 0.4t = 54 \quad \text{or } t = 135° \text{ above } 1450°, \text{ or}$$

the slag is at 1585° C.

The fused $CaSiO_3$, from its original constituents at zero degrees to 1585° C., has absorbed 569.13 calories.

In cooling down to 1250°, its crystallization point, it loses

$$(1585-1250) \times 1 \times 0.4 = 134 \text{ calories}$$

and at 1250° will have in it, (569.13 − 134) = 435.13 calories.

This should represent its “total heat of smelting.”

According to experimental data furnished by Ackerman, this

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[1] Specific heats taken from Richards, Metallurgical Calculations, Pt. 1.

[2] C = number of calories liberated by the reaction.
t = final temperature of the products of the reaction.
m = mass of the products of reaction.
c = mean specific heat of the products of reaction between t_0 and t.

figure is 460 calories. This is good agreement considering the accuracy of the specific heat data worked with.

The Net Total Heat of Formation. — Under furnace conditions the heat evolved by the formation of the silicate will not go toward superheating the formed slag as above outlined, but will be utilized on other furnace units, so that the fuel requirement may be kept as low as possible. Then we have that 415.13 calories must be furnished to cause the formation of the slag, and of the 154 calories yielded by the combination 100 calories are absorbed as latent heat, making a total of 515.13 calories in the *slag* at 1450°. There are 54 calories in excess available, so that the net calories which must be furnished are $(515.13-54) = 461.13$ calories. This will be called the "*net total heat of formation.*"

The Specific Heat of Slags. — The specific heat of a substance at any temperature t (above 0° C.) is expressed by the equation

$$S = \alpha + \beta t + \gamma t^2$$

in which the last term may be disregarded in all ordinary calculations; therefore

$$S = \alpha + \beta t$$

in which α is the specific heat at 0° C. and B is a constant for any given substance. The mean specific heat between 0 and t, Sm, is expressed by the equation

$$Sm = \alpha + 0.5\ \beta t.$$

The mean specific heat between any two temperatures t and t_1 is expressed by the equation

$$Sm = \alpha + 0.5\ \beta\ (t + t_1).$$

The specific heat of a compound (in this case, silicate) may be closely calculated from Woestyn's rule, viz.:

$$100S = P_1S_1 + P_2S_2 + P_3S_3 \ldots \text{etc.},$$

in which S is the specific heat of the slag (or compound), $P_1 - P_2 - P_3$ are the percentages of SiO_2 and bases present, and $S_1 - S_2 - S_3$ are the specific heats of these substances.

The following table gives the specific heats of silica and the common bases. (See table on page 280).

The specific heat S at any temperature may be approximately calculated, the value at zero degrees α being known, from the fol-

TABLE XLII. SPECIFIC HEAT OF SILICA AND THE COMMON BASES

Substance	Specific Heat at 0°	Mean Specific Heat Between 0° and 100°	Formula for Mean Specific Heat with Increase of Temperature
SiO_2	0.1833 0.1841	0.1913	[1] 0.1833 + .000077 $t°$
Al_2O_3	0.2081 [1] 0.1902	0.1976	[1] 0.2081 + .0000876 $t°$
Fe_2O_3	0.1607	0.1670	[1] 0.1456 + .000188 $t°$
MnO	0.1511	0.1570	
MgO	0.2347	0.2439	[1] 0.2420 + .000096 $t°$
CaO	0.1715 [1] 0.1580	0.1640	[1] 01715 + .00007 $t°$
FeO	0.146	0.1520	
K_2O	0.139	0.144	
ZnO	0.1212	—	0.1212 + .0000315 $t°$
Na_2O	0.225	0.2340	

lowing formula, $S = \alpha + 0.00078\ \alpha t$ and the mean specific heat Sm between zero degrees and t from

$$Sm = \alpha + 0.00039\ \alpha t \text{ (for } 0.00039\alpha = \beta).$$

The mean specific heat between 0 and t being known from the above formula, the mean specific heat between any two temperatures t and t_1 can be calculated from the formula

$$Sm_1 = \alpha + 0.00039\alpha \times (t + t_1).$$

TABLE XLIII. SPECIFIC HEATS OF CERTAIN SLAGS

Chemical Composition	Mineral Composition	Melting-Point deg. C	Sm. Between 0° and Melting-Point	S at Melting-Point	S in Molten Condition
—	$CaMgSi_2O_6$	1225	0.281	—	—
—	$(CaMg)SiO_3$, 3Ca: 1Mg	1200	0.264	—	—
—	$CaSiO_3$	1250	0.288	—	—
—	$(CaMg)_4Si_3O_{10}$	1200	0.262	—	—
—	$CaAl_2Si_2O_8$'	1220	0.294	0.35	0.37–0.40
—	$(MgCa)SiO_3$, 0.85Mg: 0.15Ca	1300	0.310	0.40	0.42–0.45
SiO_2, 31.38; FeO, 45.20, CaO, 23.42%	$4CaO.6FeO.5SiO_2$ [2]	1058 [3]	(24°–1058°) 0.255	0.326	— —
SiO_2, 35.5; FeO, 39.7; MnO, 1.0; CaO, 11.4; MgO, 2.7; Al_2O_3, 9.2%	—	1114 [4]	0.2355	0.269	—

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[1] From J. W. Richards, Metallurgical Calculations, Part I. Other data from Vogt. *Ibid.*

[2] H. M. Howe, T. A. I. M. E., XVIII, 724.

[3] Formation temperature 1190° C.

[4] J. W. Richards, Metallurgical Calculations, Part III, 474. W. S. Landis.

It will be noted that the specific heat of the slags in the molten condition is somewhat higher than at the melting-point. In the molten condition of the slag the specific heat may be considered practically constant. The melting-points as given in the above table are low for the pure mineral compounds, and are for the minerals with an admixture of small amounts of impurities. The following are the melting-points of some pure silicates.[1] $MgSiO_3$, 1565°; $CaSiO_3$, 1512°; $FeSiO_3$, 1500°–1550°; $MnSiO_3$, 1470°–1500°; $ZnSiO_3$, 1479°; $SrSiO_3$, 1287°; $BaSiO_3$, 1368.5°; Mg_2SiO_4, about 1900°; Zn_2SiO_4, 1484°; and Sr_2SiO_4, 1593° C.

The Latent Heat of Fusion of Slags. — In the equation for the "total smelting-heat" given on page 277, the latent heat of fusion is designated by the term R. The latent heat of fusion of a slag is the amount of heat absorbed without any rise of temperature being manifested in passing from the solid into the liquid state. This amount of heat will be absorbed in melting a slag already formed, and also when it is produced by smelting a mechanical mixture of its constituents. Conversely, this amount of heat is liberated without a fall in temperature, when the molten slag passes to the solid state, with this exception, viz., if the slag congeals to a glass (solid solution), the latent heat of fusion is not liberated, but remains latent in the solid mass. The latent heat of fusion is identical with the "heat of crystallization." In the case of slags, there is frequently, in rapid cooling, dependent upon composition, a congealing to glass, either wholly or partially, so that in determinations of the "total heat" in slags, this latent heat is not or only partially liberated. This fact is of importance when it is considered that, other things being equal, the value of a slag, metallurgically, is determined by the amount of heat it takes to form it. This data may be determined by calorimetric experiments, as the "total smelting heat." If in the experiments the slag congeals to a glass, the figure determined does not include the latent heat, and is therefore low, and not trustworthy data as to what heat it takes to form the slag. See the remarks on page 277 concerning the relation of "heat of formation" and "total smelting heat." When slags are to be resmelted it is evident that chilled slag, *i.e.* glassy slag, is advantageous, in so far as it will take less heat to remelt this than slowly cooled or crystallized slag.

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[1] Gerh. Stein, Zeit. Anorg. Chem., LV, 158 (1907).

TABLE XLIV. TOTAL SMELTING HEAT AND LATENT HEAT OF CERTAIN SLAGS

Composition						Total Smelting Heat	Latent Heat Fusion	Formula
SiO_2	Al_2O_3	CaO	MgO	MnO	FeO			
43.9	8.6	31.4	10.2	0.3	4.5	424 cal.[1]	91.0 cal.[1]	—
56.77	5.3	12.20	22.75	1.63	1.66	434 cal.[1]	94.0 cal.[1]	—
55.90	3.33	4.31	—	26.66	11.80	368 cal.[1]	45.7 cal.[1]	—
—	—	—	—	—	—	444 cal.	102.0 cal.	$CaMgSi_2O_6$
—	—	—	—	—	—	404 cal.	90.0 cal.	$(CaMg)_4Si_3O_{10}$ 0.7Ca: 0.3Mg
—	—	—	—	—	—	413 cal.	100.0 cal.	$(CaMg)SiO_3$ 3Ca: 1Mg
—	—	—	—	—	—	458 cal.	105.0 cal.	$CaAl_2Si_2O_8$
30	5.5	1–3	2–3	ZnO	53			
to	to	—	—	1.5 –	to			
36	8	—	—	2.6	59	306–309 cal.	85.0 cal.	—
—	—	—	—	—	—	—	130.0 cal.	Mg_2SiO_4
—	—	—	—	—	—	—	125.0 cal.	$Mg_2Si_2O_6$
—	—	—	—	—	—	—	100.0 cal.	$CaSiO_3$

The Viscosity and Superheating of Slags. — The viscosity, or resistance to flow, of slags is of as much importance from a metallurgical standpoint as is the melting-point. Many slags of *low melting-point* are so viscous at that temperature that they will not flow freely from the furnace, in fact may not flow at all. No exact standards of fluidity have been applied to slags, but making the subdivisions of — viscous-fluid, — thinly fluid, it may be said that the degree of fluidity of a slag is a function of chemical composition and of temperature. With any slag of given composition fluidity increases with a rise of temperature, but this increase of fluidity is by no means the same for different slags for the same increase of temperature. Thus considering slags A and B of different compositions, with A melting at $T°$ C. and B at $T^{1}°$ C., the latter being the higher temperature, it will require a certain amount of superheating to make the slags sufficiently fluid for metallurgical purposes. But it may be found that the slag B needs less superheating to attain the required degree of fluidity than A, so that while A has the lower melting-point, the lesser amount of superheating necessary for B to gain the requisite fluidity may make it the economical slag as regards the consumption of heat.

[1] Approximate.

From experience it may be stated that —

1. The viscosity of slags increases, other factors being equal, with the degree of acidity (*i.e.* silicate degree) above the orthosilicates. The more acid silicates are decidedly more viscous than the more base silicates, at the same temperatures (referring to melted slags).

2. As regards bases present, FeO decreases the viscosity, and MnO acts in a still greater intensity in this direction; PbO has the same effect. In the Ca–Mg silicates with some Al_2O_3, viz., blast-furnace slags, those high in Mg are more thinly fluid than those high in lime. The effect of MgO is, however, not nearly so pronounced as that of FeO or MnO. In basic slags, *i.e.*, low silicate degree, the chief base being lime, Al_2O_3 has the effect of increasing the fluidity, but in acid slags the effect of Al_2O_3 is to markedly increase the viscosity, when it amounts to more than 10 per cent.

From the glass industry it is known that the presence of much K_2O and Na_2O in acid lime silicates decreases the fluidity, the effect of K_2O being more pronounced than that of Na_2O.

The Relation of Slags to Mattes and Metals Produced in the Furnace. — It is necessary to consider slags in relation to other furnace products made at the same time. For example, in iron smelting in the blast furnace, the molten products are slag and cast iron; in copper smelting — slag, matte, and sometimes, but rarely, metallic copper; in lead smelting, slag, matte, and lead bullion. Taking more specifically the case of copper-matte smelting, we have the two molten products — a silicate slag and a sulphide matte, — which are practically immiscible but still have a slight reciprocal solubility increasing with temperature. This solubility is of importance in so far as any sulphide which is soluble in the slag is carried away with it and is lost.

A distinction must be made here between particles of sulphide or matte which are mechanically entangled in the slag due to an inefficient separation by specific gravity, and sulphide which is actually dissolved in the slag. In the case of iron smelting in the blast furnace, somewhat different conditions exist, as there must be considered the molten slag and iron which are practically insoluble in each other, but aside from which there exists a relatively small amount of sulphides, chiefly calcium sulphide, but also some manganese and iron sulphides which are soluble in both slag and iron. As these sulphides are deleterious constituents of iron, it is desirable to have a slag of such a nature as will dissolve a relatively large amount of sulphide, compared to what the iron will dissolve, so as to free the latter as much as possible from this constituent. In fact, the removal of sulphur in blast-furnace smelting is attained by the solubility of the sulphides (CaS) in the slag. In lead smelting we have the same general condition existing as in iron smelting, viz., a molten metal, lead, and a silicate slag practically insoluble in each other, and then a sulphide-matte, which, however, in this case is present in large amount. The question to be considered here is, what is the reciprocal solubility between sulphide and slag on the one hand, and sulphide and metal on the other? The relationship of these various substances above outlined to each other comes under certain laws of physical chemistry as discussed by Nernst,[1,2] the division of a substance between two solvents, and reciprocal solubility.

Molten silicate slags have the property of dissolving some sulphide, which on cooling is found in the slag as mono-sulphide (RS) in crystals, and crystallites in which R is Ca, Mn, Fe, and Zn chiefly. Similarly the sulphide or matte is capable of dissolving small amounts of slag. Upon analysis, certain small quantities of silica are almost invariably found in mattes, even though the mechanical separation may have been perfect. The solubility of certain sulphides in slag is considerable and the amount dissolved is a function of the temperature and the nature of the slag. The solubility increases rapidly with the temperature, and the more basic slags are capable of dissolving larger quantities of sulphide than the more acid or siliceous slags. Slags high in lime and manganese and of low silicate degree are capable of dissolving from 6 to 7 per cent. of RS, chiefly as CaS and MnS, and in especial cases, as high as 8 per cent. RS. In the case of copper and lead smelting the above data holds generally true, except that the sulphide dissolved in the slags is ZnS or FeS. In basic slags comparatively high in zinc the amount of sulphide dissolved may be as high as 6 or 8 per cent. In slags high in iron the amount of dissolved sulphide is less, usually not more than 2½ to 3 per cent. In acid slags the amount is considerably less

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[1] W. Nernst, Theoretische Chemie, 5 ed., 1907, pp. 488, 490.

[2] Jüptner, H. v., Stahl und Eisen, 1902, I.

than this. Cu_2S is soluble in silicate slags, but to a very small extent, so that considering a slag in contact with matte, both in the molten condition, the slag will dissolve iron sulphide from the matte in preference to copper sulphide. Lead sulphide, silver sulphide, and nickel sulphide, like copper sulphide, are practically insoluble in silicate slags. It is noted that in copper smelting, high silica slags are lower in copper contents than the more basic slags.[1]

Some Considerations Bearing on Technical Metallurgical Practice. *Alumina in Slag.* — The question of alumina in slags is much discussed by metallurgists owing to its deleterious effect under certain conditions, and the problem as to whether it is present as a base, *i.e.* in the form of silicate, or as an acid, viz., as aluminates, in certain slags, is a very old one. It will have been seen from the foregoing sections that alumina may be present in either form, dependent upon the composition of the slag. If it occurs as an acid, it usually takes the form of a spinel which crystallizes out of the slag at a high temperature and may be the cause of much trouble. If it is desired to carry considerable alumina without the formation of spinel, it is essential to pay particular attention to the nature of the other bases present so that those mineral compositions can form which will carry alumina as a base, viz., in the ortho-silicates, melilite, gehlenite, or anorthite, and in the bi-silicates, augite. Magnesia and zinc greatly aid in the formation of spinel, and therefore the presence of either zinc or magnesia in considerable quantity with alumina may give rise to the formation of spinel and cause trouble. Alumina present in amounts of less than 10 per cent. will in many cases cause a lowering of the formation temperature of the slag, but in amounts of 6 to 10 per cent. will increase the viscosity somewhat. Amounts of more than 10 per cent, even though it pass into the slag as a base, raise both the formation temperature and the viscosity materially. For detailed data, see previous sections of this chapter.

Zinc in Slags. — Zinc is present in slags in the form of silicate or, as just mentioned, sometimes in considerable proportion as a sulphide. When in the form of silicate it enters freely into the minerals of the olivine group, as already discussed in previous pages of this chapter. In order to facilitate the entrance of zinc

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[1] W. A. Heywood, Eng. and Min. Journ., March 10, 1904.

TABLE XLV. Com

Type of Slag	Locality	Com			
		CaO	FeO	MgO	Al_2O_3
		%	%	%	%
Basic Bessemer process slag	Pottsdown, Pa.	45.26	12.0	5.90	4.01
Iron blast furnace	Pennsylvania	33.84	0.98	17.08	9.51
Iron blast furnace	Domnarfvet, Sweden	33.44	0.74	14.35	5.81
Iron blast furnace	Bangbro, Sweden	30.70	0.54	8.47	5.80
Iron blast furnace	Norton on Tees, England	24.36	1.85	0.60	9.18
Iron blast furnace	Muirkirk, Md	25.35	3.20	2.11	12.84
Iron blast furnace	Pennsylvania	47.39	0.94	5.38	5.48
Iron blast furnace	Pennsylvania	35.46	0.74	19.88	4.05
Basic Bessemer process slag	N. E. Steel Co., Middlesboro, Eng.	45.04	2.10	6.42	1.50
Acid Bessemer process slag	Bangbro, Sweden	0.32	31.19	0.11	2.24
Acid Bessemer process slag	Bethlehem, Pa.	0.75	13.89	0.24	$Al_2O_3+P_2O_5$ 5.76
Acid open hearth process slag	Steelton, Pa.	—	27.39	—	—
Basic open hearth process slag	Steelton, Pa.	38.06	23.99	4.17	—
Basic open hearth process slag	Steelton, Pa.	43.46	14.81	4.23	—
Puddling furnace slag	*Manufacture wrought iron*	0.81	52.43	Fe_2O_3 19.62	0.38
Heating cinder	—	—	Fe_2O_3+FeO 71.29	—	7.78
Copper blast furnace slag	Ducktown, Tenn., 1874	2.52	44.70	4.80	8.15
Copper blast furnace slag	Ducktown, Tenn., 1904	6.30	51.40	1.37	4.84
Copper blast furnace slag	—	19.50	26.20	—	14.80
Copper converter slag	Arizona	—	65.30	Ag 0.16 oz.	—
Copper reverberatory furnace slag	Butte, Mont.	4.60	38.60	—	6.00
Copper reverberatory furnace slag	Butte, Mont.	1.2	47.31	—	8.00
Lead blast furnace slag	Montzen, Belgium	11.40	51.40	1.44	—
Lead blast furnace slag	Laurium, Greece	17.33	29.88	trace	11.38
Lead blast furnace slag	Tombstone, Ariz.	7.50	11.56	—	6.34

position of Slags

osition						Reference
SiO_2	MnO	P_2O_5	Na_2O K_2O	CaS	TiO_2	
%	%	%	%	%	%	
5.10	5.56	21.37	0.80	—	—	Fertilizer slag W. H. Morris, T. A. I. M. E., XXI, 232.
32.73	0.77	0.22	—	2.39	2.35	B. F. Fackenthal, T. A. I. M. E., XXI, 348.
42.05	2.96	—	—	—	—	R. Ackerman, T. A. I. M. E., XXII, 275.
47.70	5.67	—	—	0.50	—	R. Ackerman, T. A. I. M. E., XXII, 275.
27.83	—	—	—	—	36.18	Titaniferous ores. Ilmenite W. M. Bowron, T. A. I. M. E., XI, 159.
46.85	7.53	—	2.72	0.34	—	F. P. Dewey, T. A. I. M. E., XVII, 470.
39.95	—	—	—	—	—	F. Firmstone, T. A. I. M. E., XXIV, 499.
37.82	—	—	—	1.82	—	F. Firmstone, T. A. I. M. E., XXIV, 499.
5.80	3.50	18.10	Fe_2O_3 15.42	S 0.32	—	Stead and Ridsdale, Trans. Lond. Chem. Soc., 1887, p. 601.
40.50	25.43	—	—	—	—	Manganiferous iron R. Ackerman, T. A. I. M. E., XXII, 275.
64.16	12.80	Fe 2.38	—	—	—	Chas. F. King, T. A. I. M. E., IX, 264.
50.73	19.60	—	—	—	—	H. H. Campbell, T. A. I. M. E., XXII, 440.
8.00	7.29	15.13	—	—	—	H. H. Campbell, T. A. I. M. E., XXII, 440.
9.85	8.26	15.38	—	—	—	H. H. Campbell, T. A. I. M. E., XXII, 440.
16.39	6.41	3.84	—	—	—	Used for paint Axel Sahlin, T. A. I. M. E., XX, 385.
20.06	0.21	0.27	—	—	Cu 0.40	Used for paint Axel Sahlin, T. A. I. M. E., XX, 385.
37.20	tr.	—	ZnO 2.24	S 0.17	Ag 0.28	Carl Henrich, T. A. I. M. E., XXV, 217.
31.04	0.51	—	Zn 2.01	S 1.36	Cu 0.45	W. A. Heywood, E. & M. Jour., 77, 395.
36.80	—	—	ZnO 2.50	—	Cu 0.20	S. E. Bretherton, Peters, Princ. of Copper Smelt., p. 331.
32.57	Ni 0.19	Pb 2.25	Zn 0.42	S 0.26	Cu 3.18	James Douglas, Trans. I. M. & M., vol. 8, 1.
37.80	—	—	—	—	Cu 0.37 to 0.69	L. S. Austen, T. A. I. M. E. XXXVII, 473.
42.8	—	—	—	—	Cu 0.40	H. O. Hofman, T. A. I. M. E., 34, 293.
29.33	—	Pb 0.50	Zn 4.25	S 1.86	Ag 0.25 oz	A. Firket, Annales des Mines, Belgium, 1901, p. 237.
25.20	2.88	Pb 0.80	Zn 9.87	S 0.78	Ag 0.30 oz	H. F. Collins, E. & M. Jour., 87, 883.
29.60	43.25	Pb 1.40	Ag tr.	—	—	Special Lead Smelting Condition. J. A. Church, T. A. I. M. E. XXIV, 561.

into this form, high iron is necessary. When iron is absent and the slags are high in lime or magnesia and some alumina is present, there is a tendency to form zinc spinel, *i.e.* zinc aluminate, and also the mineral willemite, zinc silicate of a high melting-point and crystallizing out at a high temperature, like the spinel. If it is desired, therefore, to carry much zinc in the slag, the bases must be proportioned so that the zinc may enter into the olivine group of minerals. The presence of zinc in amounts above 5 to 8 per cent. raises the melting-point of the slags and increases their viscosity very decidedly.

The preceding table gives the composition of various typical slags.

CHAPTER IX

MATTE, BULLION, AND SPEISE

MATTE. — A *matte* is an artificial sulphide of a metal, or a mixture or conglomerate of such sulphides, frequently containing in minor quantities metallic copper and iron, etc., as also included slag, arsenides, and antimonides. It is an important intermediate product in copper and nickel smelting, and in lead smelting, and its treatment for the contained valuable metals comprises an important branch of the metallurgy of copper, lead, and nickel.

Mattes serve also as "collectors" of the precious metals, gold and silver. In a furnace charge in which metallic lead or copper is not produced, the matte formed will contain practically all the gold and silver.

Preliminary to a consideration of matte proper, the metallic sulphides and the several binary systems they enter into are considered.

I. *The various binary systems of the metallic sulphides and the binary systems of various sulphides and their respective metals entering into the constitution of matte.* — The chief sulphides found in matte are cuprous sulphide, Cu_2S; ferrous sulphide, FeS; and lead sulphide, PbS. Zinc sulphide, ZnS, is present in subordinate amounts; silver is present, probably as sulphide Ag_2S, in very small amount. The condition of the gold is not definitely known.

The metals present in the free state, or nearly so, are iron and copper. Other impurities, such as antimony and arsenic, are present in most mattes, in small amounts, and their condition is not considered. The sulphides enumerated above are considered as chemical compounds, though, judging from their thermal analysis, Friedrich[1] does not believe this theorem to be absolutely established.

The binary systems of the sulphides discussed are: FeS–Cu_2S;

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[1] Metallurgie, V, 57 (1908).

$PbS–Cu_2S$; $Ag_2S–Cu_2S$; $ZnS–Cu_2S$; $FeS–PbS$; $Fe_7S_8–PbS$; $FeS–ZnS$; $PbS–Ag_2S$; $PbS–ZnS$; and $Ag_2S–ZnS$; and the systems of metals and their respective sulphides are: Fe–FeS; $Cu–Cu_2S$; and Pb–PbS.

The end members of the sulphide series, and their melting-points.—It has been mentioned that the sulphides are considered as chemical compounds, but the end members of the various binary systems are rarely the pure compound; in fact, it will be shown that the end member may consist of the sulphide plus either sulphur or the metal in a small excess. Thus, the iron sulphide member may be $FeS + Fe$ or $FeS + S$; the cuprous sulphide member, $Cu_2S + Cu$, or $Cu_2S + S$, etc.

1. **Iron Sulphide.** — The subject of iron sulphide has been thoroughly investigated by Le Chatelier and Ziegler,[1] who came to the conclusion that the proto-sulphide of iron, FeS, is a chemical compound, and that no sub-sulphide of iron exists. This has also been demonstrated by other investigators. Le Chatelier and Ziegler show that, at a temperature of 1200° C., the compound FeS begins to lose sulphur by vaporization, the result being a mixture of FeS and Fe, and that at 1500° C. this decomposition is very appreciable. They also show that iron oxide, probably Fe_3O_4, may be present in the sulphide and will form a eutectic with iron sulphide. Thus, ordinary iron sulphide is a ternary system, showing under the microscope FeS and Fe and a eutectic of FeS and Fe_3O_4. (See remarks on ternary systems further on in this chapter.) Treitschke and Tammann [2] have also investigated the system of FeS–Fe, and confirm the results of Le Chatelier and Ziegler. They give the melting-point of FeS by extrapolation at 1300° C., which is high.

The eutectic between Fe and FeS has a composition of 16 per cent. Fe and 84 per cent. FeS, and freezes at 970° C. The components of the eutectic, however, are not pure Fe and FeS, but mixed crystals of FeS dissolving 2 per cent. Fe, and Fe dissolving a small proportion of FeS.

In the mattes produced in copper and lead smelting the FeS of the matte is, in most cases, derived from some higher sulphide,

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[1] Bulletin de la Soc. d'Encouragement pour l'Industrie Nationale, etc., CIII, 368 (1902).

[2] Treitschke und Tammann, Über das Zustandsdiagramm von Eisen und Schwefel, Zeit. für Anorganische Chemie, XLIX, 320 (1906).

FeS_2, pyrite; Fe_7S_8, pyrrhotite; or $CuFeS_2$, chalcopyrite; or other copper-iron sulphides. As the temperature of smelting almost invariably exceeds 1200° C., the final product, as regards the iron sulphide, is a member of the series FeS–Fe, the amount of metallic iron present depending upon the temperature reached. The vaporization of sulphur from FeS increases rapidly with the temperature, but is not great until 1400° or 1500° C. is reached, so that the amount of metallic iron in most mattes is not great, and is usually in solution in the FeS, and possibly in the Cu_2S. Some mattes, however, produced at a high temperature may have a large quantity of metallic iron present. That iron oxide, Fe_3O_4, may be present with iron sulphide is shown by the researches of Le Chatelier and Ziegler, and confirmed by Treitschke and Tammann. Iron oxide and iron sulphide can be coexistent below a temperature of about 1100° C.,[1] but with certain concentration (high FeS) and temperatures above 1100 or 1200° C., the two substances react, with the production of metallic iron and SO_2:

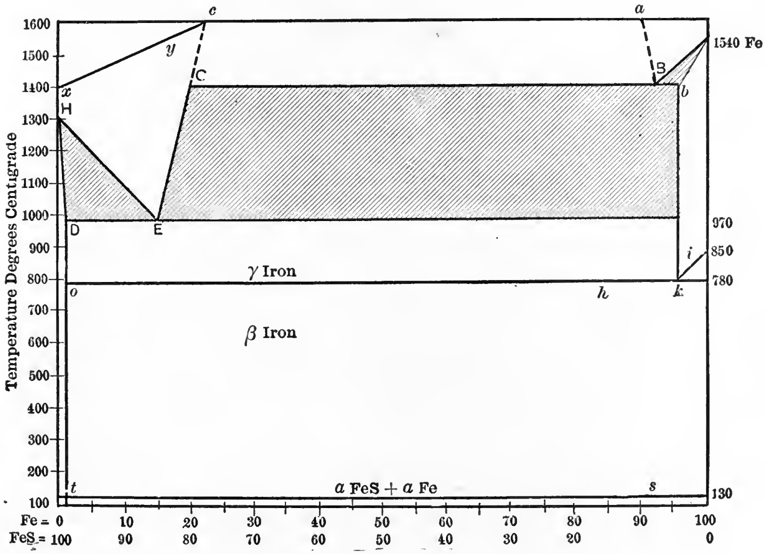

Fig. 86. — The system Fe–FeS.

$$5\,Fe + 2\,SO_2 \rightleftarrows 2\,FeS + Fe_3O_4.$$

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[1] Heyn und Bauer, Metallurgie, III, 84 (1906).

In the mattes examined there is no definite microscopic evidence of iron oxide, although it is evident that, under certain conditions, its existence is possible. The most favorable conditions for the production of mattes containing iron oxide are to be found in reverberatory smelting.

The system FeS–S has not been extensively investigated, but from the references in Table XLVI it is shown by independent observers that its melting-point is above that of FeS. The melting-point of pure FeS can be obtained practically only by extrapolation or interpolation, in so far as heating above its melting-point, which is necessary to make the determination, causes some decomposition.

TABLE XLVI. MELTING-POINT AND COMPOSITION OF THE FeS–S SYSTEM

Substance	Melting-Point	Chemical Composition		Reference
		Fe %	S %	
FeS	1171° C.	63.59	36.41	Friedrich, Metallurgie, V, 56.
FeS	1194° C.	63.59	36.41	Bornemann, Metallurgie, V, 64
FeS + Fe	1189° C.	63.70	36.21	Bornemann, Metallurgie, V, 64.
FeS + S	1203° C.	63.25	36.75	Bornemann, Metallurgie, V, 64.
FeS + S	1192° C.	61.75	38.25	Friedrich, Metallurgie, V, 56.
FeS ?	1133° C.	?	—	Röntgen, Metallurgie, III, 479.
FeS ?	1300° C.	?	—	Tammann, Zeit. für Anorganische Chemie, XLIX, No. 3, 320.

According to Le Chatelier and Ziegler, and Treitschke and Tammann, iron sulphide has a transformation point at 140° C., with possibly a second point somewhat higher. This dimorphic change is accompanied by a contraction and shrinkage on cooling, and accounts for the fissured and porous appearance of this sulphide in mattes.

From the foregoing it would seem that the end member as regards iron sulphide is apt to be either FeS containing some Fe, or FeS containing some S, the iron or sulphur in excess being in solution in the FeS if present in not too great an amount. Considering the temperature of the production of mattes, which is almost invariably above 1200° C., and the sulphur content of matte as determined by chemical analysis, the iron sulphide of the matte is without question a member of the series FeS–Fe:

Mattes were examined which contained much metallic iron. These were produced by partial pyrite-smelting, with a slag of from 48 to 49 per cent. of SiO_2, requiring a high temperature for fusion.

These facts also explain the production of the so-called "iron sows" found most frequently in partial pyrite-smelting with highly siliceous slags requiring high temperatures. The sows represent the segregated iron from the matte.[1] It is also probable that at these high temperatures the reaction between FeS and Fe_3O_4 in the presence of much FeS contributes to the formation of metallic iron.[2]

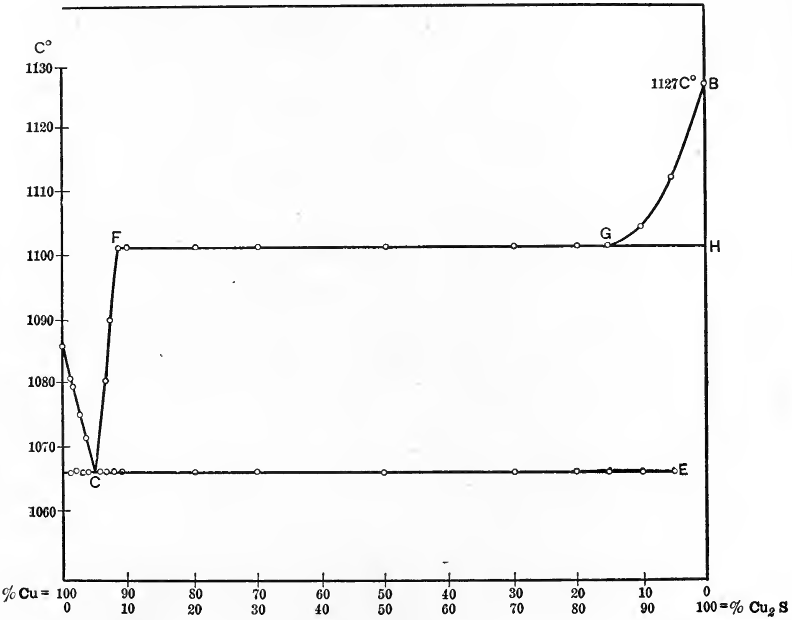

FIG. 87. — The system Cu_2S–Cu.

2. **Cuprous Sulphide.** — This substance presents the same general aspect as iron sulphide. It is a chemical compound of the formula Cu_2S, and is the only sub-sulphide known as far as the researches go.[3] Fig. 87 shows the curve of the system Cu_2S–Cu. It is of the same type as that of FeS–Fe, except that in this case the eutectic lies near the metal side, and has a compo-

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[1] See also Peter's Principles of Copper Smelting, p. 403 (1907).

[2] Engineering and Mining Journal, LXXVIII, 333 (1904).

[3] Heyn und Bauer. *Ibid.*

sition of 3.8 per cent. of Cu_2S and 96.2 per cent. of Cu, and freezes at 1067° C. Cu and Cu_2S are practically insoluble in each other in the solid state. An addition of either sulphur or copper to the sulphide has the effect of lowering the melting-point. Table XLVII gives data on the melting-point of cuprous sulphide.

TABLE XLVII. MELTING-POINT AND COMPOSITION OF Cu_2S.

Substance	Melting-Point	Chemical Composition	Reference
$Cu_2S + S$	1127° C.	Cu_2S, 99.71 per cent.	Heyn & Bauer, Metallurgie, III, 78
Cu_2S	1135° C.	Cu_2S, 100 per cent.	Friedrich, Metallurgie, V, 52
$Cu_2S + S$	1101° C.	Cu, 78.6 per cent.	Friedrich, Metallurgie, V, 52
Cu_2S ?	1085° C.	?	Röntgen, Metallurgie, III, 479
$Cu_2S + S$	1152° C.	Cu, 78.94 per cent.	Hofman, Trans., XXXVIII, 142
$Cu_2S + Cu$	1110° C.	Cu_2S, 95 per cent. Cu, 5 per cent.	Heyn & Bauer, *Ibid.*

Copper sulphide, like iron and other sulphides, has the property of losing sulphur by volatilization above its melting-point.[1] From the foregoing data, and taking into consideration the temperature of smelting in the production of mattes, and the evidence furnished by chemical analysis and metallographic researches outlined later, it is evident that the end member on the cuprous sulphide side is one of the series Cu_2S–Cu.

Cuprous sulphide undergoes a dimorphic change at 103° C.[2] At this temperature copper which has previously been in solution is probably forced out as the so-called "moss copper" of mattes.

3. **Lead Sulphide.** — PbS is the lowest sulphide, no subsulphides being known. The system Pb–PbS, which has been worked out by K. Friedrich and A. Leroux,[3] shows a curve dropping from the melting-point of the sulphide to that of lead with no eutectic point and a practical insolubility of the constituents in each other in the solid state. Table XLVIII gives the data of the melting-point of PbS. (See table on next page.)

PbS, like other sulphides, suffers dissociation above its melt-

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[1] Friedrich, Beiträge zur Kenntnis der Schwefelmetalle, Metallurgie, V, 50 (1908); also V, 122 (1908).

[2] Landolt und Börnstein, Phys. Chem. Tabellen, 3d ed., 277 (1905).

[3] Blei und Schwefel, Metallurgie, II, 536 (1905).

TABLE XLVIII. MELTING-POINT OF PbS

Substance	Melting-Point	Chemical Composition		Reference
		Pb %	S %	
PbS	1120° C.	86.6	13.4	Friedrich, Metallurgie, V, 51
PbS + S	1130° C.	85.9	14.1	Friedrich, Metallurgie, V, 51
PbS + Pb	1114° C.	87.1	12.9	Friedrich, Metallurgie, V, 51
PbS ?	970° C.	—	—	Weidmann, Metallurgie, III, 660

ing-point, and loses sulphur, and it is markedly volatile as a whole.[1] The loss of sulphur, however, is not so marked as in the case of iron sulphide and cuprous sulphide. The end member in the case of lead sulphide in mattes is probably very nearly PbS.

4. **Zinc Sulphide.** — This sulphide enters into the constitution of matte to but a limited extent. Its melting-point has not been determined, due to its marked volatility at high temperatures and the fact that the boiling and melting-points lie very close together. Friedrich places the melting-point by extrapolation close to 1670° C.

THE BINARY SYSTEMS OF THE SULPHIDES IN DETAIL.

a. **Ferrous Sulphide-Cuprous Sulphide.** — This system has been investigated by Hofman [2] and Röntgen.[3] and K. Bornemann and F. Schreyer,[4] also by Baykoff and Troutneff.[5] The curves of Röntgen and Bornemann resemble each other, differing, however, much in detail. They are very complex and show a number of compounds. These of Hofman and Baykoff also resemble each other, and are much simpler than the first-mentioned curves, showing no chemical compounds. The investigation of this system is very difficult and final results are still to be obtained. Fig. 88 shows the Hofman curve and Fig. 89 that of Röntgen. Röntgen shows a main eutectic of the following composition: FeS, 67

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[1] K. Friedrich, Metallurgie, V, 51 (1908); Friedrich und Leroux, Metallurgie, II, 536 (1905).

[2] T. A. I. M. E., XXXVIII, 142 (1908).

[3] Metallurgie, III, 479 (1906).

[4] Metallurgie, VI, 619 (1909).

[5] Revue de Metallurgie, p. 519 (1909).

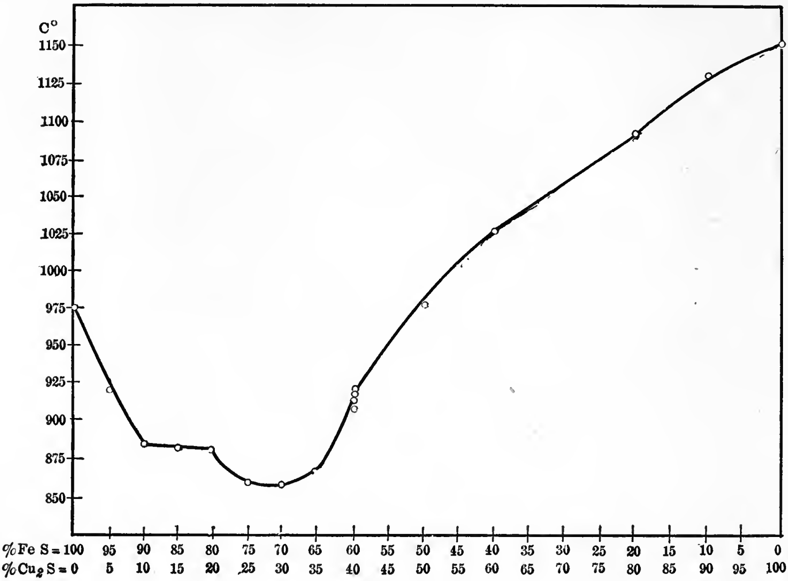

FIG. 88. — The system FeS–Cu_2S. (Hofman)

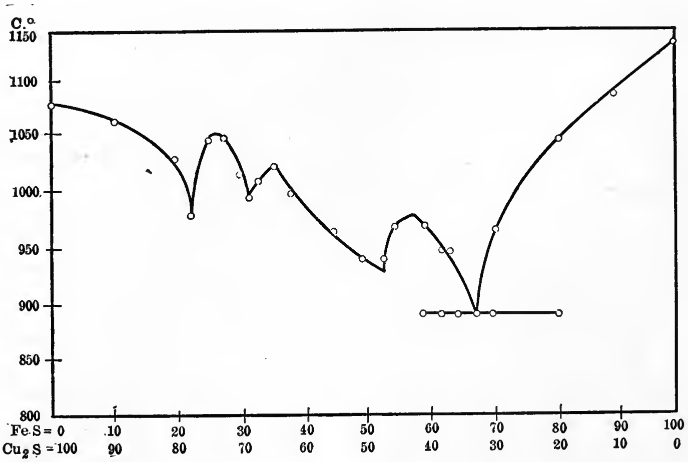

FIG. 89. — The system FeS–Cu_2S. (Röntgen)

and Cu_2S, 33 per cent., freezing at 895° C. Hofman shows a eutectic, determined chiefly by metallographic work, of FeS, 86, and Cu_2S, 14 per cent., freezing at 860° C.; Bornemann, at 66.3 FeS, 33.7 per cent. Cu_2S, freezing at 978° C. In mattes the eutectic composition is very close to Cu_2S, 21 to 22, and FeS, 78 to 79 per cent., which corresponds to Cu, 17 per cent.

Hofman gives the eutectiferous range as extending from 20 to 90 per cent. FeS, assuming the existence of mixed crystals, one of 10 per cent. of Cu_2S in 90 per cent. of FeS, and the other of 20 per cent. of FeS in 80 per cent. of Cu_2S. The examination of mattes confirms this view, although in somewhat different limits, again referred to. In mattes no intermediate chemical compounds have been detected.

b. Lead Sulphide-Cuprous Sulphide. — This system, which has been investigated by K. Friedrich,[1] has the freezing-point curve shown in Fig. 90. The end members in the investigation were not absolutely pure, the cuprous sulphide member being represented by Cu_2S, 99.6 per cent., and the lead sulphide member by PbS, 99.6 per cent. The series is eutectiferous throughout, implying but little reciprocal solubility of the constituents in the solid state. The eutectic has a composition of Cu_2S, 51 per cent.,

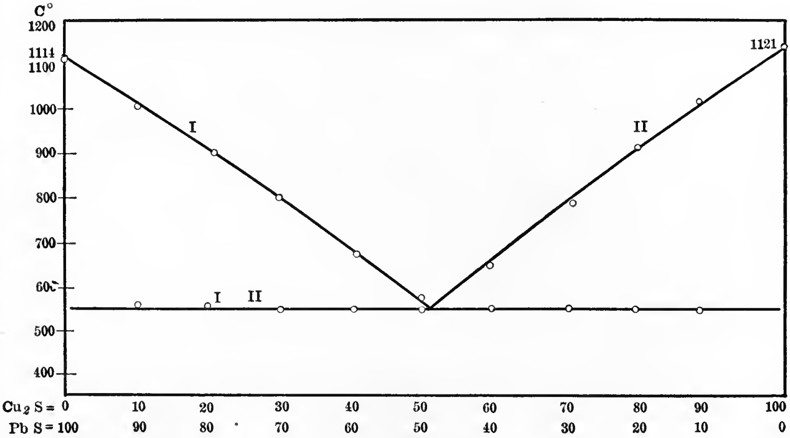

FIG. 90. — The system Cu_2S–PbS.

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[1] Bleiglanz-Kupfersulfür, Metallurgie, IV, 671 (1907).

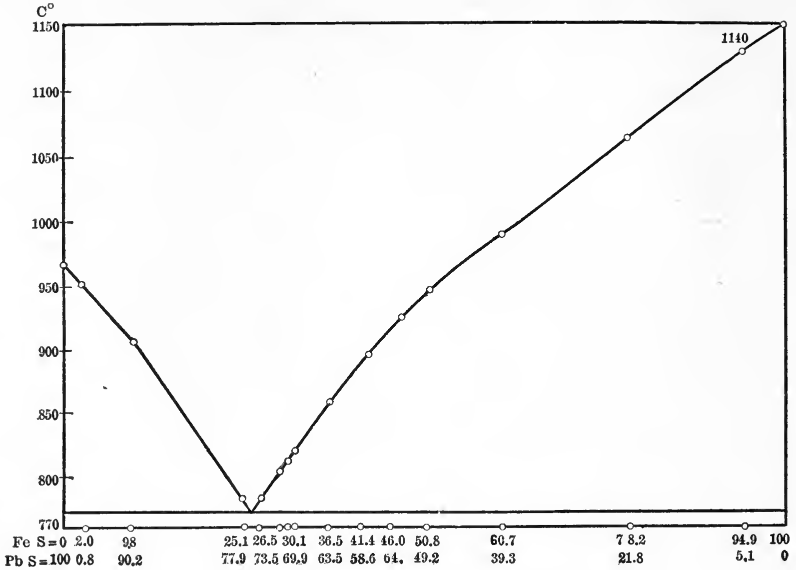

Fig. 91. — The system FeS–PbS.

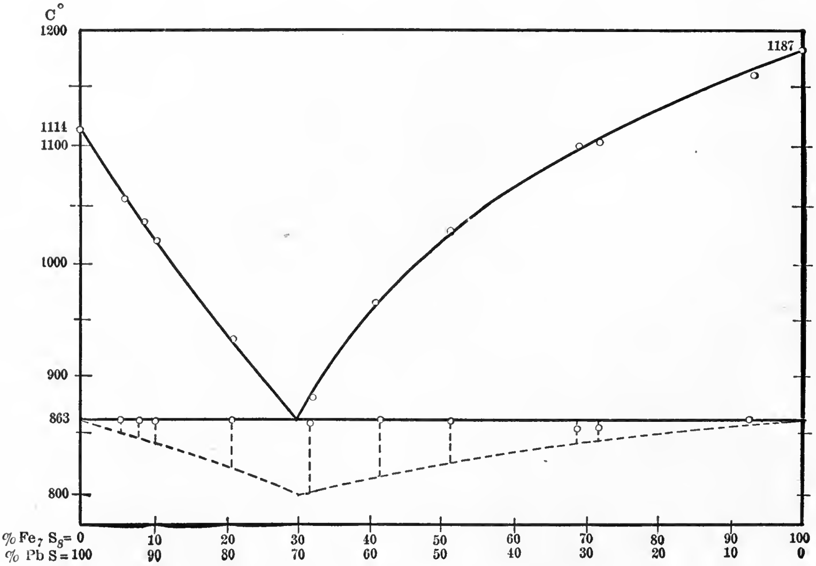

Fig. 92. — The system Fe_7S_8–PbS.

and PbS, 49 per cent., with the freezing-point at 540° C. This is the important system in lead-copper mattes.

c. Lead Sulphide-Ferrous Sulphide. — This system has been investigated by Weidmann.[1] The related system of lead sulphide-pyrrhotite has been investigated by Friedrich,[2] with practically the same result. The freezing-point curves are shown in Figs. 91 and 92 respectively. In neither case are the end members the pure sulphides, but they are very nearly pure.

Weidmann places the eutectic at FeS, 25.8, and PbS, 74.2 per cent., with the freezing-point at 782° C. Friedrich gives the eutectic at Fe_7S_8, 30, and PbS, 70 per cent., with a freezing-point at 863° C. Both investigators show the eutectic range to be from ordinate to ordinate, implying a practical reciprocal insolubility of the constituents in the solid state.

d. Silver Sulphide-Cuprous Sulphide. — K. Friedrich has investigated this system,[3] the freezing-point curve of which is reproduced in Fig. 93. The system consists of an unbroken series of mixed crystals. Neither the thermal investigations nor the

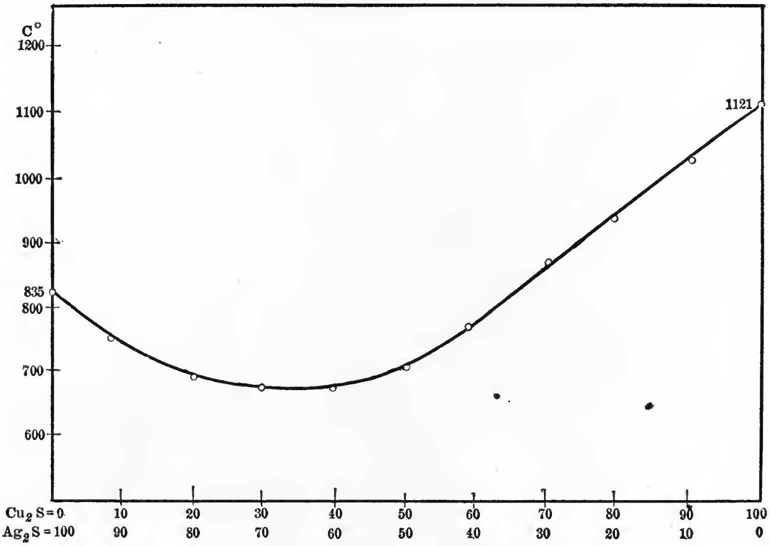

FIG. 93. — The system Ag_2S–Cu_2S.

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[1] Bleistein, Metallurgie, III, 660 (1906).

[2] Bleiglanz-Magnetkies, Metallurgie IV, 480 (1907).

[3] Schwefelsilber-Kupfersulfür, Metallurgie, IV, 671 (1907).

microscopic sections give any indications of a eutectic. The end members were not absolutely pure sulphides. The Ag_2S had a melting-point of 835° C., and the Cu_2S of 1121° C. The curve shows a minimum at 677° C., at a composition of Ag_2S, 70, and Cu_2S, 30 per cent.

This is the only system of all those under discussion in which the constituents form an unbroken series of mixed crystals, implying a very powerful solvent action. There seems little doubt that in the presence of cuprous sulphide, any silver present in the matte is held in solution by the cuprous sulphide. From the results of the system under discussion the silver in mattes is probably present as silver sulphide, unless the temperature at which the matte is produced is unusually high.

e. Silver Sulphide-Lead Sulphide. — This system has been investigated by K. Friedrich[1] and is chiefly of interest in connection with the manner in which the precious metals are carried in mattes. The freezing-point curve of the system is shown in Fig. 94. Neither of the end members was a pure sulphide. The

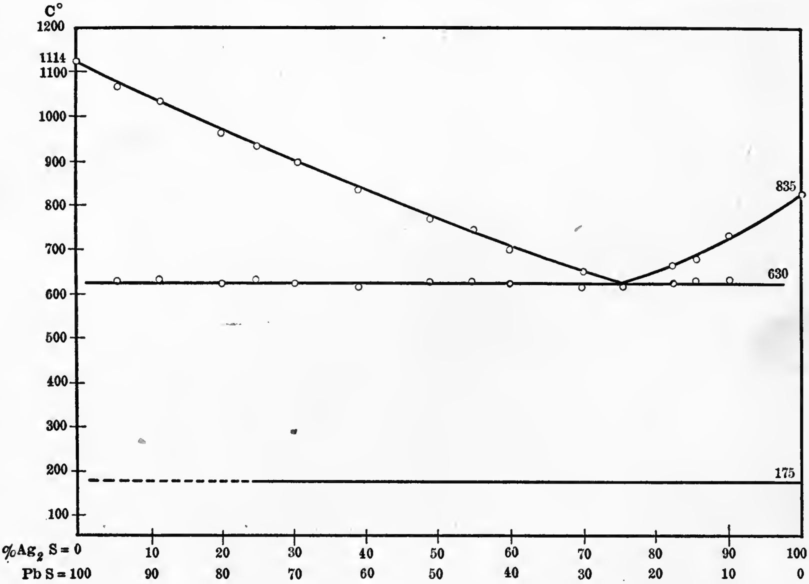

Fig. 94. — The system Ag_2S–PbS.

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[1] Bleiglanz-Schwefelsilber, Metallurgie, IV, 479 (1907).

melting-point of the Ag_2S was 835° C., and that of the PbS, 1114° C. A eutectic occurs of the composition Ag_2S, 77, and PbS, 23 per cent., which has a freezing-point of 630° C. The eutectiferous range does not extend across to the ordinates, but there is a reciprocal solubility of 2 per cent. forming two series of mixed crystals.

Lead sulphide, has, therefore, an appreciable solvent action on silver sulphide sufficient to assume all of the silver in mattes to be in solution in the lead sulphide, provided cuprous sulphide is absent. The solvent action of cuprous sulphide on silver sulphide is undoubtedly more powerful than that of lead sulphide.

f. Silver Sulphide-Ferrous Sulphide. — This system has not been investigated, but it is known that ferrous sulphide has practically no solvent action on silver or on gold. Metallic iron, however, has a powerful solvent action on gold, the system iron-gold forming two series of mixed crystals.[1] Metallic iron, however, has practically no solvent action on silver.[2] Cuprous sulphide and copper, as is well known, have a powerful solvent action on gold.

g. Zinc Sulphide-Cuprous Sulphide; Zinc Sulphide-Ferrous Sulphide; Zinc Sulphide-Lead Sulphide; and Zinc Sulphide-Silver Sulphide. — These systems have been investigated by K. Friedrich.[3] and their freezing-point curves are shown in Figs. 95, 96, 97, and 98. Zinc is frequently present in matte as a minor constituent, as a rule rarely above 3 or 4 per cent., and most frequently less than this amount.

Zinc sulphide-cuprous sulphide do not alloy, and form no eutectic. Zinc sulphide is practically totally insoluble in cuprous sulphide, and vice versa.

Zinc sulphide-iron sulphide possess a eutectic at a composition of FeS, 95, and ZnS, 5 per cent., with a freezing-point at approximately 1145° C. Zinc sulphide possibly forms a mixed crystal with iron sulphide up to 3 per cent. Whether iron sulphide is soluble in zinc sulphide is doubtful.

Zinc sulphide-lead sulphide possess a eutectic of a compo-

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[1] Bolles, T. A. I. M. E., XXXV, 666 (1905). Pierce, T. A. I. M. E., XVIII, 454–457 (1889–90). Spilsbury, T. A. I. M .E., XV, 767 (1886–7). E. Isaac und G. Tammann, Über Eisen-Gold Legierungen, Metallurgie, IV, 469 (1907).

[2] Bolles, *Ibid.;* Pierce, *Ibid.;* Spilsbury, *Ibid.*

[3] Die Zinkblende als Steinbilder, Metallurgie, V, 114 (1908).

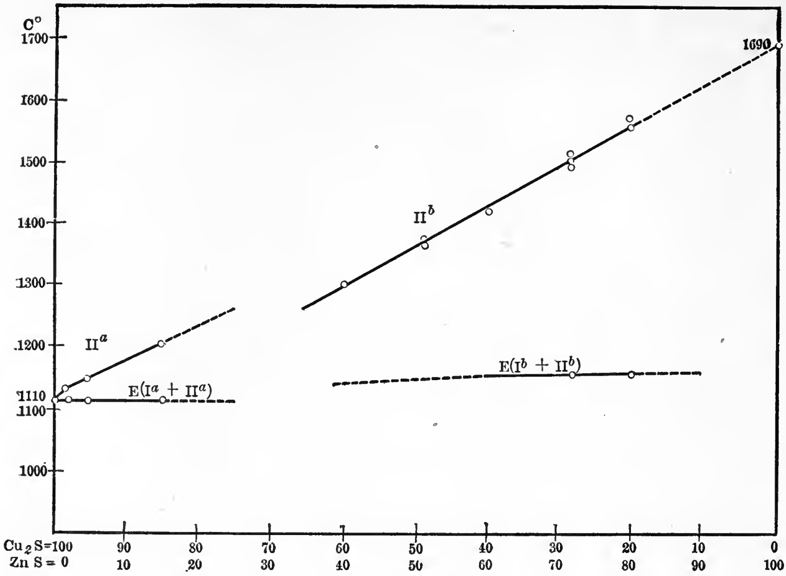

FIG. 95. — The system Cu_2S–ZnS.

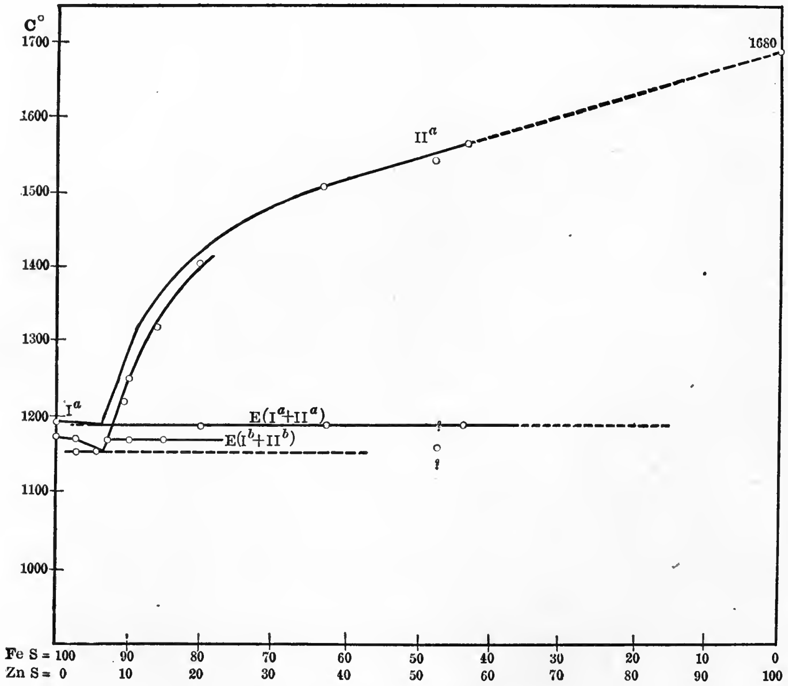

FIG. 96. — The system FeS–ZnS.

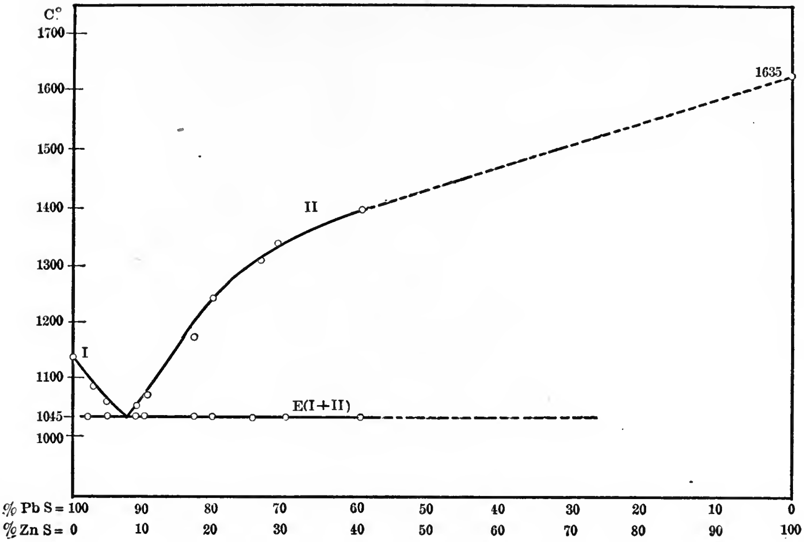

FIG. 97. — The system PbS–ZnS.

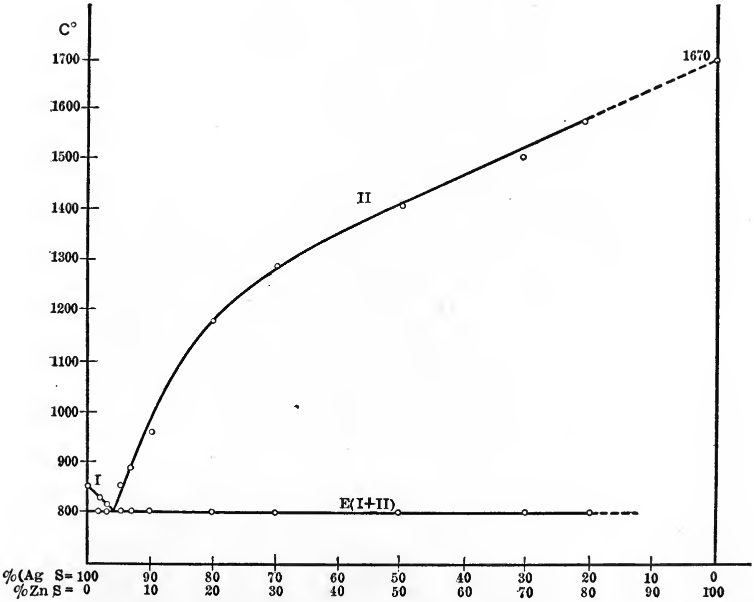

FIG. 98. — The system Ag_2S–ZnS.

sition PbS, 92, and ZnS, 8 per cent., with a freezing-point of approximately 1045° C. Zinc sulphide is practically insoluble in lead sulphide when solid, and probably vice versa.

Zinc sulphide-silver sulphide possess a eutectic of the composition ZnS, 3, and Ag_2S, 97 per cent., with a freezing-point at 800° C. ZnS is practically insoluble in Ag_2S. Ag_2S is probably practically insoluble in ZnS, or only soluble to a very limited extent. This is of interest again in connection with the condition of the precious metals in mattes, already discussed.

Matte. — In a microscopic examination of copper mattes and copper-lead mattes, derived from several metallurgical operations, the following constituents were found to be present, either all or in part.[1]

1. *A substance hereafter called "D"* — Under direct-reflected daylight it varies from a gray-blue to a sky-blue to a purple-blue color. With high-power incandescent electric light the blue color is somewhat lighter. This material may be either pure cuprous sulphide (Cu_2S), or $Cu_2S + Cu$, passing from this to a mixed crystal of Cu_2S–Cu, holding in solution FeS–Fe to a probable extent of 25 per cent. of FeS–Fe in 75 per cent. of Cu_2S–Cu. When nearly pure Cu_2S, it always shows the characteristic crystal boundary-lines of that substance; its color is then gray-blue to sky-blue. As the amount of iron increases the color passes to darker blue and purplish blue.

In sections of mattes high in copper, showing large fields of this material, if rapidly cooled, thus giving a fine-grained structure, a cloudy yellowish effect is often obtained, which is either an incipient eutectic, "B" (mentioned below), or the precipitation of FeS–Fe, from a saturated solution on cooling. The substance "D" is rarely porous, and usually presents a rather smooth uniform surface. In relief polish it shows itself to be the softest of the various constituents usually present in mattes. It frequently contains within itself in seams a substance hereafter called "F," of metallic luster and a copper color, which tests show to be pure or nearly pure metallic copper. This substance is further described below.

2. *A substance hereafter called "C."* — Under direct reflected daylight it shows usually a gray brass yellowish color. With

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[1] Fulton and Goodner, "The Constitution of Copper-Iron and Copper-Lead-Iron Mattes," T. A. I. M. E., XXXIX, 548 (1908).

incandescent electric illumination a lightening of the color is observable. In mattes very low in copper it sometimes has a rosin color like that of very pure blende. This material is either pure iron sulphide, FeS, or more usually FeS dissolving some Fe (2 per cent.), or, in the presence of Cu_2S, is a mixed crystal of FeS–Fe, dissolving as a maximum approximately 5 per cent. of Cu_2S. Cavities and blow-holes are of frequent occurrence in this material. This substance readily takes on a tarnish when exposed to the air, assuming a purplish tinge.

3. *A conglomerate substance, a eutectic, hereafter called "B."* Its individual constituents are the substances "D" and "C." In some of the mattes examined this eutectic is very clearly developed. As already mentioned, the eutectic composition between copper and iron sulphide occurs at what corresponds to about Cu_2S, 21, and FeS, 79 per cent., so that mattes low in copper show the existence of eutectic very much better than those high in copper. The eutectic in the mattes examined was both fine textured and coarse textured, dependent upon the rate of cooling. Some of the mattes examined consisted almost entirely of eutectic. Many of the specimens show a very strong tendency to the coalescence of the individual constituents of the eutectic, so that the phenomena of eutectic and large masses of both free mixed crystals "D" and "C" can be found in an apparent violation of the phase rule. This coalescence of the individual constituents of the eutectic is more marked as the amount of eutectic decreases, *i.e.* the percentage of copper increases, and in mattes of from 45 to 60 per cent. of copper the substance "C" frequently occurs in isolated masses thrown out by the coalescence or segregation of the substance "D" (of the eutectic), with the great mass of excess substance "D." In very rapidly cooled mattes it takes powers of from 400 to 900 diameters to resolve the eutectic into its constituents, but in slowly cooled mattes low powers show it plainly.

4. *A substance hereafter called "A."* — Under direct reflected daylight and electric light it has a brilliant white color. It is usually present in irregularly rounded and elongated grains, often of considerable size, evidently of roughly spherical or ellipsoid form. This substance answers to all tests for metallic iron. It is not a common constituent of mattes; in fact, it is usually absent except in those produced in conjunction with a highly siliceous slag, at a high furnace temperature. It is usually sur-

rounded by eutectic "B" or the mixed crystals "C" and "D." Wherever it is in contact with "D" seems to be a favorite place for the appearance of seams filled with "F" or metallic copper. In relief polish "A" shows itself to be the third hardest substance present, coming after "C." It is found in considerable quantities in some of the matte specimens mentioned above, constituting from one-third of the bulk downward.

5. *A substance hereafter called "F."* — In direct reflected daylight and electric light it shows a copper color, and answers to all tests for metallic copper. It most frequently fills long thin seams and occurs as minute crystals in cavities. Practically, it invariably occurs in fields of "D," and may be found in mattes of any copper tenor from the lowest to the highest, though more of it occurs in mattes high in copper, as will be noted later. It is the so-called "moss copper" of mattes.

6. *A substance hereafter called "G."* — In direct reflected daylight or electric light it shows a light purple color. It is generally in the form of crystals of rhomboidal cross-section, sometimes very much elongated. It is transluscent. Some of the crystals have zonal inclusions. At times, instead of crystals irregular grains of this substance are found. Its perfect crystal shape proclaims it to be the first of the constituents of the matte to take form. In most mattes but little of this substance is present, and in a number of specimens it is practically absent. It could not be positively identified, but evidence points it out to be either zinc sulphide or phosphide of iron. It occurs most plentifully in mattes containing considerable zinc. The mixed crystal "C" is probably capable of dissolving about 3 per cent. of ZnS.

7. *A substance hereafter called "L."* — In direct reflected daylight and electric light it shows a light gray color. It has a uniform peculiarly smooth appearance. Tests show it to be practically pure lead sulphide, PbS. It is found only in mattes containing lead in appreciable quantities.

8. *A conglomerate substance, a eutectic, hereafter called "K."* — Its individual constituents are "L" (lead sulphide) and "D" (mixed crystal, cuprous sulphide-iron sulphide), already described in detail. The eutectic is usually rather fine in texture, very delicate and smooth in appearance, and of typical structure. It shows the same tendency to coalescence that the

eutectic "B" does. The eutectic between lead sulphide-copper sulphide has been discussed under the binary systems.

9. *A substance hereafter called "M."* — By direct reflected daylight and electric light it has a light green gray color. It appears usually very sparingly as long thin strings of crystal grains. Its positive identification was not possible, but it is probably included slag.

The above seven substances and the two eutectics comprise all the constituents of copper-iron and copper-iron-lead mattes found.

Iron-Copper Mattes. — All iron-copper mattes examined show themselves decidedly to be conglomerates. There is a distinct eutectic present, often very beautifully developed, especially in slowly cooled mattes. This eutectic is best defined in mattes of low copper content, as already mentioned. In mattes of 35 per cent. of Cu and above it will, in most cases, be faint or absent, due to the strong coalescence of the individual constituents of the eutectic. In a number of specimens examined this coalescence could be plainly traced, some specimens showing on the one side of the section perfectly developed fine eutectic structures, which gradually passed to a coarse eutectic structure, and from that to the two individual constituents of the matte, "C" and "D," in isolated fields. When the matte contains about 60 per cent. of copper or 75 per cent. Cu_2S–Cu, and 25 per cent. FeS–Fe, no more "C" is visible, as 25 per cent. of FeS–Fe is the amount of this substance soluble in Cu_2S–Cu, forming the saturated mixed crystal "D." In mattes approximating this composition, but just below it, in fact down to 40 per cent. of copper, eutectic is practically never found, due to the strong segregation above mentioned, and the substance "C" is present in isolated fields within substance "D."

A number of specimens contained many cavities and cracks, these being mainly in substance "C." Cavities are but rarely found in substance "D." When the composition of the matte approaches that of "white metal," substance "D" shows well developed cleavage and crystal boundary planes. Inclusions, like gas bubbles, are frequently present. The substance "F," or metallic copper, is of common occurrence, and may be found in mattes of almost any copper tenor. It most generally occurs as thin, flat sheets and wires, which, in the microscopic section, appear as long, thin seams. These invariably occur in substance "D," so that this must be looked upon as the source of the metallic copper. This substance "F" (metallic copper), usually increases in quantity with the copper content of the matte. It is present in considerable quantity in many mattes which do not show its presence to the naked eye. The substance "G," or zinc sulphide, is a common constituent, although usually present in small amounts. Its general form is that of rhomboidal, translucent, purplish crystals, well developed, though it may be present as irregular grains in some very rapidly cooled mattes. The constituent "A," metallic iron, is present only in mattes produced under certain conditions, which have been discussed.

Copper-Iron-Lead Mattes. — In general appearance the structure of these mattes is similar to that of the copper-iron mattes, except that the eutectic usually present is "K," that of Cu_2S and PbS. In some cases both eutectics, "B" (Cu_2S–Cu, FeS–Fe), and "K" (PbS, Cu_2S–FeS), are found. The presence of lead sulphide, in commercial lead-copper mattes, usually reduces the amount of FeS, so that, in many instances, all of this substance is in solution in the Cu_2S–Cu.

The eutectic "K" shows the same tendency of the coalescence of its individual constituents, "D" and "L," that the eutectic "B" does, though in most mattes where it is not present in great amount there is no opportunity for this coalescence as it is the last of all the constituents to freeze.

The reason for the structure of mattes is developed in the section which follows. Figs. 99 to 104 inclusive show micro-photographs of iron-copper, and iron-copper-lead mattes.

The Constitution of Mattes. — It is desirable to append a discussion of the theoretic constitution of the most complex of the mattes under examination, *i.e.* the iron-copper-lead mattes, in order to explain the results obtained in the microscopic examination. The above matte should be considered as belonging to a ternary system, the members of which are assumed to be Cu_2S, PbS, and FeS, though in reality the end members will be Cu_2S–Cu, PbS and FeS–Fe, as previously outlined. There is no reason for viewing this as a quaternary system, Cu–Fe–Pb–S, since the sulphide compounds actually exist at the temperatures under discussion. It seems to be most generally assumed that in a ternary system the freezing-point of the ternary eutectic lies

FIG. 99. — Copper matte showing the eutectic "B." The light portion is the substance "D" and the dark portion is "C," being the entities making up the eutectic.

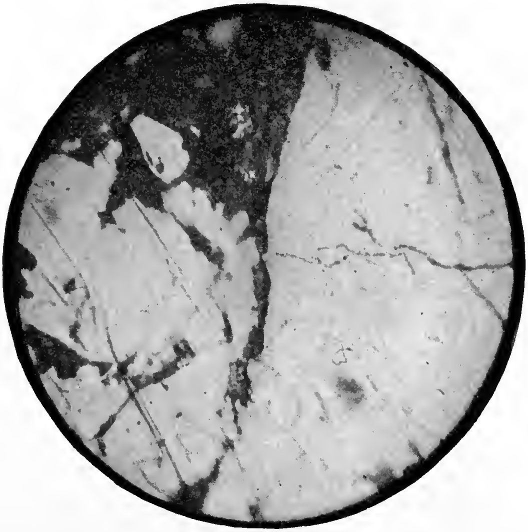

FIG. 100. — Copper matte. The light portion of the field is "D." The dark portion is "F," metallic copper.

below that of any of the eutectics of the binary systems entering into the ternary system. It can, however, be mathematically demonstrated, graphically and analytically, by an application of Raoult's and van't Hoff's law, of the depression of the freezing-point, that the ternary eutectic point may lie either below, at the same height (temperature ordinate), or above the lowest of the binary eutectics. In general, it is apt to lie above the lowest binary eutectic, when the freezing-points of the eutectics of the other two binary systems are relatively much higher than that of the third or lowest. Raoult's and van't Hoff's law of the depression of the freezing-point is applicable only to substances insoluble in each other in the solid state. It applies practically to two of the binary systems, $PbS–FeS$ and $PbS–Cu_2S$, and not to $Cu_2S–FeS$. The graphical demonstration of a ternary system can well be made according to the equilateral prism method, the freezing-point curves of the binary systems being plotted on the sides of the prism, ordinates indicating temperatures. In the case of simple V curves, the point of intersection of the three surfaces passed through, each two branches of the V curves common to one constituent of the ternary system marks the position of the ternary eutectic, as regards both composition and temperature of freezing.

Three binary systems, $PbS–Cu_2S$, $FeS–PbS$, and $FeS–Cu_2S$, enter into the ternary system under discussion. These have been fully discussed, but it is desirable to repeat the composition and freezing-points of their eutectics. $Cu_2S–FeS$: eutectic composition, Cu_2S, 21, FeS, 79 per cent.; freezing-point, 895° C. $Cu_2S–PbS$: eutectic composition, Cu_2S, 51, PbS, 49 per cent.; freezing point, 540° C. $PbS–FeS$: eutectic composition, FeS, 25.8; PbS, 74.2 per cent.; freezing-point of eutectic, 782° C.

From a graphical demonstration, taking into account the nature of the $Cu_2S–FeS$ curve, it is evident that the ternary eutectic point lies above that of the lowest binary eutectic, viz., $PbS–Cu_2S$ at 540° C. Therefore the ternary eutectic is a "hidden eutectic" and it follows from analysis that no true ternary eutectic, *i.e.* a conglomerate of the three substances, FeS, PbS, Cu_2S, can exist in the solid mass. In no instance was there found any indication of a ternary eutectic in the mattes examined, but very decided cases of two binary eutectics. If the ternary eutectic freezing-point is lower than that of any of the three binary eutec-

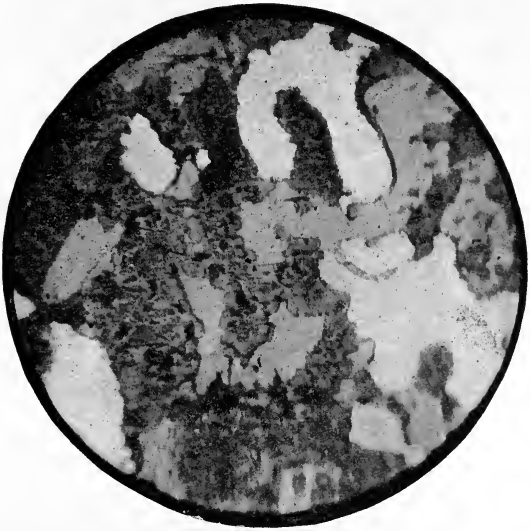

FIG. 101. — Copper matte. The white portion is metallic iron. The next lightest portion is substance "D." The next darkest portion is substance "C," in which the still darker spots are cavities.

FIG. 102. — Copper matte. Same as shown in Fig. 99, but under increased magnification.

tics, a ternary eutectic conglomerate should be found. From analysis it would also appear that the main eutectic to be found in a case such as the above is that of the lowest freezing-point, *i.e.* PbS–Cu_2S, or "K." This was invariably present in the lead-copper-iron mattes examined.

In order to demonstrate the constitution more clearly, there is outlined below the freezing of copper-lead-iron matte, making certain assumptions as follows:

1. That the composition of the "hidden" ternary eutectic is PbS, 40; FeS, 25; Cu_2S, 35 per cent., with a freezing-point at 600° C.

2. For the sake of simplicity in calculation the eutectic composition of the binary eutectics is assumed as follows:

a. Cu_2S–FeS containing Cu_2S, 20; FeS, 80 per cent., or taking into account that 80 per cent. of Cu_2S dissolves 20 per cent. of FeS, a eutectic composition of FeS, 75; Cu_2S–FeS, 25 per cent., with a freezing-point at 895° C.

b. PbS–FeS containing PbS, 72, and FeS, 28 per cent., freezing at 782° C.

c. Cu_2S–PbS containing Cu_2S–FeS, 50, and PbS, 50 per cent., freezing at 535° C., this again taking into account the solubility of FeS in Cu_2S.

Case I. — Taking 100 g. of matte of the following composition: FeS, 25; PbS, 25; and Cu_2S, 50 per cent., and recalculating in order to provide for the FeS dissolved in the Cu_2S, we have 62.5 g. of Cu_2S–FeS, 12.5 g. of FeS, and 25 g. of PbS. Above 600° C., the ternary eutectic point, the excess substance is all that portion of the matte in excess of the ternary eutectic composition. The ternary eutectic composition of this matte, according to the percentage assumption above, is 25 g. of PbS, 27.3 g. of Cu_2S–FeS, and 10.1 g. of FeS, a total of 62.4 g. The excess substance is therefore 35.2 g. of Cu_2S–FeS and 2.4 g. of FeS, a total of 37.6 g. As the matte cools towards 895° C., the point at which the eutectic between Cu_2S and FeS forms, the first true excess, Cu_2S–FeS, freezes out, and when 895° C. is reached, 34.4 g. of this substance or substance "D" will have separated out. Then at 895° C. the eutectic between Cu_2S and FeS freezes out, the amount being 3.2 g., composed of 2.4 g. of FeS and 0.8 g. of Cu_2S–FeS.

The mother metal is now of ternary eutectic composition and simply cools from 895° C. to 600° C., remaining molten during

FIG. 103. — Copper-lead matte. In the center of the field, faintly shown, is the eutectic "K." The light portion surrounding it is substance "D." The darker substance adjoining it on the bottom to the left is substance "C," in which are some cavities.

FIG. 104. — Copper-lead matte. The eutectic "K" and fields of substance "D."

this interval. Since a binary eutectic between PbS and Cu_2S exists which has a lower freezing-point (535° C.) than that of the "hidden" ternary eutectic, no true ternary eutectic conglomerate can freeze out at 600° C., but at this temperature the "excess substance, over the lowest binary eutectic, will separate out. This excess substance, according to calculation, is 10.1 g. of FeS, and 2.3 g. of Cu_2S–FeS, and is in reality in surfusion, and while, according to calculation, it represents an excess of 3.2 g. of FeS, and 9.2 g. of eutectic "B" (6.9 g. of FeS and 2.3 g. of Cu_2S–FeS), it probably freezes out at once, showing only incipient eutectic structure. The mother metal now has the eutectic composition of the eutectic between PbS and Cu_2S–FeS and cools down to 535° C., when it freezes to the eutectic "K," or Cu_2S–FeS, 50, and PbS, 50 per cent., or, in actual amount, 50 g. composed of 25 g. each of the above-named substances, or "D" and "L."

It is to be noted that this manner of freezing, with the separating out of the eutectic "B" at higher temperature while a large mass of mother metal is molten, gives the greatest possible opportunity for the coalescence of the individual constituents of this eutectic, so that it is to be expected that segregated fields of the individual substances rather than eutectic structure should be found. This was the actual result of the microscopic examination of the copper-lead-iron mattes. The eutectic "B" was found, but only in isolated instances.

Case II. — Taking 100 g. of matte of the following composition: Cu_2S, 18; PbS, 20; and FeS, 62 per cent., and recalculating to provide for the FeS dissolved in the Cu_2S, we have Cu_2S–FeS, 22.5; PbS, 20; and FeS, 57.5 per cent. The ternary eutectic of this matte according to the percentage composition is 20 g. of PbS, 21.8 g. of Cu_2S–FeS, and 8.1 g. of FeS. The excess substance is therefore 0.7 g. of Cu_2S–FeS, and 49.4 g. FeS. As the matte cools towards 895° C., FeS separates out as the first true excess, and when this temperature has been reached, 47.3 g. of this substance, or "C," will have separated out. Then the eutectic "B" freezes, amounting to 2.8 g., composed of 0.7 g. of "D" and 2.1 g. of "C." The mother metal is now of ternary eutectic composition and cools to 600° C., when the excess substance, 8.1 g. of FeS and 1.8 g. of Cu_2S–FeS, separates out, as described in Case I. The remaining mother metal now cools and finally freezes to 40 g. of eutectic "K," as described for Case I.

Case III. — Taking 100 g. of matte of the following composition: PbS, 70; FeS, 20; and Cu_2S, 10 per cent. (this is of unusual composition as regards ordinary lead-copper-iron mattes, and is taken here only to outline the method of freezing), and recalculating to provide for the FeS dissolved in the Cu_2S, we have PbS, 70; Cu_2S–FeS, 12.5; and FeS, 17.5 per cent. The ternary eutectic of this matte according to the percentage eutectic composition is 12.5 g. of Cu_2S–FeS, 11.4 g. of PbS, and 4.6 g. of FeS. The excess substance is therefore 58.6 g. of PbS and 12.9 g. of FeS, but it must be borne in mind that in order to form the final binary eutectic, "K," 12.5 g. of PbS are required; therefore the real amount of the excess is 57.5 g. of PbS and 12.9 g. of FeS.

As the matte cools towards 782° C. (the point at which the eutectic between FeS and PbS forms), PbS separates out as excess substance, until at 782° C., 24.3 g. has separated out; then the eutectic of these two substances freezes, amounting to 46.1 g., and composed of 33.2 g. of PbS and 12.9 g. of FeS. The mother metal then simply cools to 600° C., the ternary eutectic point, when "excess substance," FeS, freezes out, amounting to 4.6 g. The remaining mother metal, then of eutectic "K" composition, cools to 535° C., when it freezes as the eutectic "K," amounting to 25 g. The composition of the matte as frozen then is:

First excess, PbS, or "L"		= 24.3 g.	
" binary eutectic, PbS–FeS	PbS	= 33.2 g.	46.1 g.
	FeS	= 12.9 g.	
Second excess, FeS, or "C"		= 4.6 g.	
" binary eutectic Cu_2S, FeS–PbS, or "K"	Cu_2S, FeS	= 12.5 g.	25 g.
	PbS	= 12.5 g.	
Total		100.0 g.	

These three cases illustrate the manner of freezing of a copper-lead-iron matte, and tend to explain the constitution as found by microscopic analysis. The freezing of an ordinary copper-iron matte is much simpler and need not be further discussed. There seems to be reason to believe that in the case of copper-iron matte containing metallic iron the method of freezing is a similar one, as is indicated by the absence of any evidence of ternary conglomerate eutectic, but the presence of fields of metallic iron, indicating it as the first excess substance to be frozen out.

The case of the probable zinc sulphide crystals, substance "G," is explained in the same manner. If the iron and zinc sulphide do enter into any eutectic during freezing, the very powerful tendency toward coalescence, already discussed, explains their presence as isolated constituents.

The Relation of the Microscopic Constitution to the Chemical Composition of Mattes. — It has been frequently noted that the sulphur content of mattes does not correspond with that called for by considering the copper, iron, lead, etc., combined as the sulphides, Cu_2S, PbS, and FeS. Table XLIX gives the composition of mattes based on the theory that the metals are present as sulphides only.

TABLE XLIX. CALCULATED COMPOSITION OF MATTES HAVING THE METALS PRESENT AS SULPHIDES

Copper	Iron	Sulphur	Total
%	%	%	%
00.0	63.64	36.36	100 = FeS
7.99	57.28	34.73	100
11.985	54.094	33.92	100
31.96	38.184	29.856	100
47.94	25.456	26.604	100
63.92	12.728	23.352	100
79.9	0.00	20.1	100 = Cu_2S

The range of sulphur in true mattes, including lead mattes, is from 18 to 27 per cent. A very common figure for ordinary copper-iron mattes is in the neighborhood of 23 or 24 per cent. The sulphur is lowest in copper-iron-lead mattes and highest in copper-iron mattes containing much iron. It is plain that the sulphur content is below that called for by the assumption that all of the metal present is combined as the sulphide. From what has gone before it is not necessary to give further explanation. Considering the temperature of the production of most mattes, it is evident that the end members are not Cu_2S, FeS, PbS, etc., but are $Cu_2S + Cu$, $FeS + Fe$, $PbS + Pb$. This is also borne out fully by the microscopic examination. Witness the almost invariable presence of metallic copper, and in certain rare instances the large amount of metallic iron. In ordinary mattes the metallic iron is not visible microscopically, being in solution in the FeS and possibly in the Cu_2S–FeS to some extent. When present, however, in any quantity, it shows up very plainly. Some further discussion is necessary in reference to the metallic copper.

According to the researches of Heyn and Bauer[1] and of other observers, metallic copper is insoluble in cuprous sulphide in the solid state. The work of the above-named authors did not include the dimorphic point of Cu_2S, which occurs at 103° C. It has been observed that metallic copper, so-called "moss copper," is sometimes present in mattes of a low copper tenor, as low as 10 per cent. of copper. In watching the cooling of casts of this matte it was noticeable that this "moss copper" appeared suddenly when the matte was nearly cold, relatively speaking, but still too hot to bear the hand upon it. This is confirmed by C. S. Palmer[2] and also by E. L. Larison.[3]

In view of these facts it is suggested that the dimorphic point, 103° C., marks the throwing out of metallic copper from solution in the Cu_2S–FeS. It has already been shown that this metallic copper originates exclusively in fields of Cu_2S–FeS, or substance "D," and not in FeS, or "C." The presence of "moss copper" in mattes of such low copper content will seem unusual, but the explanation readily follows when it is considered that these mattes were produced by partial pyrite smelting with a slag containing from 46 to 49 per cent. of SiO_2, necessitating a high temperature. The presence of metallic iron in considerable quantity in these mattes indicates the temperature employed. Ordinarily, "moss copper" visible to the naked eye is not seen in mattes containing less than 30 per cent. of copper.

Matte as a Carrier of the Precious Metals. — As to which constituents of a matte act as solvents for the precious metals has already been discussed. To recapitulate: Cuprous sulphide and silver sulphide form an unbroken series of mixed crystals, and there is little doubt that when cuprous sulphide is present, silver is in solution in this substance as sulphide. Metallic copper, usually present in copper mattes, has a powerful solvent action on both silver and gold. Cuprous sulphide has a powerful solvent action on gold. Lead sulphide has a considerable sol-

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[1] Metallurgie, III, 84 (1906).

[2] Mining and Scientific Press, XCIII, 604 (1906).

[3] Mining World, XXVII, 550 (1907).

vent action on silver sulphide, but probably only a limited one on gold. Zinc sulphide has very little solvent action on silver sulphide and probably little on gold. Metallic iron has a powerful solvent action on gold and but a very limited one on silver. Ferrous sulphide has practically no solvent action on silver sulphide or on gold. Arsenic and antimony are present usually in very small amounts, and in view of the well-known feeble solvent action of "speise," it is believed that their presence has practically no significance as a solvent for the precious metals. The substances in mattes, therefore, which dissolve precious metals and give the matte value as a "collector" are cuprous sulphide, metallic copper, lead sulphide, and metallic iron. In order to collect both gold and silver satisfactorily, cuprous sulphide, or metallic copper, which implies the first, is essential.

A matte may contain at times unusual substances such as BaS from the reduction of barite or heavy spar in ore, molybdenum, in appreciable percentage, and also minor quantities of such elements as selenium, tellurium, bismuth, arsenic, antimony, etc., as shown in Tables L and LI. Nickel-copper matte is a common furnace product from some ores. The system nickel sulphide (Ni_3S_2), iron sulphide (FeS), is a complex one and has been investigated by Bornemann[1]. (See tables on pages 319 and 320.)

When arsenic and antimony are present in considerable percentage "speise" is formed. Arsenides and antimonides and sulphides are not miscible to any great extent, and when both are present in a fluid mass, they separate into two layers by liquation.

The appearance of matte varies considerably. Copper mattes are usually hard and dense, and when high in iron frequently porous and full of blow-holes. Lead mattes, on the other hand, are rather soft and crumbly in nature. The color of copper mattes varies from a blue gray white in the so-called "white metal," which is practically cuprous sulphide, to a dark brass color in the mattes high in iron and low in copper. Intermediate between these two are blue and purple tints. These colors refer to fresh fractures.

METALLIC FURNACE PRODUCTS. **Bullions.** — These are intermediate furnace products produced in metallurgical operations and are subjected to refining processes for the production of pure metals, or alloys of definite composition. In lead and cop-

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[1] Metallurgie, V, 13 (1908).

TABLE L.[1] COMPOSITION OF MATTE

Type of Matte	Chemical Composition, per cent.														
	Cu	S	Fe	Fe_3O_4	Ni	Co	Zn	Pb	Bi	Sb	As	Te	Se	oz. per ton	
														Ag	Au
									Ba			SiO_2	CaO	%	%
Copper blast furnace	11.20	25.47	61.68	—	—	—	No	.005	0.047	No	0.22	0.66	0.21	0.092	0.0457
Sudbury copper nickel ores	26.91	26.95	31.23	—	14.14	0.235	—	—	—	—	—	—	—	—	—
Sudbury copper nickel ores	14.69	24.96	31.89	—	28.17	—	—	—	—	—	—	—	—	—	—
Reverberatory copper furnace	60.76	23.25	11.43	1.13	0.0076	0.0034	2.41	0.59	0.042	0.079	0.045	0.0112	0.0038	60.4	0.30
Blast-furnace matte	54.89	23.36	20.25	—	0.0341	0.024	0.34	0.1178	0.0044	0.0232	0.0171	0.0088	0.0113	6.0	0.10
Nickel-copper matte	24.54	23.24	28.65	7.32	15.56	0.55	—	0.0272	0.0008	0.0068	0.0042	0.0	0.0	5.3	0.05
Copper blast furnace	57.83	22.47	15.28	—	—	—	2.09	0.0719	0.0014	0.0143	0.013	—	—	13.4	0.51
Copper blast furnace	55.0	23.96	13.85	2.58	—	—	1.24	3.025	0.0174	0.2693	0.0914	0.0474	0.1172	127.0	2.28
Copper blast furnace	21.36	22.95	41.03	10.44	0.002	0.1984	0.24	0.0226	0.0	0.0	0.0041	0.0	0.0082	2.4	0.0
Copper blast furnace	61.52	22.52	13.68	—	0.0645	0.4140	0.2333	0.0270	0.0008	0.0032	0.0013	0.0	0.0	2.2	trace

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[1] E. Keller, Min. Ind., IX, 240 (1900), except first three analyses.

TABLE LI.[1] COMPOSITION OF MATTES

Type of Matte	Metallographic Constitution Refers to Preceding Description of Constituent								Chemical Composition Per cent.				
	A	B	C	D	F	G	L	K	Cu	Fe	S	Pb	Zn
Copper blast furnace, highly siliceous slag	little	much	—	—		—	—	—	19.94	50.85	25.63	—	—
Copper blast furnace, highly siliceous slag	considerable	much	same as excess		—	—	—	—	13.89	60.54	—	—	—
White metal from converting lead-copper matte	no	no	no	large uniform fields	—	—	some in spots	—	74.26	1.41	16.24	3.26	—
Lead blast furnace matte	no	no	no	considerable as excess	considerable	some	no	considerable	55.45	6.25	18.42	18.34	—
Lead blast furnace matte	no	no	no	considerable as excess	some	some	no	much	45.46	11.70	18.55	23.23	—
Reverberatory copper furnace matte	no	a little	considerable	much as excess	some	some	no	little	41.51	22.47	24.75	4.91	3.43
Lead blast furnace matte	no	some	some	some as excess	—	—	—	some	35.46	21.97	20.11	11.41	—
Copper blast furnace pyritic smelting	no	much	some as excess	small fields	—	—	—	—	10.49	54.66	26.27	—	—
Copper blast furnace pyritic smelting	no	some	considerable	much	considerable	—	—	—	41.10	29.45	24.23	—	—
"White metal" from converter	no	no	no	large fields	some	—	—	—	80.84	0.55	19.60	—	—
Copper blast furnace matte	no	some	considerable	much	some	—	—	—	40.25	29.78	24.91	—	—
Copper blast furnace matte	no	some	considerable	considerable as excess	very little	considerable	—	—	36.48	32.66	25.20	—	3.05
Copper reverberatory furnace oil-fired	no	some	considerable	considerable	little	some	—	—	45.10	26.63	24.54	—	—

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[1] Fulton and Goodner, T. A. I. M. E., XXXIX, 584 (1908).

per smelting, lead and copper are produced that contain the gold and silver. The term "bullion" is applied to copper and lead when they contain gold or silver or both. Precious metal bullions are produced in gold and silver milling processes and are often complex in nature. Table LII gives the composition of various products of this type.

TABLE LII. COMPOSITION OF METALLIC FURNACE PRODUCTS

Material	Chemical Composition									
	Ag oz. per Ton	Au oz. per Ton	Pb %	Bi %	Sb %	As %	Te %	S %	Fe %	Cu %
Black copper[1] . . .	364.0	1.00	2.531	0.31	2.789	0.627	0.856	0.487	5.46	—
Black copper[1]	62.2	0.14	0.78	0.0035	0.238	0.052	0.0095	0.796	0.17	—
Lead bullion[2]	41.18	Co 0.00016	98.929	0.0048	.7203	.0064	Ni 0.0023	Zn 0.0028	0.0064	0.1862
Lead bullion[2]	41.20	Co 0.00035	98.965	0.0082	.5743	.0074	Ni 0.0068	Zn 0.0024	0.0089	0.2838
Gold bullion[3] from cyanide process . .	per cent 7.3	per cent 60.3	7.00	—	—	—	Ni 2.2	Zn 15.00	2.20	6.50
do	9.2	72.6	4.90	—	—	—	—	7.1	1.40	4.80

	Total C	Graphite	C. Carbon	Si	P	Mn	S
Gray pig iron	3.70	3.52	0.18	2.85	0.03	1.31	0.03
Forge iron	3.09	2.30	0.79	1.35	0.04	0.36	0.28
White iron	2.20	0.20	2.00	0.71	0.47	0.50	0.19
Mottled iron	3.685	2.375	1.31	0.401	0.066	0.115	0.63

Interesting questions arise in reference to the sampling of these metallic products. Lead and copper bullions are frequently shipped from the plant producing them to refining works. The material is purchased or checked in on the assays and analysis of samples taken in various ways, such as dip samples from the molten metallic bath in the furnace or lead kettles, or by a systematic punching of a certain number of bars by a belt punch, the punchings forming the sample, or by saw samples, certain bars being sawed in half and the sawdust taken as the sample. Gold and silver bars are usually sold to the government mints and are sampled either by dip, punch, or chip samples. It is very important that accurate samples be obtained, on account of the large monetary value involved. As will be noted from the table of analyses, the bullions are complex alloys of a number of metals

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[1] E. Keller, T. A. I. M. E., XXVII, 106 (1897).

[2] Hampe, Zeit. für Berg-Hütten-u. Salinenwesen, XVIII, 203.

[3] Rose, Metallurgy of Gold, 331 (1902).

and non-metallic elements, and during the freezing of the bars, segregation may take place which will effect a very uneven distribution of the precious metals throughout the bar. For this reason dip samples from the molten metal, in which diffusion has made the mass uniform, are most accurate. It is, however, not always practicable for samples of this kind to be taken. The nature of the distribution of the metals throughout the bar is dependent upon what other metals are present and their quantity. If molten lead containing silver be poured into a mold and permitted to cool slowly it might be expected, from an inspection of the freezing curve of silver-lead (page 101), that the silver would concentrate toward a eutectic and that the part of the bar to freeze last, viz., the upper middle part, be richest in silver, the outside of the bar, in contact with the mold, chilling quickly, be of average composition, segregation not having time to take place, while the rest of the bar be lowest in silver. This has been found to be true for certain lead bullions.[1] When, however, other metals are present, as for instance antimony with which silver forms an intermetallic compound, Ag_3Sb, having a freezing-point of 560° C., it is evident that silver will be taken up by antimony and the whole course of the freezing changed, the metal first frozen being richer in silver than that last frozen, unless silver antimonide and lead form a series, in which occurs a eutectic, which would cause liquation toward the center. In most lead bullions [2] the exterior of the bar is richer in silver than the interior. A similar phenomenon is shown by copper bullion,[3] some copper bullions being richer in the center while others are richer in the exterior layers. The segregation in copper bullion is much more pronounced than in lead bullion, and the unequal distribution is again to be looked for in the nature and quantity of impurity present, and to be explained by the selective freezing of the alloy. The problem is, however, a very complex one, due to the number of metals present, and the explanation cannot be based on the consideration of a single binary system. The segregation taking place in impure gold bullion produced in cyanide mills is very pronounced, due chiefly to the presence of zinc and lead, but may

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[1] R. Rosenlecher, Berg- und Hüttenmännische Zeit., Sept. 28, Oct. 5, 1894.

[2] A. Raht, Mineral Industry III, 414 (1894). G. M. Roberts, T. A. I. M. E., XXVIII, 413 (1898).

[3] E. Keller, T. A. I. M. E., XXVII, 106 (1897).

again be obviated by the presence in certain proportion of a metal like silver.[1] In gold-platinum bullion considerable segregation takes place, the center of the ingot being enriched in platinum. The anomalous behavior of silver-copper bullion has been referred to on page 98. Segregation also plays an important part in the casting of steel ingots, the impurities generally concentrating toward the center of the ingot.

SPEISE. — Speise is a furnace product produced chiefly in lead blast furnace smelting, when considerable arsenic is present in the ores. It is produced under essentially reducing conditions. In smelting oxidized copper ores containing arsenic, under reducing conditions, it is one of the furnace products. In lead refining works, it is produced at times in a reverberatory furnace termed the "residue furnace," which smelts the skimmings and various other by-products of the "liquating" or softening furnace in which the lead undergoes a partial refining preliminary to desilverization.

A speise is essentially an artificial arsenide, although antimonide speises are also known. The base concerned in a speise is most frequently iron, though nickel and cobalt will usually enter the speise if they be present, as will also some copper. Essentially, however, a speise is an arsenide of iron into which enter the nickel and cobalt and small quantities of lead and other metals. Speises are often produced in conjunction with matte, and such speises always contain sulphur, pointing to a certain solubility of matte in speise. The solubility of speise in matte is comparatively small.

Speise has a certain solvent power for gold and silver, but to what constituent of the speise this is due has not been determined. The system iron-arsenic has been investigated by K. Friedrich[2] within the limits of 91.6 and 44 per cent. iron. He found the existence of the compounds Fe_2As, Fe_3As_2 and probably FeAs. The mixture of Fe 91.6–As 8.4 per cent. has a melting-point of 1384° C. The compound Fe_2As freezes at 919° C. and FeAs at 1030° C. The compound Fe_3As_2 is the product of a reaction in the solid alloy which takes place at 800° C. At a concentration of 30 per cent. As and 70 per cent. Fe, a eutectic occurs, between Fe_2As and a mixed crystal richer in iron, which freezes

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[1] Ed. Matthey, Proc. Royal Soc., LX, 21 (1896).

[2] Eisen-Arsen, Metallurgie, IV, 129 (1907).

at 830° C. The melting-points of concentrations between 70 and 44 per cent. iron lie between 830° C. and 1027° C. In general, the speises are conglomerates of various mixed crystals into which the above compounds enter. Table LIII gives the composition of a number of speises.

TABLE LIII.[1] COMPOSITION OF SPEISES

Material	Chemical Composition, per cent.										
	Ag	Au	Cu	Pb	Mo	Fe	Zn	Ni	S	As	Sb
Lead furnace speise	0.0085	tr	0.3628	1.49	.211	60.57	tr	0.0876	5.82	31.47	tr
do	0.0301	.009	0.2566	2.503	.2155	70.478	"	0.0981	4.4695	21.80	0.1450
do	oz 35.0	oz .05	—	—	—	59.10	—	—	6.88	31.54	—
do	per cent 0.02	tr.	0.409	3.245	—	56.70	—	0.783	10.0	26.75	1.608
Copper speise[2]	—	—	52.0	35.0	—	—	—	—	1.38	2.75	3.34
do	—	—	26.0	16.7	—	22.0	—	—	4.13	11.0	13.5

See also, K. Friedrich, Ni–As. . . Metallurgie, IV, 200 (1907).
Cu–As. . . " II, 477 (1905).
Pb–As. . . " III, 41 (1906).
K. Friedrich und A. Leroux, Zn–As. . . " III, 477 (1906).
Ag–As. . . " III, 192 (1906).
and other systems of similar nature in Vol. V, Metallurgie.

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[1] Hofman, Metallurgy of Lead, p. 354 (1899).

[2] Hühn, Glück Auf., p. 1165 (1905).

CHAPTER X

REFRACTORY MATERIAL FOR FURNACES

1. **General.** — A refractory material is any substance used in furnace construction under such conditions as to be subjected to the effect of high temperatures, that will withstand the temperature encountered and not melt, and also will resist such abrasion or corrosion as may occur at the places where it is used. The number of good refractory substances is not large and the variety of conditions under which they are used is considerable. A refractory material must possess the following properties.

1. *It must be comparatively infusible*, viz., it must have an appreciably higher melting temperature than that which is attained in that part of the furnace in which it is used. The temperatures attained in metallurgical furnaces vary much; thus the range is wide from 1000 or 1100° C., found in ore-roasting furnaces, to the 3500 or 3600° C. attained in certain electric furnaces. The temperatures found in the iron blast furnace may be as high as 1960° C. just in front of the tuyeres, while in the Bessemer converter and the open-hearth furnace for steel, 1600° C. are often obtained. While very high temperatures may be reached in certain portions of a furnace, such as in the interior of the lower part of the blast furnace, those parts of the furnace in which the refractory material is employed, as the walls, may not be subject to such high temperatures, due to the effect of a constant and rapid radiation of heat. A fair grade of fire-clay brick will melt at approximately 1400° C., while impure magnesia melts at about 1920° C. and graphite is practically infusible.

2. *Resistance to abrasion.* — Refractory material may be used in such parts of furnaces where it is subjected to heavy wear by abrasion. Thus in the upper parts of the iron blast furnace, the fire-brick lining of the interior walls is subject to abrasion by the rough edges of the irregular pieces of ore, coke, and limestone of the descending charge. The question of abrasion is one of relative hardness and toughness of the materials that come in

contact. In this connection it must be borne in mind that the hardness of the refractory material at the high temperature at which it may be used, is not that which it has at ordinary temperatures. It may be very materially softened, though far from its melting-point. Thus magnesia softens very appreciably at 1500° C. As examples of the occurrence of abrasion may be mentioned the gas and air ports of open-hearth steel furnaces, which in turn are exhaust ports for the products of combustion. These products of combustion in the early part of the melt may carry considerable flue-dust, in the form of sharp particles of ore and limestone, which, due to the high velocity at which they are carried, cause considerable abrasion on the refractory material of which the ports are constructed. In reverberatory smelting furnaces for copper ore there is at times much abrasion of the interior walls where the liquid charge is in contact with the wall. The charge is in more or less constant motion (particularly in copper-refining furnaces, due to the working or "rabbling" of the charge). While a perfectly liquid charge would not cause abrasion, the part of the charge in contact with the walls may be unmelted due to the lower temperature prevailing here on account of radiation from the walls, and the solid unmelted ore particles, more or less hard, working up and down, abrade the wall.

3. *Resistance to chemical corrosion.* — The linings of furnaces are subject to chemical action from the furnace charge or contents under certain conditions. In general the lining of the furnace must be of such a nature as not to be unduly corroded by the furnace charge. Thus in reverberatory copper-smelting furnaces in which a slag of rather low silica contents may be produced, the walls might be lined with a silica fire brick, which would be of high temperature resistant qualities, but would be quickly corroded by the slag abstracting silica from it, and by the matte, its iron oxidizing in the presence of air and taking up silica. The proper lining would be a highly aluminous clay brick, or a magnesia brick, or still better, if the cost permitted it, a "neutral" material like chromite, not acted on by slag or matte. Under certain conditions it may be desirable to have a furnace lining that suffers corrosion, thereby furnishing material for the slagging of oxides. Thus in the converter for copper matte, the lining is made of "gannister" — crushed quartz, or a highly siliceous ore mixed with just sufficient clay to bind the particles.

This is tamped into place in considerable thickness. During the blowing of the matte, the ferrous oxide formed, unites with the silica in the lining to form ferrous silicate, a fluid slag. If the silica were not provided for, infusible scoria of magnetic and ferric oxide would result. Most recent practice, however, lines the converters with basic magnesia brick, not attacked by the ferrous oxide, and introduces siliceous material in the form of an addition to the charge, thus avoiding the heavy expense of labor in continuously having to reline the converters.

Aside from the corrosion of furnace lining the nature of the lining may exercise an important function in the chemical reactions of the metallurgical processes. In the basic open-hearth process for making steel the removal of phosphorus is an important consideration. It is found essential that the part of the lining in contact with the molten bath should be "basic," *i.e.* not contain an appreciable amount of silica, since this if be present above a certain amount, the phosphorus which oxidizes and enters the slag as a lime phosphate and is thus removed is again reduced by the action of silica and metallic iron present and reënters the steel bath. The lining of these furnaces is generally magnesia. Corrosion of refractory lining is also frequently caused by metallic vapors and gases.

4. *Property to withstand sudden changes in temperature.*—Under certain conditions of use the refractory material in furnaces may be subjected to sudden changes of temperature. This occurs around furnace openings or doors in reverberatory furnaces and is due to the cooling effect of inrushing air. Magnesia brick is subject to spalling and cracking under such conditions. Chromite brick will withstand sudden changes of temperature.

5. *Low heat conductivity.* — It is essential to conserve as much heat as possible within the furnace, and reduce the loss by radiation to a minimum. Fortunately most refractory materials have low conductivity, though there is much variation in this respect with the several materials. This is further referred to in the paragraph on the physical properties of refractory materials.

Furnaces are often built of a number of different refractory materials, the choice in particular parts of the furnace being dependent upon the conditions existing. Thus magnesia, highly refractory, but a good heat conductor, may be backed up by silica brick, practically a non-conductor, to keep the radiation loss as low as possible.

6. *Résumé.* — It is evident that no one refractory material can possess to a high degree all the aforesaid properties. Thus silica brick can resist high temperatures, but as it is not firm or tough cannot resist abrasion successfully. It is also subject to corrosion by basic slags, viz., those low in silica. It could not be used, therefore, where resistance to abrasion and non-corrosive qualities under the conditions stated are called for. It is therefore essential to choose such a refractory material as possesses to the highest degree most of the properties called for under the conditions of use. The material must also be reasonably cheap; thus, chromite in many cases is an ideal refractory material, but its relatively high cost prohibits its use, so that often a less suitable material will be used in its place.

Classification of Refractory Material. — The slags produced in the furnaces are the chief agents in the corrosion of refractory linings, and as these slags are in the main silicates, viz., compounds in which silica — SiO_2 — is the acid radical, or are metallic oxides, which readily unite with silica, we base the classification of refractory materials on their behavior to silica. The chief divisions are therefore: 1. Acid refractories—those which are not corroded by silica or siliceous slags, but are corroded by oxide slags, or basic slags, viz., of low silica tenor. 2. Basic refractories, those which are not corroded by oxide slags, or basic slags, but are corroded by silica or siliceous slags. The dividing line is not a very sharp one; thus fire clay is usually classed as an acid and sometimes as a "neutral" refractory, but as it differs widely in composition, from aluminous to siliceous varieties, it has no definite classification. 3. A third division is added, viz., those refractories that are not attacked by either basic or acid slags, such as chromite and graphite. These are classified as "neutral refractories." The accompanying list enumerates the chief refractories in use:

1. *Siliceous refractories.*
    a. Fire clay, aluminous fire clay, siliceous fire clays.
    b. Dinas and silica brick.
    c. Gannister — quartz furnace sand.
2. *Basic refractories.*
    a. Magnesite and magnesia.
    b. Dolomite — lime.
    c. Bauxite.

3. *Neutral refractories.*
    - *a.* Chromite.
    - *b.* Graphite.
    - *c.* Carborundum and siloxicon.

Most of these refractories are put on the market in various forms, in the shape of crushed and ground material, standard bricks, and shapes, and tiling suitable for furnace construction, special forms, as muffles and retorts, and special shapes of brick and tiling for particular uses. The shapes are usually molded, pressed, and burnt at comparatively high temperatures, the mode of manufacture frequently having decided influence on certain of their important properties, such as resistance to abrasion, conductivity, etc. It is not within the province of this work to go into the manufacture of the finished material in detail. The nature and properties of the material only will be discussed.

1. ACID REFRACTORIES. **a. Fire Clay and Fire-Clay Brick.** — Fire clay and its products in point of quantity used is the most important refractory material. The essential constituent of all clays, including fire clay, is the mineral kaolinite — a hydrated silicate of alumina — $Al_2O_3 \cdot 2\,SiO_2 \cdot 2\,H_2O$, containing SiO_2, 46.5; Al_2O_3, 39.5; H_2O, 14 per cent. This mineral possesses the property of being very plastic when mixed with a comparatively small per cent. of water and may thus be readily molded into shapes. Clays are mixtures of kaolinite, with other minerals, in various proportion, but with enough kaolinite present to preserve plasticity. Kaolinite is a decomposition product of aluminous minerals like the feldspars, and when forming clay beds is often intermixed with quartz particles in the form of sand; undecomposed particles of feldspar; mica; pyrite or its decomposition product ferric oxide; titanium oxide, probably in the form of rutile; lime, and magnesia, usually in combination with silica, or as carbonates or as constituents of residual feldspar, to which is also due the presence of the alkalies, K_2O, Na_2O.

The essential constituents of fire clay are — alumina and silica, which should in almost all instances comprise from 92 to 98 per cent. of the mass of the clay. The other constituents are usually classed as "fluxes." They are impurities which will lower the refractoriness of the clay appreciably. The fluxes are — ferric oxide, Fe_2O_3; titanium oxide, TiO_2; lime, CaO; magnesia, MgO; and the alkalies, sodium and potassium oxides, K_2O and Na_2O.

It is generally stated that the total fluxes should not exceed 3 to 4 per cent., but under certain conditions, such as in a very coarse textured clay high in alumina, they may even mount to 10 per cent. and the clay still be a fire clay, though not of a high refractoriness. The relative amount of the different fluxes present also has its influence; ferric oxide probably tending to lower the refractoriness of a clay more than the other fluxes present, particularly if carbonaceous matter be present in the clay.

The silica in a fire clay is present as combined silica, with alumina, and possibly a small amount with some of the fluxes, and as non-combined silica or quartz sand. That which is present as quartz sand acts as a flux to the kaolinite and lowers the melting-point of the mixture until a eutectic point at 90 per cent. SiO_2 is reached at 1600° C. From that point it rises again to the melting-point of silica. Fig. 105 gives the melting-point curve of silica-alumina as determined by Shepherd and Rankine.[1] The melting-point of silica is given by Day and Shepherd as 1625° C.,[2] but by Roberts-Austen as 1775° C., and by Boudouard as 1830° C.[3] The melting-point of alumina is given by Hempel as 1880° C., which is probably low. There is one compound in the series corresponding to the mineral sillimanite $Al_2O_3 \cdot SiO_2$, melting at 1811° C. Kaolinite, dehydrated, is shown on the diagram by a dotted line.

Fire clay is used as a refractory material chiefly in the form of fire brick and other molded forms. The ordinary mode of manufacture is to temper the natural clay in pits with water, molding the mixture by hand or in "soft mud" machines into bricks, re-pressing and drying them, and then burning the same in down-draft kilns at a temperature between 1330 and 1370° C. (seger cones 10–12). Often mixtures are made of burnt fire clay, etc., in certain proportion, with raw clay. This is done to obtain coarse textured brick and reduce shrinkage. In burning there is considerable shrinkage, due to the driving out of the combined water. The amount of shrinkage is largest with the highly aluminous clays and least with the sandy clays and ordinarily amounts to 5 to 12 per cent.

The texture of the fire clay and that of the brick have an im-

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[1] Am. Journ. Science, 4th Series, 28, 293 (1909).

[2] Journ. Am. Chem. Soc., XXVIII, 1096 (1906).

[3] Journ. I. and S. I. (1905), No. 1, 350.

portant bearing on its refractoriness. If the clay be in very fine particles or grains the brick made from it will be of lower refractoriness than one of the same chemical composition that has a large percentage of coarse particles. This texture is an inherent property of the clay, but in fire brick may be obtained by suitable mixtures. Chemical composition being on a par, the refractoriness of fire brick is much increased by the coarseness of texture. The general structure of the brick usually is that of comparatively coarse grains imbedded in a ground mass of fine grains. The greater in quantity this ground mass is, the more easily will the brick show incipient fusion. The principle governing this is the same as that of the "formation temperature" of slags, page 272.

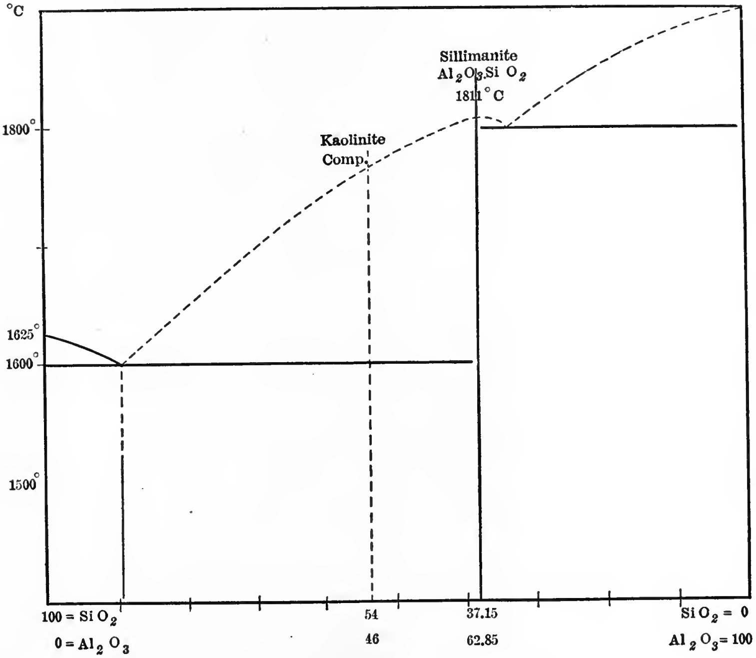

FIG. 105. — The Al_2O_3–SiO_2 series.

While the refractoriness of fire brick is increased by the coarseness of texture, obtained by mixing the crushed burnt clay and the raw clay and reburning, the resistance to corrosion and abrasion is often greatest in those bricks that are hard and dense, as when made almost entirely from a fine-grained raw clay.

TABLE LIV. COMPOSITION OF FIRE CLAYS

Locality	Chemical Composition									
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O + Na_2O	Water	Moisture	TiO_2	FeO
Woodbridge, N. J.[1]	46.90	35.90	1.10	—	—	0.44	12.80	1.50	1.30	—
Woodbridge, N. J.[1]	71.80	18.92	0.88	—	—	0.48	6.70	0.50	—	—
Woodbridge, N. J.[1]	40.64	41.19	3.27	0.65	tr	tr	14.74	—	—	—
Mexico Dist., Mo.[2]	52.0	33.0	1.50	0.50	0.10	0.7	12.0	—	—	—
St. Louis, Mo.	62.0	24.0	1.90	0.70	0.30	0.7	10.5	SO_3 0.35	1.0	1.2
Flint Clay, Mo.[2]	40.8–48	37–43.2	0.15–0.83	0.28–1.93	0–0.58	0.2–1.20	13.3–15	—	—	—
Mt. Savage, Pa.[3]	55.21	31.18	0.07	0.18	0.11	0.23	13.02	—	—	—
Sharon, Pa.[3]	44.04	39.44	FeO 0.94	0.07	0.11	0.72	14.13	—	—	—
Haydenville, O.[3]	76.24	16.87	0.16	0.50	tr	1.09	5.14	—	—	—
Scioto Co., O.	44.60	40.05	0.80	0.27	tr	tr	14.23	—	—	—
Pueblo, Col.[3]	63.22	24.72	0.43	0.30	0.13	tr	8.63	—	0.68	—
Golden, Col.[3]	50.35	33.64	0.75	—	tr	0.58	11.75	2.13	0.80	—
Rapid City, S. D.[3]	76.78	14.43	0.18	2.18	0.95	tr	4.62	—	—	—

Tensile strength of fire clays. — This property has a practical bearing in so far as a clay possessing considerable tensile strength can more readily be molded and worked than one that does not. It also permits of the addition of considerable non-plastic material, as burnt clay, quartz, etc. The tensile strength of air-dried fire clay varies from about 50 to 285 lbs. per square inch.

The composition and refractoriness of fire brick. — The refractoriness of fire brick is dependent on the clay from which it is made, but to some extent also on the mode of manufacture, as bearing on the texture, density, hardness, etc. The accompanying table gives the composition, refractoriness, and texture of a number of different manufactures of fire brick.

The price of fire brick varies with refractoriness and general excellence; thus at the present time (1909) the price in St. Louis is $10 to $35 per M. It is evident that the type of brick to be used, viz., whether highly aluminous, or high in silica, must be carefully determined by the conditions of use. A number of formulas[4] have been proposed and used to calculate the refractoriness of fire brick from the chemical composition, such as

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[1] H. Ries, T. A. I. M. E., XXXIV, 254 (1904).

[2] H. A. Wheeler, T. A. I. M. E., XXXV, 720 (1905).

[3] H. Ries, Clays—Occurrence, Properties, and Uses (1906).

[4] H. O. Hofman, T. A. I. M. E., XXIV., 42 (1894).

TABLE LV.[1] COMPOSITION OF FIRE BRICK

Locality	Chemical Composition						Seger Cone[3] of Fusion	Texture
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	Alkaline Earth and Alkalies	Sum of Fluxes		
Missouri	51.59	38.26	1.84	1.97	6.34	10.15	32–33	Angular flint clay particles, coarse.
Pennsylvania	53.05	41.16	2.65	1.80	1.34	5.79	32–33	Angular flint clay particles, coarse.
Pennsylvania	49.44	40.94	3.68	2.23	3.71	9.62	31–32	Angular flint clay particles, very coarse.
Colorado	93.57	2.53	0.62	0.27	3.01	3.90	32–33	Quartz particles, rather fine.
Colorado	72.47	19.78	1.67	0.81	5.27	7.75	29	Quartz particles, medium coarse.
Kentucky	50.31	41.21	2.55	2.45	3.48	8.48	31	Flint clay particles, rather fine.
Kentucky	44.77	43.08	2.78	2.54	6.83	12.15	31–32	Flint clay particles, medium coarse.
Ohio	55.97	36.22	3.44	1.57	2.80	7.81	31	Flint clay particles, coarse.
Ohio	50.82	43.51	1.71	1.80	2.16	5.67	31	Quartz particles, coarse..
Ohio	67.61	25.66	2.42	1.55	2.76	6.73	28	Quartz particles, medium coarse.
New York	77.66	9.87	1.29	3.89	7.29	12.47	27–28	Some quartz particles, fine.
Ohio	69.69	25.72	1.90	1.37	1.32	4.59	29	Flint clay particles, coarse.
Texas	75.78	21.81	1.39	0.77	0.25	2.41	29–30	Fine uniform grain.
Illinois	60.69	28.01	2.51	1.17	7.62	11.30	29	White flint particles, medium.
Indiana	77.01	15.29	1.89	0.93	4.88	7.70	27	Some quartz particles, fine.
Pennsylvania	61.28	27.13	2.90	1.37	7.31	11.58	26	Flint clay particles, fine.
Indiana	60.76	31.66	5.67	1.58	0.33	7.58	26	Fine grain.
New Jersey[2]	75.20	21.09	1.37	1.72	0.62	—	33	—
New Jersey[2]	82.30	14.84	1.70	0.71	0.45	—	31	—
New Jersey[2]	68.70	26.50	1.25	2.65	0.90	—	27	—
New Jersey[2]	77.30	18.99	2.06	1.05	0.60	—	31–32	—

[1] R. F. Weber, T. A. I. M. E., XXXV, 637 (1905).

[2] H. Ries, T. A. I. M. E., XXXIV, 254 (1904).

[3] For corresponding temperatures, see table of seger cone melting-points, p. 187. These temperatures are, however, not very accurate, as it is not possible to standardize seger cones by thermo-electric couple above 1600° C.

Bischoff's and Seger's and Wheeler's,[1] this last also taking into account the texture, but while they give fair results for any one particular clay, they are not of universal application. Refractoriness is now determined in experimental laboratory furnaces.

b. Dinas Brick, Silica Brick. — The original Dinas or silica brick is made from pure sandstone, occurring in the Vale of Neath in Wales. The composition of the best stone is: SiO_2, 98.31 per cent.; Al_2O_3, 0.72 per cent.; Fe_2O_3, 0.18 per cent.; CaO, 0.22 per cent.; alkalies, 0.18 per cent.; moisture, 0.35 per cent. The lowest percentage of SiO_2 is about 96.50 per cent., with a corresponding increase of fluxes. The material is not plastic like clay. The rock is burnt in furnaces, to calcine it, then thrown hot into water to disintegrate it, after which it is coarsely ground and mixed with 2–3 per cent. of lime in the form of milk of lime and molded into shapes. Much care must be exercised in handling the molded shapes as they are not tough. They are burnt in kilns at fairly high temperatures, sufficient to cause a formation of lime silicate which forms on the outside of the grains and acts as cement or binding material. The average per cent. of silica in "Dinas" brick is 95.64 per cent.

This brick is of a coarse texture, and rather friable and brittle. It will not withstand abrasion, and of course is highly corroded by basic slags. It is used in parts of furnaces where it must withstand high temperature, but is not subject to corrosion or abrasion, such as in the roofs of open-hearth steel furnaces, roofs and flues of reverberatory copper furnaces, etc. In the United States, much silica brick is used, and some of it is imported Dinas brick, while a large part is manufactured here — chiefly in Pennsylvania. An analysis of American brick gave SiO_2, 94.07 per cent.; $Fe_2O_3 + Al_2O_3$, 3.66 per cent.; CaO, 1.39 per cent.; MgO, 0.19 per cent. There is a difference between Dinas and ordinary so-called silica brick, in that in Dinas brick the binding material is lime silicate, while in many silica brick the binding is clay. Almost any brick high in silica is termed silica brick, though it may be of low refractoriness. As already pointed out, the lowest refractoriness of fire brick lies in the vicinity of 90 per cent. SiO_2, not taking into account the fluxes. True silica brick should contain not less than 95 per cent. SiO_2, and is now made in the United States, of very high quality.

c. Gannister. — The term gannister was originally employed

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[1] H. A. Wheeler, Eng. and Min. Jour., March 10, 1894.

to designate a close-grained dark-colored argillaceous sandstone found in the Carboniferous formation near Sheffield, England. An approximate composition is: quartz, 83 per cent.; clay, 13 per cent; impurities and moisture, 4 per cent. The term is now applied to any similar rock, consisting chiefly of quartz and containing just sufficient clay material to act as a bond and not enough fluxing ingredients to lower its refractoriness materially. Gannister, however, is made most extensively by mixing crushed quartz, quartzite or highly siliceous ore, with enough clay to act as a binding material. It is not molded into shapes, but is used to form furnace bottoms, by tamping it into place, to line steel and copper converters by molding it into the iron shells with special molding devices.

Thus at Mount Lyell, Tasmania,[1] copper converters are lined with gannister made from a white quartzite that has the following composition: SiO_2, 91.44 per cent.; Fe_2O_3, 1.54 per cent; Al_2O_3, 3.09 per cent., mixed with a small percentage of clay of this composition: SiO_2, 62.52 per cent.; Al_2O_3, 23.89 per cent.; Fe_2O_3, 0.26 per cent.; CaO, 0.25 per cent.; MgO, 0.4 per cent.; water, 12.68 per cent. At Butte, Montana,[2] at some plants an argillaceous: granular sandstone is used, of the following composition: SiO_2, 64.4 per cent.; FeO, 7.6 percent.; Al_2O_3, 16.5 per cent.; CaO, 1.1 per cent.; MgO, 1.8 per cent.; loss on ignition, 4.7 per cent. This material is sufficiently plastic to be used without the admixture of a bond.

Furnace Sand. — The smelting bottoms or hearths of reverberatory furnaces for copper smelting, and for the regenerative reverberatory furnace for acid open-hearth steel, must be monolithic in character to prevent the cutting effect of the molten charge and its consequent escape from the furnace. For this purpose certain sands are used. Over the brick construction of the hearth is spread a thin layer of sand ½ to 1 in. thick, and the furnace is fired until this begins to sinter and agglomerate, then another layer is spread, and the furnace again fired, and this is repeated until a total thickness of 10 to 20 in. is obtained, forming a solid monolithic bottom, without joints or cracks. The sand for the purpose must contain sufficient fluxing material to cause sintering, though the texture of the sand and the nature of

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[1] Robt. Sticht, Min. Ind., XVI, 425 (1907).

[2] H. O. Hofman, T. A. I. M. E., XXXIV, 305 (1904).

the fluxes in it are important. The temperature that can be attained in the furnace it is to be used in also has its bearing. Compositions of sands that have been used for this purpose are as follows:

No. 1. SiO_2, 97.25 per cent.; Al_2O_3 and Fe_2O_3, 0.16 per cent.; CaO, 0.08 per cent.; MgO, 0.39 per cent.; alkalies, 0.36 per cent.; water, 0.24 per cent.; loss on ignition, 0.36 per cent. (For steel furnace.)

No. 2. SiO_2, 86.0 per cent.; CaO, 5.7 per cent.; MgO, 0.8 per cent.; Al_2O_3, 1.6 per cent.; Fe_2O_3, 1.2 per cent.; CO_2, etc., 4.5 per cent. (Reverberatory copper furnace.)

2. BASIC REFRACTORIES. — **a. Magnesia.** With the great development of the basic open-hearth steel process calcined magnesite as a refractory material has been extensively used. Magnesite is the mineral form of magnesium carbonate, and is often associated with impurities, chief among which is lime and iron carbonate, and silica. In the United States, California produces some magnesite. The bulk of that used, however, is imported from the island of Euboea, Greece, and from Styria in Austria. Both calcined magnesite and magnesia brick are imported. The requirements of magnesia for open-hearth steel practice are approximately 89–90 per cent. MgO; about 3 per cent. SiO_2; not more than 0.5 per cent. Al_2O_3; about 5.0 per cent. Fe_2O_3 and not more than 1 per cent CaO.[1] The silica and ferric oxide are essential in order to cause sintering, which binds the grains in the brick and also permits it to be used in building up furnace hearths.

Compositions of magnesites and magnesia brick used for refractory purposes are given in the accompanying table. (See on next page.)

Magnesite is calcined in kilns with about 10 per cent. coke, or in special continuous kilns, fired by lignite coal, or in reverbertory furnaces, oil fired as in California. In making brick about 90 per cent. of the thoroughly burnt magnesite is mixed with 10 per cent. of incompletely burnt material, which causes the brick to set. It is then compressed by high hydraulic pressure and burnt at the proper temperature. Other modes of manufacture are also in use. Magnesite bricks are dense and hard, and are better conductors of heat than ordinary fire brick, which is an undesirable property. They expand somewhat on heating

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[1] Mineral Industry, XVII, 628 (1908).

TABLE LVI. COMPOSITION OF MAGNESITE

Locality	Chemical Composition						
	MgO	CaO	Fe_2O_3	Al_2O_3	SiO_2	CO_2	water
[1] Euboea *b*	46.28	0.41	0.03	0.07	2.27	49.85	1.15
[2] Euboea *b*	47.69	1.29	1.20*a*	—	0.50	49.33	—
Austria *c*	85.32	1.12	8.571	0.929	2.84	0.50	—
[3] Hungary *c*	91.1	1.88	5.7	0.10	0.98	—	—
[3] Hungary *c*	89.36	2.66	7.4	0.10	0.16	—	—
[4] California *b*	44.39	1.49	0.49*a*	—	0.90	50.06	—
[4] California *b*	47.10	0.62	0.25*a*	—	0.10	51.98	—
[2] Euboea *d*	88.90	3.40	2.40*a*	—	3.90	—	—
[2] Steiermark *d*	86.20	0.75	5.70*a*	—	2.95	—	—
[2] Mitterdorf	82.10	1.15	8.20*a*	—	7.65	—	—
[5] Grecian magnesite brick American manufacture.	93.03	4.20	0.72	—	2.16	—	—

a. Includes Fe_2O_3 and Al_2O_3. *b*. Crude magnesite. *c*. Calcined magnesite. *d*. Brick.

and do not stand well sudden changes of temperature such as caused by drafts of cold air, spalling and flaking off under these conditions. Contrary to common belief they may be laid in contact with ordinary fire brick or even silica brick without any serious fluxing action taking place even at rather high temperatures. They are very refractory; the heat they will withstand is about 1800 to 1900° C. The melting-point of pure magnesia is given from 1920° C.[6] to 2250° C. (Hempel). A magnesia brick with high iron showed incipient fusion at the edges at 1900° C., and was molten at 2000° C.[7]

At high temperatures magnesia brick softens somewhat, but its refractoriness is not affected thereby. It should not be subject to much load when hot.

For laying magnesia brick in place[8] it is essential as with all fire brick to lay them with practically no joints, but "skin to

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[1] Mineral Industry, XVII, 630 (1908).

[2] A. E. Hunt, T. A. I. M. E., XVI, 720 (1887).

[3] Mineral Industry, XI, 457 (1902).

[4] F. L. Hess, Mineral Industry, XV, 556 (1906).

[5] J. D. Pennock, T. A. I. M. E., XXVI, 269 (1896).

[6] Goodwin and Morley, Trans. Am. Electro. Chem. Soc., May, 1906.

[7] A. Lampen, Journ. Am. Chem. Soc., XXVIII, 852.

[8] F. T. Havard, E. and M. Jour., LXXXVI, 802 (1908).

skin," so called. The mortar that may be used is very finely ground magnesia mixed with enough tar to make it plastic. This is kept hot in pans, and the trowels used in applying it are also sometimes heated to make the joint as thin as possible. Linseed oil may be used in place of tar. It is not desirable to use water with magnesia. Magnesium chloride, a by-product of the potash salt industry, may be used in solution, with ground magnesia for mortar purposes, or magnesia mixed with hydrochloric acid will answer the same purpose. Tar and magnesia is considered most desirable.

Magnesia brick and crushed magnesia may be used with advantage in the construction of reverberatory lead refining furnaces, and lead cupeling furnaces, where the slag consists chiefly of basic oxides, ordinarily greatly corrosive to fire-clay brick. The hearth or "test" of cupeling furnaces especially may be constructed of magnesia, in place of marl, clay, Portland cement and limestone, or bone ash, under certain conditions.

The crucibles of lead blast furnaces may with advantage be constructed of magnesia, as well as the forehearths or "settlers," for the separation of matte from slag in lead and copper smelting when these are of the large, round, stationary type. For small movable forehearths which frequently "freeze up" and must be torn down and relined, magnesia is too expensive to warrant its use. Magnesia brick is used as the lining of copper converters in the new practice now being introduced, replacing gannister. Magnesia also finds application in the construction of copper reverberatory furnaces. Due to their softening at high temperatures with consequent rapid abrasion, magnesia brick are, where practicable, surrounded by water jackets to increase radiation and thus preserve the bricks. In basic open-hearth steel furnaces the bottoms are formed of crushed magnesia in a similar manner to that described under furnace sand, except that the layers spread are much thinner.

b. Dolomite and Lime. — Lime has been suggested and used to a limited extent as a refractory material. It is cheap and of a high refractoriness, CaO melting at 1900° C. (Hempel). It has, however, one property which makes it practically useless for this purpose, its slaking with water to form calcium hydrate. It may be used in the calcined state mixed with tar and tamped into place, for bottoms, but is not satisfactory. Bricks cannot be made of it as they do not stand storing.

Dolomite, the lime-magnesian carbonate, has been quite extensively used as a source of refractory material for the lining of basic open-hearth steel furnaces and basic steel converters, but is now replaced almost entirely by magnesia. Calcined dolomite does not slack in air to any very appreciable extent, as nearly pure lime does, but it has a tendency to do so, for bricks made from it do not withstand the weather well, like magnesia bricks do. The wear of dolomite lining, in the furnace is much greater than that of magnesia lining but its cost is much less. In the furnace it cannot be laid in direct contact with acid brick, but there should be a neutral layer of chromite or carbon brick inserted. Table LVII gives the composition of certain dolomites and dolomite brick that have been used as refractory material.[1]

Table LVII. Composition of Dolomite

Locality and Material	Chemical Composition						
	SiO_2	Fe_2O_3 Al_2O_3	$CaCO_3$	$MgCO_3$	CaO	MgO	CO_2
Germany, Hörde	2.02	2.30 —	61.31	34.42	—	—	—
" Ilsede	1.35	2.05	—	—	30.12	19.21	44.97
France, Dion	0.10	4.00 1.50	—	—	31.40	16.40	42.20
Hungary, Dombrowa	2.00	3.20 1.30	—	—	31.00	16.00	45.40
U. S., Virginia	15.40	5.38	—	—	27.12	17.48	35.24
German brick	5.95	4.30	—	—	56.15	32.40	—
" "	4.86	3.95	—	—	59.10	30.03	—
French brick	2.30	8.20	—	—	60.10	30.01	—
Austrian brick	3.10	2.60	—	—	61.25	31.60	—
Pennsylvania brick	7.40	3.25	—	—	51.05	37.20	—

c. **Bauxite.** — Bauxite is the hydrated oxide of alumina, $Al_2O_3 \cdot 2\,H_2O$, and rarely occurs pure, being almost always associated with silica, titanium oxide, and ferric oxide, the latter often in large amount. Bauxite is mined most extensively as an aluminium ore, and its application as a refractory material has been limited. It is, however, coming into use as a lining for rotary cement kilns, and is again advocated as a substitute for magnesia in basic open-hearth steel furnaces. It is cheaper than magnesia. It is now successfully made into very hard and tough brick, said to have a tensile strength of 10,000 lbs. per square inch. Its

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[1] Hunt, T. A. I. M. E., XVI, 719 (1887).

application in many branches of metallurgy where a basic material is called for is to be expected. Some bauxites are not readily attacked by acid or basic furnace charges and act similar to chromite, as a neutral material. Table LVIII gives the composition of some bauxites and bauxite bricks.

TABLE LVIII. COMPOSITION OF BAUXITE[1]

Locality	Chemical Composition				
	Al_2O_3	Fe_2O_3	SiO_2	TiO_2	H_2O
1. Arkansas	62.05	1.66	2.00	3.50	30.31
"	46.40	22.15	4.89	—	26.68
2. Alabama	61.00	2.20	2.10	3.12	31.58
3. "	40.93	22.60	8.99	—	20.43
4. Georgia	58.62	1.51	4.27	3.79	31.44
5. Baux, France	60.00	25.00	3.00	—	12.00
6. " "	75.00	12.00	1.00	—	12.00
7. Arkansas, calcined bauxite	87.30	1.43	6.40	3.99	0.88

Bauxite brick[2] is now made at St. Louis from Arkansas bauxite. The crude bauxite is washed at the mines to remove free silica and is then calcined at 2500° F. to drive out the combined water. But little water goes off until 2390° F. is reached. The shrinkage is about 30 per cent.

The calcined bauxite is bonded with about 4 per cent. of high-grade fire clay, or else sodium silicate, or lime, pressed into bricks and burnt at a high temperature. A brick $9 \times 2\frac{1}{2} \times 4\frac{1}{2}$ in. weighs $7\frac{1}{2}$ lbs. The bauxite for the manufacture of brick must be carefully chosen. It should contain some silica and iron oxide, the combination and incipient fusion of which aid to make a firm brick. Those bricks highest in alumina are most refractory. If considerable iron oxide is present, iron aluminates probably form, which are also refractory. Silica lowers the refractoriness of the brick, and should, for a basic refractory material, not exceed 12 per cent. Good bauxite brick readily resists abrasion.

3. NEUTRAL REFRACTORY MATERIAL. **a. Chromite.** — The mineral chromite is a chromate of iron, and when pure, of the following composition: Cr_2O_3, 68 per cent.; FeO, 32 per cent. It

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[1] Mineral Industry, XIII, 40.

[2] A. J. Aubrey, E. and M. Jour., LXXXI, 217 (1906).

frequently contains magnesia (MgO) which replaces iron oxide, and alumina, which replaces chromic oxide, and silica as an impurity. The accompanying table gives the composition of chromite ore used as refractory material.

TABLE LIX. COMPOSITION OF CHROMITE

Locality	Composition						
	Cr_2O_3	Al_2O_3	FeO	MgO	SiO_2	CaO	Fe_2O_3
Turkey	51.70	14.10	14.20	14.30	3.50	1.70	—
New Caledonia	55.70	16.20	16.60	9.80	0.25	0.25	—
North Carolina [1]	58.00	15.52	14.45	8.26	3.20	0.70	—
North Carolina [1]	59.20	7.15	25.02	4.42	3.20	0.92	—
Newfoundland [2]	49.23	7.50	17.21	18.66	6.57	—	—
For open-hearth furnaces	38–40	24.5	15.0	—	3.25	—	17.5
Chromite brick, Harbison Walker Refractories Co.	43.98	20.47	12.92	13.52	5.60	3.25	—

The chromite used in the United States is largely imported from New Caledonia; a little is produced in California. Chromite brick is very refractory, dense, and hard. It resists the chemical action of both siliceous and basic slags about equally well, withstands abrasion and rapid changes of temperature better than any other refractory used. Chromite is employed as a neutral parting between acid and basic refractories, for repairing and patching worn spots in open-hearth furnaces, for the lining of air and gas ports in open-hearth furnaces, and occasionally for building furnace bottoms and fore-hearths for lead and copper blast furnaces and for the lining of copper converters. Its use would become much greater but for its high cost. Thus while at Pittsburg the highest grade of fire-clay brick may be bought for $35 per M., chromite brick cost $175 per M. or five times as much.

b. Graphite. — Carbon in the form of graphite or coke is employed as a refractory material, particularly in the manufacture of crucibles used for making crucible steel and for melting metals and alloys and for constructing parts of electrical furnaces. Carbon is the most refractory material known. Its melting-point

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[1] J. H. Pratt, T. A. I. M. E., XXIX, 17 (1899).

[2] G. W. Maynard, T. A. I. M. E., XXVII, 283 (1897).

has not been attained. It softens somewhat and vaporizes at the temperature of the electric arc, about 3700° C. The material used for crucibles is chiefly Ceylon "plumbago" or graphite. For this purpose the graphite must be quite pure, and contain 90 per cent. and over of carbon, with low contents of iron oxide and silica. The crushed graphite is mixed with a varying percentage of good fire clay, in part raw and in part calcined, and the crucibles formed on a "wheel," similar to that used in the manufacture of pottery. The amount of clay taken is generally from 50 to 75 per cent., depending on the grade of the crucibles. Special brands contain less clay. The crucibles are carefully dried and annealed at a high temperature in a reducing atmosphere in special kilns. Special forms, as retorts, for distillation of zinc scums containing gold and silver from the lead desilverization process, and for other purposes, are made of graphite. Crucibles must be capable of withstanding sudden changes of temperature without cracking; and also, to a reasonable extent, the corrosion due to metallic oxides. Graphite crucibles do not withstand well the effect of oxidizing flames, or oxidizing fluxes, which cause excessive corrosion by the burning out of the graphite.

Artificial graphite made in the electric furnace by the Acheson graphite process is also used to some extent in the manufacture of crucibles, and for carbon blocks for electric furnace use. This graphite is made from anthracite. Carbon bricks have been used somewhat, but not extensively, in lining the hearth and bosh walls of the iron blast furnace, where the necessity of a highly refractory material, and one that can resist corrosion, is essential.

Bricks of this type have been made of graphite and clay, coke and clay, and coke and tar.[1]

Coke and tar brick — carbon, 87.26 per cent.; ash, 12.74 per cent.

Coke and clay brick — SiO_2, 21.51 per cent.; Fe_2O_3, 1.41 per cent.; Al_2O_3, 12.05 per cent.; CaO, 0.67 per cent.; MgO, 0.29 per cent.; carbon, 64.23 per cent.

Graphite as a refractory material can only be used under reducing conditions; when used under oxidizing conditions it is very rapidly destroyed.

Other Refractories. — **Carborundum and Siloxicon.** Carborundum is produced in the electric furnace by the heating

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[1] James Gayley, T. A. I. M. E., XXI, 102 (1892).

together of sand, sawdust, and coal at a high temperature. It is a carbide of silicon — SiC, and is crystalline in its nature. It is crushed and made into shapes and forms, by mixing with about 15 per cent. of fire clay, and then burning the resultant brick. Tar, glue, sodium silicate, etc., may also be used as a bond. Carborundum is highly refractory, withstanding temperatures of 2220° C.,[1] at which temperature it will begin to dissociate into carbon and vapor of silicon. Siloxicon is made in the electric furnace and is a product similar to carborundum. It is made with less carbon than carborundum, resulting in a product containing unreduced silica. Its composition is variable, but may be represented by the formula Si_2C_2O. Siloxicon is made into bricks by mixing the crushed material with water to moisten it, molding into brick and burning at a high temperature. Siloxicon is not readily attacked by siliceous or oxide slags.

The silicon in carborundum and siloxicon oxidizes slowly at high temperatures, viz., when heated above 1470° C. and the refractoriness is partly destroyed thereby. The materials are used as a refractory substance for lining melting furnaces for copper and brass founding, for some electric furnaces, and to some extent in lining clay zinc retorts.[2]

Some Physical Properties of Refractory Material. — Specific gravity and weights per cubic foot and average refractoriness are shown in the accompanying table.

TABLE LX. SOME PHYSICAL PROPERTIES OF REFRACTORY MATERIALS

Material	Specific Gravity	Wt. per Cu. Ft. Lbs.	Incipient Melting Point
Aluminous fire-clay brick	2.56	112–150	1400° to 1750° C.
Silica brick	2.53	128	1600° to 1800° C.
Magnesia brick	3.44–3.54	160–170	1850° to 2000° C.
Bauxite brick	—	130	1850° C to 2000°.
Chromite brick	—	175	2000° and above.
Magnesite calcined	—	112	—
Plumbago-graphite	—	140	above 3500° C.
Chrome ore dust	—	160	—

The heat conductivity of refractory material is of importance

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[1] S. A. Tucker and A. Lampen, Journ. Amer. Chem. Soc., XXVIII, 858.

[2] Mineral Industry, XIV, 63 (1905), XV, 92 (1906).

in furnace construction, as the loss by conduction of heat through the furnace walls may be a serious item, not alone in fuel cost, but also as a factor in attaining the high temperature desired. Insulation against loss by radiation is therefore necessary. The accompanying formula permits of the calculation of loss by conduction through furnace walls.

$$H = \frac{S}{l} Kt.$$[1]

H = gram calories per second which pass from one end of conductor to other.

S = cross-section of conductor in cm.

l = length of conductor in cm.

K = conductivity constant.

t = difference in degrees centigrade in temperature between faces.

The factors S and l apply to furnace dimensions, S denoting surface of wall and l expressing thickness of wall. The thicker the wall, the less heat will be lost. There is, however, a limit to this, for in many furnaces the temperature reached is so high as to exceed the refractoriness of the material, unless walls are thin enough to cause sufficient loss of heat by conduction to prevent temperature from rising too high within the furnace. In these cases economy would be gained if a more refractory material could be employed so that the walls or roof might be thickened. Table LXI[2] gives the factor K for refractory materials. (See table on next page.)

The factor K expresses heat conductivity as follows. If a piece of refractory material be considered whose thickness is 1 cm. and whose surfaces are plane and parallel and differ 1° C. in temperature, then K expresses the number of small calories that pass per second, per square centimeter of surface.

This factor varies with the temperature and usually increases with the temperature with the possible exception of chromite brick. It should be used therefore as specific heats are (Chapter VIII, page 280), but such exact data is not available. The figures given are a mean specific conductivity between 500 and 1000° C.

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[1] Carl Hering, Elec. Chem. and Met. Ind., VI, 495; VII, 11, 72.

[2] S. Wologdine and A. L. Queneau, Conductivity, Porosity and Gas Permeability of Refractory Materials, Electro. Chem. and Met. Ind., VII, 383.

TABLE LXI. PHYSICAL CONSTANTS OF REFRACTORY MATERIAL

Material	Conductivity		
	K. Average Between 500–1000° C.	Kg. Calories per Hour per Sq. Meter Surface per One Degree Diff. in Temperature with Walls One Meter Thick	Relative Conductivity
Graphite brick	0.025	9.00	100 per cent.
Carborundum brick	0.0231	8.32	92.4
Magnesia brick	0.0071	2.54	28.4
Chromite "	0.0057	2.05	22.8
Fire-clay "	0.0042	1.50	16.7
Building "	0.0035	1.26	14.0
Bauxite "	0.0033	1.19	13.2
Silica.. "	0.0020	0.71	7.8
Kieselguhr (diatomaceous earth)	0.0018	0.64	7.1

The heat conductivity of any given refractory material is a function of the temperature of burning. The higher the burning temperature the greater the conductivity. The proper burning temperature is that which corresponds to the maximum occurring during use. If this is not reached further shrinkage may take place in the brick, which will cause trouble in the furnace.

Silica brick when burnt at a low temperature has the lowest heat conductivity of any refractory, except silica sand in the form of diatomaceous earth.

The conductivity of *fire-clay* refractories is practically that of the air included within the pores of the material. The greater the permeability the greater is the conductivity.

The Permeability of Refractory Brick to Gases. — Some materials, like fire-clay brick and magnesia brick and bauxite brick, increase in density with an increased burning temperature, and at the same time become more permeable to gases, which property in certain instances is greatly increased. Silica brick decreases in density with an increase of burning temperature, but also increases in permeability. Conductivity increases with permeability.

Increased porosity does not imply increased permeability. Permeability is rather closely related to density, the greater

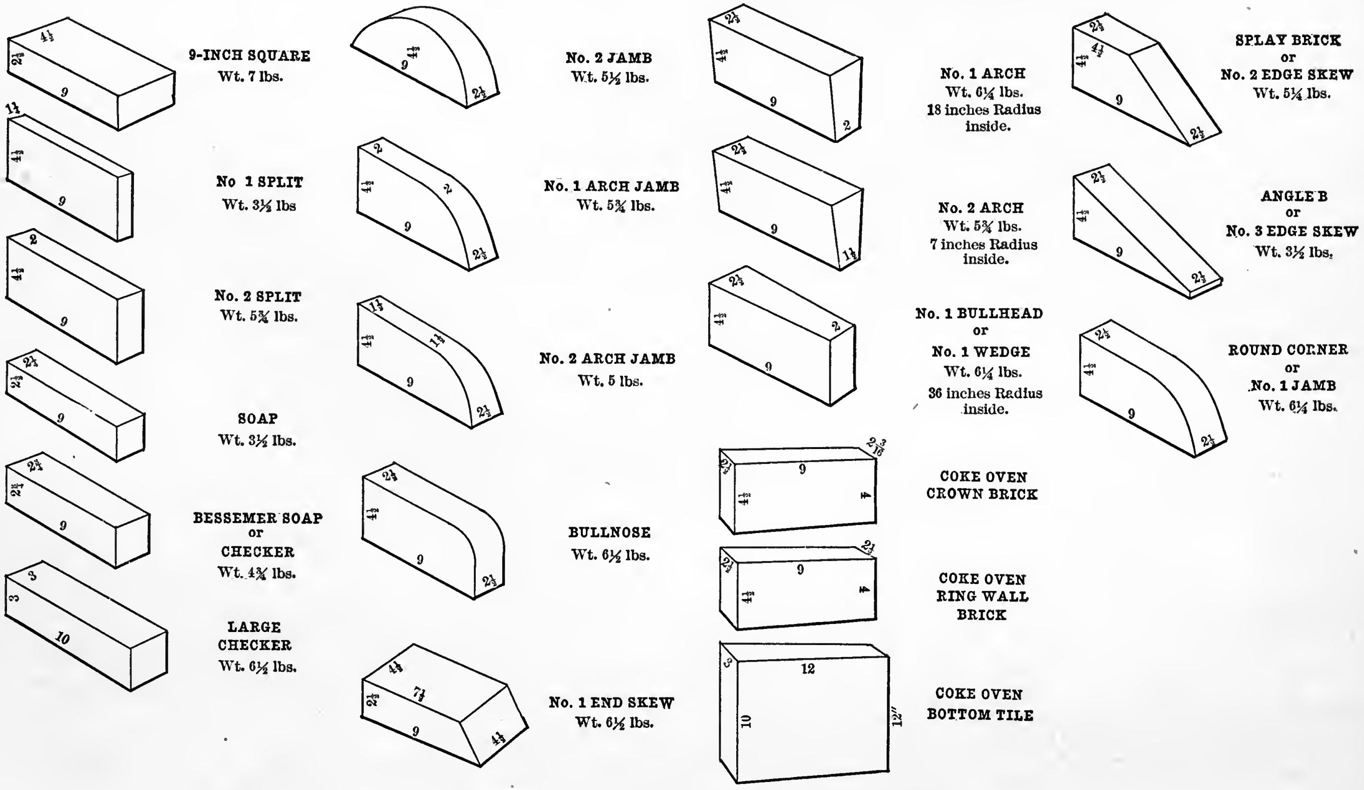

Fig. 106. — Common shapes of refractory material.

the density, the greater the permeability. The factor of permeability is of importance in connection with retorts, for zinc distillation, etc., which should be practically tight. The permeability of refractory material, aside from the burning temperature employed, is dependent upon its original physical constitution, viz., whether it is granular or flaky. The latter is conducive to low permeability.

Expansion of Refractory Material with Temperature.—Very little data is available on this subject. It is generally conceded that fire-clay brick contracts slightly on heating, while silica, magnesia, and chromite brick expand slightly. At about 800 to 1200° C. magnesia brick expands 0.11 in. in 12 in., and silica brick about 0.10 to 0.125 in. in 12 in. The accompanying plate shows the usual shapes and sizes common in refractory material.

CHAPTER XI

FUELS

Definition. — A fuel is any substance the burning of which, either directly or in the form of its distillation products, (gas) with air, gives rise to sufficient heat to carry on industrial and metallurgical operations on a commercial scale. Fuels are extensively used in metallurgical operations for the production of heat and the high temperatures necessary to bring about certain reactions; in fact, a great part of the common metallurgical reactions take place only at comparatively high temperatures. While the great mass of fuel is carbonaceous fuel, such as coal, coke, wood, etc., fuel in the metallurgical sense also includes certain sulphides, as pyrite and pyrrhotite, which are made use of in pyritic smelting; and silicon, phosphorus, manganese, contained in relatively small quantities in pig iron, and which act as a fuel in converting this to steel in Bessemer converters.

Classification of Fuels. — Fuels may be classified into two main groups: (I) natural fuels, such as coal, wood, natural gas, etc., which may be used without especial preparation, and (II) artificial or prepared fuels, the product of natural fuel treated in a certain manner, viz., coke, the residual product of distilling certain coals, and charcoal, the residuum from the distillation of wood. This classification is not of much importance and is not further mentioned in the treatment of the subject.

The fuels are discussed in the order named: (1) wood; (2) charcoal; (3) peat; (4) coal; (5) coke; (6) oil; (7) gas; (8) sulphides.

(1) **Wood.** — The use of wood as a metallurgical fuel is comparatively rare, except in remote districts where coal or coke is not available. It was used extensively in the United States in the Rocky Mountain region, during the early develop-

ment of the mineral resources, in its natural form for reverberatory smelting of gold and silver bearing lead and copper ores, and in the form of charcoal, for blast-furnace smelting. In Pennsylvania and other eastern states it was used extensively in the manufacture of charcoal iron. It has also been used in the form of short blocks, replacing coke or anthracite coal in part in copper blast furnace smelting. It is best suited for reverberatory smelting and with a properly designed grate and furnace can be successfully employed.[1] In some regions it is still used extensively as a fuel for generating steam, but its growing scarcity is fast diminishing its use.

Wood is composed of three substances, (*a*) cellulose or woody fiber, $C_6H_{10}O_5$, making up the main bulk of the wood; (*b*) the constituents of the sap, chiefly a soluble gum, lignin, of the same composition as the fiber, and amounting to about 13 per cent. of the wood; and (*c*) water. The sap may differ chemically rather widely in various wood, but the ultimate analysis in carbon, hydrogen, and oxygen is practically the same for all woods. The amount of water varies in different kinds of wood, and in the same woods, at different seasons. The water in wood is of importance, as its presence diminishes its calorific power, or the heat units that can be derived from it, since part of these are consumed in vaporizing this water. The amount of water in freshly-cut wood will range from 26 to 28 per cent. in wood such as ash, to 35 to 40 per cent. in oak and pine, and 50 to 52 per cent. in poplar; for wood cut when the sap is least, viz., in January. When the wood is cut in the spring, *e.g.* April, the amount of water is about 10 per cent. greater than the above figures.

When wood is freshly felled, it is useless as a fuel. It must be *air-dried* before use. Wood for fuel purposes is usually cut into 4-ft. lengths and split longitudinally into pieces 4 to 8 inches in diameter and piled into stacks, a pile 8 ft. long and 4 ft. high of 4-ft. wood making a *cord.* In this form it is exposed to the air, preferably in such positions as are protected from snow and rain, for from 6 to 12 months. It may be piled under rough sheds, although in reasonably dry climates this is not necessary. In ordinarily wet climates, it takes wood about 18 months to reach the maximum attainable dryness;

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[1] J. T. Canfield, E. and M. Jour., LXXIII, 525.

in dry climates this may be reached in much less time. Resinous woods, such as pine, fir, spruce, dry more rapidly than non-resinous woods such as oak, poplar, elm, etc. *Air-dried* wood still contains from 20 to 30 per cent. of water, with an average of about 25 per cent. When this amount of water is reached, no further elimination takes place.

Wood may be *kiln-dried* by heating it to 120 to 140° C., when it will lose most of its hygroscopic water, but not all. If kiln-dried wood is again exposed to air at ordinary temperatures it will reabsorb water until it again contains 20 to 25 per cent. When wood is heated to 200° to 225° C., carbonization begins to take place, and distillation sets in.

Wood is best felled in winter, in December and January in northern climates, and should be thoroughly air-dried before using. If waste heat can be cheaply utilized to *kiln-dry* wood, it will be advantageous to do so, provided the wood is used immediately after drying.

Wood is classified into (*a*) hard wood; (*b*) soft wood. The distinction is based on the facility with which it may be worked by tools, its heat-producing power, and on its specific gravity. In hard woods, the woody cells are narrower and more closely packed than in soft woods. Thus oak, beech, walnut, elm, and maple are classed as hard woods, while pine, spruce, poplar, fir, willow are classed as soft woods. The specific gravity of wood is that of the bulk of the material, viz., the woody fiber, the water and the air contained in the pores. Wood fiber alone, with no pores and containing no hygroscopic water, has a gravity of about 1.5, independent of the kind of wood. According to Marcus Bull[1] the specific gravity of American air-dried woods is as follows.

TABLE LXII. SPECIFIC GRAVITY OF WOODS

Kind of Wood	Specific Gravity	Lbs. per Cu. Ft.	Kind of Wood	Specific Gravity	Lbs. per Cu. Ft.
Walnut	1.000	34.7	Cedar	0.565	—
White oak	.885	30.5	Yellow pine	0.551	18.9
Ash	.772	26.0	Pine	0.450	15.4
Beech	.724	24.9	Birch	0.530	18.3
Elm	.580	19.9	Poplar	0.397	13.6

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[1] Groves and Thorp, Chemical Technology, Vol. I, Fuels.

Corded wood ordinarily contains approximately 56 per cent. of actual wood and 44 per cent. of unoccupied space. One cord of oak wood, 128 cu. ft., therefore weighs 3904 lbs., and one cord of white pine 1971 lbs., and one cord of oak has, therefore, approximately 1.98 times the fuel value of a cord of pine.

Table LXII gives the ultimate composition and calorific power of wood, dried to eliminate all hygroscopic water.

TABLE LXIII. COMPOSITION AND CALORIFIC POWER OF WOOD

Kind of Wood	Carbon %	Hydrogen %	Oxygen %	Nitrogen %	Calorific Power Calories per Gram	Calorific Power B. T. U. per Lb.
Beech	49.89	6.07	43.11	0.93	4774	8591
Oak	50.64	6.03	42.05	1.28	4620	8316
Birch	50.61	6.23	42.04	1.12	4771	8586
Aspen	50.31	6.32	42.39	0.98	—	—
Willow	51.75	6.19	41.08	0.98	—	—
Ash	—	—	—	—	4711	8480
Fir	—	—	—	—	5035	9063
Pine	49.94	6.25	43.81	—	5085	9153
Elm	50.19	6.425	43.39	—	4728	8510

It will be noted that soft woods like pine have a greater heating power per unit of weight than hard woods like oak. The above figures must be reduced by 25 to 30 per cent. for *air-dried* wood on account of the contained water.

The "available hydrogen" in wood is the hydrogen in excess of that required for the contained oxygen to form water. For every 8 parts of oxygen there is required 1 part of hydrogen. Thus, in a wood containing 42 per cent. O_2 and 6.25 H_2, there is required for the oxygen, $42 : x = 8 : 1$, or 5.25 parts H_2, leaving 1 part of hydrogen "available" as a fuel constituent, with the contained carbon.

Air-dried wood, on burning, leaves an ash which varies in amount from 0.5 to 5 per cent. Pine wood contains approximately 1 to 1.1 per cent. ash, while oak and other hard woods contain 1.5 to 2.5 per cent. The ash consists chiefly of the carbonates of lime and the alkalies, with some iron and manganese phosphates, etc., and may differ widely in composition in different woods. The composition depends on the nature of the tree and the soil in which it grew. The accompanying table gives analysis of wood ashes, made by Berthier,

Table LXIV. Composition of Wood Ashes

Kind of Wood	Chemical Composition										
	CO_2 %	SO_3 %	Cl %	SiO_2 %	P_2O_5 %	K_2O %	Na_2O %	CaO %	MgO %	Fe_2O_3 %	Mn_3O_4 %
Birch . . .	28.76	0.37	0.03	4.78	3.61	12.72		43.85	1.97	0.09	0.54
Spruce . .	24.93	0.80	0.08	6.23	3.14	16.80		29.72	3.28	10.53	4.48
Fir	35.66	1.67	0.92	4.37	0.91	4.41	3.53	38.51	9.56	0.09	0.36

(2) **Charcoal.** — Charcoal is made from wood by a process of charring. This is essentially a process of destructive distillation, the heat for which is furnished by the combustion of *part* of the wood. In making charcoal in the ordinary manner, the wood is cut into 3 to 7 ft. lengths and piled into conical or hemispherical piles. It is then covered with a sod and clay covering, in which air and vent holes are cut, which may be held open or closed as the burning proceeds. The pile is set on fire and combustion starts with a very limited quantity of air, the heat generated by the burning of a portion of the wood, causing the decomposition of the woody fiber and dried sap and resulting in the expulsion of water and other volatile substances, which are given off as tar and pyroligneous acid, and leaving the larger part of the carbon and the ash of the wood in the form of charcoal. Charcoal was formerly a very important fuel for metallurgical purposes, in fact the chief fuel for this purpose. It was used in very large quantities in the manufacture of cast iron, called charcoal iron, and in the blast-furnace smelting of lead and copper ores. In the United States, in 1882, about 2,000,000 tons of charcoal were used for metallurgical purposes.[1] In the Rocky Mountain region, during the early days of its mineral development, charcoal was exclusively used as a blast-furnace fuel for lead and copper smelting. In the Great Basin in Utah and Nevada, *e.g.* at Eureka, Nevada, five lead blast furnaces consumed 4600 bushels per day at a cost of 15 to 34 cents per bushel.[2] Two hundred bushels are stated to be equivalent to one ton of good coke, so that if coke could have been procured at anything less than $50

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[1] John Birkinbine, T. A. I. M. E., XI, 78 (1883).

[2] O. H. Hahn, A. Eilers, R. W. Raymond, T. A. I. M. E., I, 100.

per ton its substitution for charcoal would have been profitable.

At present charcoal is of but little importance, except in isolated districts where wood is plentiful and cheap and other fuel is not available.

Charcoal is burnt in (*a*) piles or " meilers " and in pits covered over in a suitable manner; (*b*) in kilns, and (*c*) in retort furnaces. The first and second methods are the most common, modern charcoal burning being carried out chiefly in kilns. The yield by the different methods is approximately as follows: meilers, 30 bu. per cord; kilns, 45 bu. per cord; retorts, 60 bu. per cord. Even with the low yield of 30 bu. per cord, meilers may be the cheapest method of production as the initial expense is low, and since the meilers are built where the wood supply is located, the cost of transportation is a minimum.[1]

The charcoal obtained from different woods varies much in weight, as the accompanying data will show:

TABLE LXV. WEIGHT OF CHARCOAL FROM WOOD

Kind of Wood	Weight	Kind of Wood	Weight
White pine........	9.80 lbs. per bu.	Black ash	14.47 lbs. per bu.
Basswood	10.62	White ash	16.32
Spruce	11.25	Beech	17.02
Poplar	12.27	Yellow birch	18.75
Hemlock	12.85	Sugar maple	18.95

The yield of charcoal is about 15 to 25 per cent. of the weight of the air-dried wood. It varies with the nature of the wood, the method of burning, and the speed of burning; a slow burning will give a greater yield. Hard woods yield a hard charcoal much preferred to that of soft woods. In the West, where hard woods are absent, nut pine yields the best charcoal. Good charcoal for metallurgical purposes is black in color, and when allowed to fall on a hard surface gives rise to a sonorous ring; it will withstand considerable pressure when this is gradually applied, an important property, as in blast-furnace use it must

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[1] For methods of charcoal burning consult: T. Egleston, The Manufacture of Charcoal in Kilns, T. A. I. M. E., VIII, 373 (1880). J. Percy, Metallurgy, Vol. I, Fuels. Groves and Thorp, Chemical Technology, Vol. I, Fuels. Philips and Bauerman, Elements of Metallurgy.

be capable of withstanding pressure from the furnace charge, and not crush. When handled, it should soil the fingers but little. When ignited, it should burn without flame or smoke. It possesses the property, on account of its porosity, of absorbing large quantities of gases, absorbing 90 times its volume of ammonia gas, 35 volumes of carbonic acid gas, 9.25 volumes of oxygen, 7.5 volumes of nitrogen, or 1.75 volumes of hydrogen. Charcoal exposed to air will absorb from 5 to 12 per cent. of water. The composition of black charcoal is as follows:

TABLE LXVI. COMPOSITION OF CHARCOAL

Constituent	No. 1	No. 2	No. 3
H_2O (water)	7.23	6.04	8.21
Carbon	88.89	85.18	87.43
Hydrogen	2.41	2.88	2.26
Oxygen	1.46	3.44	0.54
Ash	3.02	2.46	1.56

The ignition point of charcoal depends upon the nature of the wood and the temperature at which it is charred. When charred at 300° C., it will ignite at 360 to 380° C.; at 432° C. it will ignite at 400° C.; at 1000 to 1500° C. it will ignite at 600 to 800° C. Charcoal made from hard wood ignites at a higher temperature than that made from soft wood. The calorific power of good black charcoal is approximately 7500 to 7800 calories. The specific heat of charcoal at room temperature is 0.2411.

(3) **Peat.** — Peat or turf is the product of the decomposition of vegetable matter, such as herbaceous plants and shrubs, etc., which accumulates in low places, as swamps and bogs, in successive seasons of growth and decay, the latter aided by warmth and moisture. Its occurrence is widespread in temperate climates. Its use as a metallurgical fuel is limited. It is used in the form of partly carbonized briquettes as peat-coke or charcoal, or as dried peat, from which gas may be produced. It is used quite extensively in European countries, Germany, Russia, and Sweden, as a domestic and steam fuel.[1] It

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[1] Robert Schorr, T. A. I. M. E., XXXV, 82 (1905). A. P. Hall and R. C. Tolman, E. and M. Jour., LXXIX, 271 (1905).

represents a fuel reserve which may be widely used in time.

The composition of peat is very variable, chiefly due to its varying content of water and ash. Freshly cut peat from bogs may contain as much as 80 to 90 per cent. water. Air-dried peat usually contains 10 to 30 per cent. of water, dependent on its nature, though it may contain 40 to 50 per cent. Practically all of the hygroscopic water may be expelled by artificial drying, but it is reabsorbed on exposure to air. The amount of ash in peat also varies within wide limits. The reason for this is that it consists not only of the natural ash of the plants, but also the mineral matter, such as sand and clay deposited at the time of the formation of the peat. The ash ranges from 1 to 33 per cent., with about 7 per cent. in good material. The composition of dried peat after deducting ash is approximately as follows: Carbon, 60 per cent.; oxygen, 34 per cent.; hydrogen, 6 per cent.; which is 10 per cent. more of carbon and 1 per cent. more of available hydrogen than contained in wood. Its higher ash contents, however, tend to annul this advantage.

Peat has received much attention in Europe in recent years and its use is rapidly increasing. It is employed in the form of dried briquettes, carbonized briquettes, and peat coke or peat charcoal. Peat coke, made by the Ziegler process, is hard, firm, and practically free from phosphorus and sulphur. It has a calorific power of from 6776 to 7042 calories per kg. and is used for smelting foundry iron, in copper refining, and for other metallurgical purposes in Germany. Peat briquettes, made by the Stauber system, have a composition of 45.14 per cent. carbon, 4.54 per cent. hydrogen, 29.34 per cent. oxygen, and 9.09 per cent. ash, and a calorific power of 3806 calories.[1]

The cost of extracting and preparing peat for use as a fuel is quite costly, and in districts where cheap coal is available, cannot enter into competition with it.

(4) **Coal.** — Coal is the most important metallurgical fuel and is used directly as coal, in the form of coke, and for the production of gas. The composition of coal varies widely and it is classified in several ways. One classification is based on the property of coking, or not coking, a coking coal being one that will melt into a fluid mass when subjected to a compara-

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[1] J. Fulton, Coke, 1905, 442. Mines and Minerals, XXV, 305 (1905).

tively high temperature without free access of air. A second classification is based on the chemical composition, viz., the relative amounts of "fixed" carbon and "volatile matter." A third classification is based on the length of flame during burning.

Coals are considered as members of a series, beginning with wood and ending with graphite, viz., wood, peat, lignite, bituminous coal, semi-bituminous coal, semi-anthracite, anthracite, graphite, the wood or vegetable tissue being the source of origin of peat and the coals. From a metallurgical point of view the classification based on length of flame, coking properties, and calorific power are of most interest. From a geological standpoint the question as to whether a coal is lignite, bituminous, or anthracite is of interest. From the standpoint of heating power the high-grade bituminous coals come first, followed by anthracite, then by ordinary bituminous, and finally by lignite. Percy's classification is (*a*) Non-coking coal free burning, rich in oxygen; (*b*) coking coal; (*c*) non-coking coal rich in carbon.

Gruner's classification is: (*a*) *Non-coking coals with long flame.* These coals approach lignite in character, yield 55 to 60 per cent. of powdery coke, and burn with a long smoky flame. The composition is as follows: C, 75 to 80 per cent.; H, 4.5 to 5.5 per cent.; O, 15 to 19.5 per cent. The ratio of O to H is 3 to 1 to 4 to 1. The calorific power is 8000 to 8500 calories.

(*b*) *Coking long flame gas coals.* These yield 60 to 65 per cent. loose, friable coke and 32 to 40 per cent. volatile matter, of which 17 to 20 per cent. is gas. The composition is as follows: C, 80 to 85 per cent.; H, 5 to 5.8 per cent.; O, 10 to 14.2 per cent. The calorific power is from 8500 to 8800 calories.

(*c*) *Bituminous or furnace coals.* These coals burn with a smoky flame and yield 68 to 74 per cent. of rather loose coke, and 15 to 16 per cent. gas. The composition is as follows: C, 84 to 89 per cent.; H, 5 to 5.5 per cent.; O, 5.5 to 11 per cent.; the ratio of O to H is 1:1. The calorific power is 8800 to 9300 calories.

(*d*) *Coking coals with short flame.* These yield from 74 to 82 per cent. of hard compact coke, and 12 to 15 per cent. gas. The composition is as follows: C, 88 to 91 per cent.; H, 4.5 to 5.5 per cent.; O, 5.5 to 6.5 per cent. The calorific power is 9300 to 9600 calories.

(*e*) *Anthracite coals*[1]. These yield 82 to 92 per cent. of soft powdery coke and 12 to 8 per cent. gas. They burn with a short flame. The composition is as follows: C, 90 to 93 per cent.; H, 4 to 4.5 per cent.; O, 3 to 5.5 per cent. The calorific power is 9200 to 9500 calories.

The calorific power in this classification is based on " combustible matter " present, viz., the composition of the coal after deducting the contents in ash. This classification is based on European coals and does not apply generally to American coals.

If a coal be heated in a closed vessel to a high temperature, gas will be given off, which consists of *volatile hydrocarbons* and some water vapor, and there remains a residue of "coke," which consists of the *fixed carbon* amd the ash. This is the basis of the method of "proximate analysis" of coal which determines the fixed carbon, volatile matter, water or moisture, sulphur and ash. In distinction to this there is the *ultimate analysis*, which determines the elemental constituents of coal, carbon, oxygen, hydrogen, nitrogen, sulphur, and the ash.

Kent's[2] classification is based on the proximate analysis of coal, recalculated to allow for ash. It is as follows:

TABLE LXVII. KENT'S CLASSIFICATION OF COALS

Type	Per cent. Fixed Carbon	Per cent. Volatile Matter	Heating Value in B.T.U. per Lb. of Combustible Matter
Anthracite	97 –92.5	3 – 7.5	14,600–14,800
Semi-anthracite	92.5–87.5	7.5–12.5	14,700–15,000
Semi-bituminous.....	87.5–75	12.5–25	15,500–16,000
Eastern bituminous ..	75 –60	25 –40	14,800–15,200
Western bituminous..	65 –50	35 –50	13,500–14,800
Lignite	less than 50	more than 50	11,000–13,500

The most recent classification suggested, and probably the most satisfactory, is that of Marius Campbell[3], which is based on the carbon-hydrogen ratio, viz., the quotient obtained by

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[1] These are really semi-anthracite and semi-bituminous coals.

[2] Wm. Kent, Steam Boiler Economy, p. 42.

[3] U. S. G. S. Professional Paper 48, 172 (1906). Report of the Coal Testing Plant and T. A. I. M. E., XXXVI, 324 (1906).

dividing the per cent. of carbon by the per cent. of hydrogen in the coal as determined by ultimate analysis.

The proposed classification is as follows; groups A, B, C, D, E, are tentative.

TABLE LXVIII. CAMPBELL'S CLASSIFICATION OF COALS

Group	Classification	Carbon-hydrogen Ratio
A	Graphite	—
B	Anthracite	00 –30
C	“	30 –26
D	Semi-anthracite	26 –23
E	Semi-bituminous	23 –20
F	Bituminous	20 –17
G	“	17 –14.4
H	“	14.4–12.5
I	“	12.5–11.2
J	Lignite	11.2– 9.3
K	Peat	9.3–
L	Wood (cellulose)	7.2–

The term semi-bituminous was used in the old Pennsylvania classification of coals,[1] and is retained, although the term is not properly used, since it would normally mean a coal between a lignite and a bituminous coal, and not a coal between a bituminous and an anthracite. The term is frequently used to describe either kind of coal.

In Table LXIX the proximate and ultimate composition of American coals are given with the calorific power, and in table LXX the proximate composition of western coals, largely used in smelting. In table LXXI the proximate composition of some foreign coals is given. In regard to moisture it is necessary to state that this is of two kinds: (*a*) the water which the coarsely crushed coal loses by drying in the air of the room until no further loss occurs, *i.e.* an equilibrium is established between the moisture in the coal and that in the air, and (*b*) that water which is lost by further drying the finely crushed, air-dried coal (60 mesh) in an air bath at 105° C. to constant weight. The second loss varies much in different kinds of coal

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[1] Persifor Frazer, T. A. I. M. E., VI, 430.

— in anthracite it will be 0.5 to 3 per cent.; in bituminous coal, 1 to 9 per cent., and in lignites as high as 20 per cent.

General. "Cannel" coal is a variety of bituminous coal usually of low specific gravity, ranging from 1.1 to 1.20, of a dull luster and non-coking. It burns with a long, smoky flame. It is high in volatile matter and low in fixed carbon, resembling lignite in composition, except that the moisture is low, like in bituminous coals. The following are proximate analyses: (*a*) Breckenridge Ky.: Volatile matter, 53.53 per cent.; fixed carbon, 34.37 per cent.; ash, 12 per cent.; S, 1.89 per cent. (*b*) Nova Scotia: Volatile matter, 66.56 per cent.; fixed carbon, 25.23 per cent.; ash, 8.21 per cent.; water, 0.23 per cent. Cannel coals are comparatively rare and not important metallurgically.

While the fuel value of coal is dependent upon its position in the classification, viz., whether it be an anthracite, lignite, etc., the amount of ash present is a very important factor. The higher the percentage of ash the less the calorific power in any given coal. Thus, a bituminous coal quite high in the classification, containing much ash, may not be as good a fuel as a lignite, low in ash. The moisture content of the coal is also important. In burning coal under boilers or in metallurgical furnaces there is a definite heat loss for every per cent. of water in the coal. If the products of combustion in which the water is present as vapor escape at 400° C., every per cent. of water causes a loss of about 8 calories; if they escape at 1200° C., a loss of about 14 calories. In table LXIX the calorific or heat-producing power of coals is given as determined by the Mahler calorimeter. This includes the heat of the condensation of the water vapor, viz., is equivalent to the products of combustion escaping at room temperature, 16° C., the water existing chiefly in the liquid form. This is not realized in practice, and the actual calories obtained must be determined by applying a correction for water.

Sulphur in coal is usually an objectionable substance, for if the coal is a coking coal and the coke is used in iron smelting, sulphur must be low. In lead and copper blast furnace smelting sulphur in coke is not detrimental. In coal for reverberatory furnaces or for the production of gas, used in iron metallurgy, sulphur is objectionable. In smelting copper ores in reverbera-

TABLE LXIX. COMPOSITION OF AMERICAN COALS[1]

LOCALITY	TYPE OF COAL	PROXIMATE ANALYSIS AIR-DRIED COAL				ULTIMATE ANALYSIS AIR-DRIED COAL					CALORIFIC POWER OF AIR-DRIED COAL
		Moisture	Fixed Carbon	Volatile Matter	Ash	H.	N.	C.	O.	S.	
Colorado	Anthracite	0.59	88.82	6.59	4.00	—	—	—			—
Pennsylvania	Anthracite	2.98	87.13	3.38	5.86	2.43	—	89.21	3.69		—
"	"	0.50	80.6	7.80	11.1	—	—	—	—	—	—
"	"	3.087	83.41	4.275	8.18	—	—	—	—	—	—
"	Semi-anthracite	1.295	83.34	8.00	6.23	—	—	—	—	—	—
Arkansas, Coalhill	Semi-bituminous	2.36	72.88	12.68	12.08	3.82	1.37	76.44	4.30	1.99	7,366 Cal. 13,259 B.T.U.
W. Virginia, Pocahontas	Bituminous	0.80	70.80	16.90	11.50	4.03	1.04	79.12	3.78	0.53	7,505 13,509
" New River	"	0.76	73.61	20.54	5.09	4.38	1.05	82.41	5.87	1.20	7,990 14,382
" Freeport bed	"	0.98	61.87	28.72	8.43	4.85	1.50	78.21	6.11	0.90	7,855 14,139
Pennsylvania, Connelsville	"	2.90	60.82	28.70	7.58	5.02	1.86	79.86	4.27	1.18	14,400
Kentucky, Eastern field	"	1.92	57.08	36.56	4.44	5.36	1.85	78.31	8.80	1.24	7,860 14,148
Alabama, Warrior field	"	1.55	53.71	32.10	12.64	4.96	1.66	72.16	7.85	0.73	7,199 12,958
Indian Territory, Hartshorne bed	"	3.71	50.31	32.61	9.77	4.97	1.78	74.0	7.66	1.44	13,414
Kansas, Weir, Pittsburg bed	"	3.74	50.01	33.11	13.14	4.91	1.09	68.22	8.30	4.34	6,891 12,404
Missouri, Rich Hill field	"	3.50	40.77	35.35	20.38	4.64	0.99	60.0	8.46	5.53	6,191 11,144
Iowa, Marion Co.	"	4.25	41.74	37.02	16.99	4.84	1.46	60.36	11.15	5.20	6,212 11,182

Wyoming, Cambria	Bituminous	2.73	37.40	37.61	22.26	4.54	0.80	55.29	12.94	4.17	5,758 10,364
Indiana, Sullivan Co.	"	8.66	42.67	34.86	13.81	5.20	1.22	62.20	14.99	2.58	6,336 11,405
Illinois, Belleville field	"	11.40	44.30	32.45	11.85	5.33	1.17	61.79	18.52	1.34	6,103 10,991
Montana, Red Lodge	"	9.05	43.03	36.70	11.22	5.25	1.36	60.41	20.0	1.76	5,987 10.777
Missouri, Bevier field	"	9.14	39.02	34.53	17.31	4.96	0.99	56.25	15.19	5.30	5,806 10,451
Iowa, Lucas Co.	"	9.22	44.52	32.71	13.55	5.35	1.22	59.89	16.57	3.42	6,105 10,989
New Mexico, Gallup	Lignite	10.86	46.90	35.14	7.10	5.73	1.05	64.34	21.14	0.64	6,353 11,435
" " Gallup	"	8.13	37.83	34.82	19.22	5.05	0.98	56.71	16.74	1.30	5,668 10,202
Texas, Wood Co.	"	10.66	40.11	39.42	9.81	5.28	1.06	57.31	25.83	0.71	5,502 9,904
Colorado, Boulder field	"	13.49	43.03	37.11	6.37	5.75	1.22	61.13	24.95	0.58	5,995 10,791
North Dakota, Lehigh field	"	15.42	33.61	38.73	12.24	5.22	0.71	52.66	27.15	2.02	5,034 9,061
" " Williston field	"	16.70	39.49	37.10	6.71	5.61	0.91	55.16	30.98	0.63	5,273 9,491
Wyoming, Monarch	"	17.69	39.56	37.96	4.79	6.09	1.09	58.41	28.99	0.63	5,753 10,355
Texas, Houston Co.	"	13.40	29.00	42.75	14.85	5.57	0.95	52.06	25.53	1.04	5,199 9,358

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[1] Based on U. S. G. S. Report Coal Testing Plant, 1906. Professional papers, No. 48, Parts I, II, III, N. W. Lord and M. R. Campbell, except analyses of anthracite, which are taken from The Pennsylvania Anthracite Coal Field, H. H. Stoeck, 22d Annual Report, U. S. G. S., Part III.

TABLE LXX. WESTERN U. S. COALS[1]

Locality	Type	Proximate Analysis					Remarks
		Moisture	Fixed Carbon	Vol. Matter	Ash	Sulphur	
Colorado, El Moro, Raton Field	Bituminous	0.75	57.07	31.13	11.05	—	Coking coal.
" Crested Butte, Grand River Field	"	0.56	71.31	22.42	5.70	—	" "
" Canon City Field	"	6.21	52.47	31.32	11.10	—	Non-coking coal.
" La Plata Field	"	0.82	55.72	37.25	6.05	—	Coking coal.
Montana, Clark's Ford Field	"	4.42	44.19	32.36	19.03	—	Non-coking coal.
" Belt Field, Great Falls	"	4.23	55.0	22.65	18.12	—	Semi-coking coal.
" Sans Coulee	"	1.00	47.7	30.00	21.3	—	Non-coking coal.
Wyoming, Hams Fork Field	"	4.70	44.56	36.52	14.85	—	" " "
" Rock Spr. Field, Sweetwater	"	4.06	56.4	32.00	7.00	—	" " "
New Mexico, Raton Field[2]	"	0.76	49.99	34.42	14.17	—	Coking coal.
Washington, Newcastle	"	7.92	53.8	29.03	8.02	1.14	" "
" Roslyn	"	2.05	54.55	33.55	6.85	0.106	" "
Utah,[3] Pleasant Valley	"	7.30	47.30	39.85	5.55	—	Non-coking coal.
" Castle Gate	"	1.68	48.65	44.29	5.38	0.47	Coking coal.
Alaska, Yukon Basin	"	0.86	66.51	25.75	6.88	—	" "
" Kadiak	Lignite	12.31	33.80	51.48	2.41	0.17	—

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[1] Various sources. U. S. G. S., 22d Rep., Rocky Mountain Coal Fields; Coals of Alaska. H. O. Hofman, T. A. I. M. E., XXXIV, 294 (1904).

[2] E. K. Judd, E. M. Jour., LXXXIV, 8 (1907).

[3] Forrester, Coal Fields of Utah, U. S. G. S., Mineral Resources, 1892.

tory furnaces, sulphur is not detrimental, but in refining copper in reverberatory furnaces, the sulphur contents of the coal used should preferably be low. Sulphur and ash in coal may often be materially reduced by washing or dressing out " bone " or slate, so that a poor coal as mined may be converted into a good fuel. Sulphur in coal occurs generally as pyrites or as gypsum. The ash of coal is of very variable composition. It consists chiefly of SiO_2, Fe_2O_3, CaO, MgO, Al_2O_3, $CaSO_4$ and small amounts of the alkalies. The amount of the different constituents varies widely. Thus: (*a*) SiO_2, 15.48 per cent.; Al_2O_3, 5.28 per cent.; Fe_2O_3, 74.02 per cent.; CaO, 2.26 per cent.; MgO, 0.26 per cent.; K_2O, 0.53 per cent.; $CaSO_4$, 2.17 per cent.; (*b*) SiO_2, 45.13 per cent.; Al_2O_3, 22.47 per cent.; Fe_2O_3, 25.83 per cent.; CaO, 2.80 per cent.; MgO, 0.52 per cent.; K_2O, 0.60 per cent.; Na_2O, 0.28 per cent.; $CaSO_4$, 2.37 per cent. (*c*) SiO_2, 60.23 per cent.; Al_2O_3, 31.63 per cent.; Fe_2O_3, 6.36 per cent.; CaO, 1.08 per cent.; MgO, 0.35 per cent.; K_2O, 0.11 per cent.; $CaSO_4$, 0.24 per cent. The ash may be of such composition as to be readily fusible, and form slag, known in this case as " clinker " at the temperature of combustion obtained in the body of the fire, as for instance (*b*), or it may be practically infusible as (*c*), or an incipient fusion only may take place.

A heavy massive " clinker " may be very objectionable, necessitating a frequent cleaning of the grates, while the entire absence of clinker may be equally objectionable as it will permit fine fuel to pass the grates. A reasonable amount of porous clinker is usually desirable.

Coking coals. The coking coals are those that can be made into a good metallurgical coke, suitable for blast-furnace smelting in iron, copper, and lead metallurgy. The coking coals belong to the bituminous class, but it is not possible to determine by the proximate or ultimate analysis of the coal whether it will or will not melt and fuse into a " coke." Coals of practically identical ultimate chemical composition will act in a widely different manner in this respect. A great deal of work has been done on this subject without result. It is well established that all coals are hydrocarbons. From this standpoint the composition of a coal may be exceedingly complex; thus coals of the same ultimate composition in O, H, C, and N may vary widely in the nature of their molecular structure, and it may

TABLE LXXI. FOREIGN COALS[1]

Locality	Type	Proximate Analysis					Remarks
		Moisture	Fixed Carbon	Volatile Matter	Ash	Sulphur	
Mexico, Coahuila Coal Co.	Bituminous	1.60	67.64	15.00	12.01	—	Coking coal.
England, Durham	Semi-bituminous	0.90	80.80	13.00	4.39	0.91	Coking coal.
" Lancashire	Bituminous	—	53.12	42.00	4.88	1.44	—
" Newcastle	"	—	57.23	39.00	3.77	1.35	—
" Wales	"	—	68.09	27.00	4.91	1.43	—
" Bwlf	Semi-anthracite	—	82.01	9.07	—	—	—
Germany, Ruhr district	Bituminous	1.84	73.97	21.04	3.15	1.11	—
" " "	"	1.70	61.36	32.65	3.10	—	—
" Saar district	"	2.03	54.43	37.14	6.40	1.21	—
" Saxon brown coal	Lignite	36.26	23.27	33.39	7.08	3.74	—

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[1] Herman Poole, The Calorific Power of Fuels, Tables of Coals (1905).

be easily conceived how certain hydrocarbon molecules may melt at comparatively low temperatures, before decomposition, while others are decomposed long before the melting-point is reached, viz., have no melting-point. It may be stated in a general way that coking coals range in volatile matter from about 17 to 33 per cent.,[1] although by no means all coals in this range will coke, and some coking coals lie outside of this range. In the process of coking, the heat for the operation is obtained from the combustion of the volatile hydrocarbons. If these are too low, good coke cannot be made in "beehive" ovens, although certain by-product ovens are suitable for the manufacture of coke from this type of coal. If the volatile matter be too high, the amount or yield of coke per ton of coal is low. The ash, sulphur, and phosphorus in coal do not seem to influence its coking properties. The ash is concentrated in the coke, hence the best coking coals are low in ash. Thus if a coal containing 10 per cent. ash yield 65 per cent. of coke, the ash contents of the coke will be 15.4 per cent.

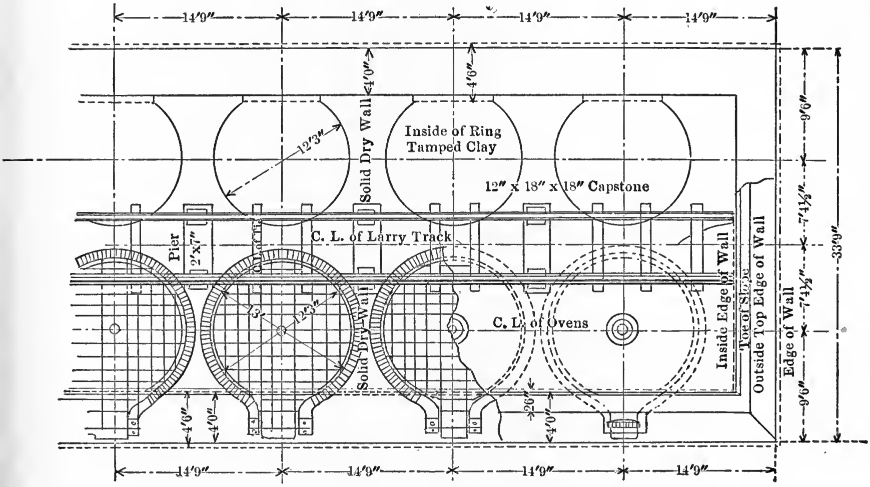

FIG. 107. — Plan of block of ovens.

(5) **Coke.** — In the United States, in 1907, there were pro-

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[1] John Fulton, Treatise on Coke, 1905, 28. F. C. Keighley, Mines and Minerals, XXVIII, 109 (1907).

duced 40,595,238 tons of coke, valued at $107,445,050 at the ovens.[1] By far the greater part of this was consumed for smelting purposes. About 85 to 87 per cent. was made in beehive ovens, and the rest in by-product coke ovens. In coking in beehive ovens, a large part of the gas produced, which is valuable as fuel, and the tar and ammonia liquor, is wasted. In the by-product oven, all the products are utilized. It is generally recognized that coking in beehive ovens entails an enormous waste, and in the more populous districts of the country they are gradually being replaced by the by-product ovens. Near cities where the gas produced finds a ready sale for fuel and illuminating purposes, by-product ovens are frequently installed. Certain large iron and steel plants also manufacture their own coke in by-product ovens, the gases obtained being used for fuel purposes. In outlying districts, distant from ready markets, as in the western states, by-product ovens are rarely installed, as the first cost is great, and the by-products do not find a ready sale. The use of the by-product oven is, however, constantly increasing.

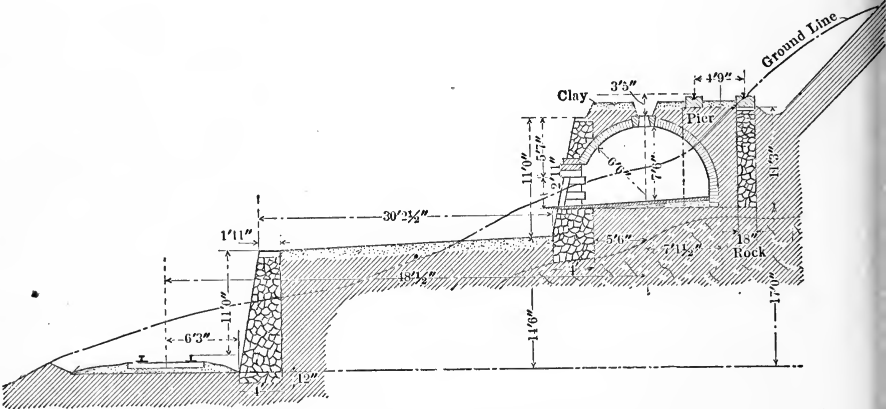

Fig. 108. — Cross-section of a bank of ovens.

Coking in beehive ovens. The "beehive" oven for coking coal is very old and is an adaptation of the conical "meiler" for burning charcoal. The name is derived from its resemblance

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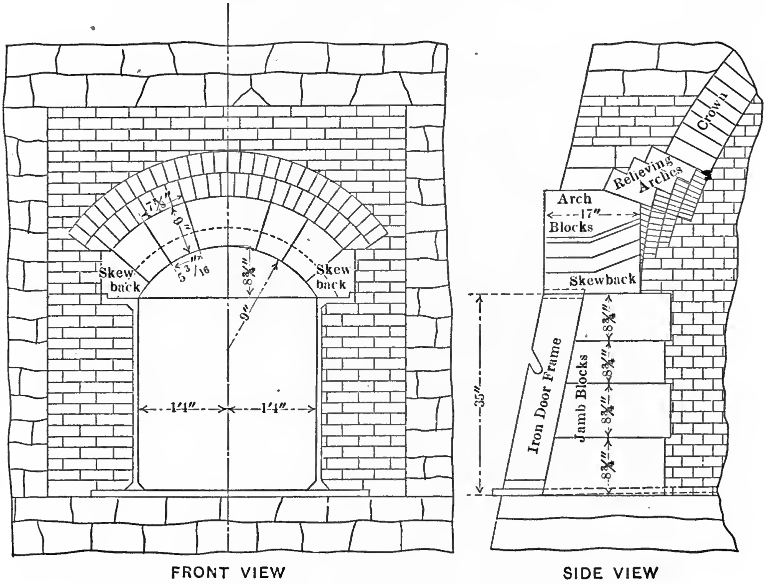
[1] Mineral Industry, XVII, 130 (1908).

to the old form of beehive. In Figs. 107 and 108 is shown the plan[1] and cross-section of ovens, and in Fig. 109 the front elevation, showing the construction of doors. The ovens are built in blocks, or double rows, or in banks, or single rows. The arrangement is such that the ovens are charged from a track on top of the ovens, by means of a special car termed a "larry," and discharged through the door in the side on to a platform, from which the coke is loaded directly into railroad cars on a track at a lower level than the platform. The ovens are generally about 12.5 ft. in diameter and 7.5 ft. high to the highest point in the crown. The circular section of the oven is built of fire brick, usually a coarse-grained brick which will withstand the severe conditions produced by highly heated surfaces coming in contact with the water used in quenching the coke. The crown of the oven is fequently built of silica brick. Tiling is used for the floor and wherever necessary special shapes are used to avoid the cutting of brick.



FRONT VIEW SIDE VIEW

Fig. 109. — Door of beehive coke oven.

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[1] Mines and Minerals, XXVII, 80 (1906).

Coking process. In starting new ovens they are preheated to a dull red heat by burning coal in them; in working ovens they are at that temperature from the previous charge. About 5 to 6 tons of coal are then charged in at the top and leveled off with a rake. The depth of the coal should be 23 to 24 in. The coal may be mine run, viz., in the form as mined, which may be fine and in small pieces as in the Connelsville district of Pennsylvania; or it may have to be first crushed. Sometimes coarse lump coal is charged. The preparation of the coal depends on the nature of it; some coals will make good coke only if finely crushed, others do not need this preparation. Certain coals must be cleaned of bone and slate by dressing and washing, in order to reduce the ash and sulphur to as low a content as possible, before coking. The door *A*, Fig. 110, is then bricked up with fire brick, the top brick being put in loosely, so that they may be removed for the admission of air when the coking process requires it. After 10 to 20 minutes white smoke will arise through the top opening, the distillation of the coal having begun; then some air is admitted at the top of the door and the gases above the coal ignite, and burn with a dull smoky flame. The coking of the coal proceeds from above downward, essentially — the volatile matter of the coal distils and burns in the oven above the coal, furnishing the heat for the operation. Some of the hydrocarbon gases rising through the mass deposit

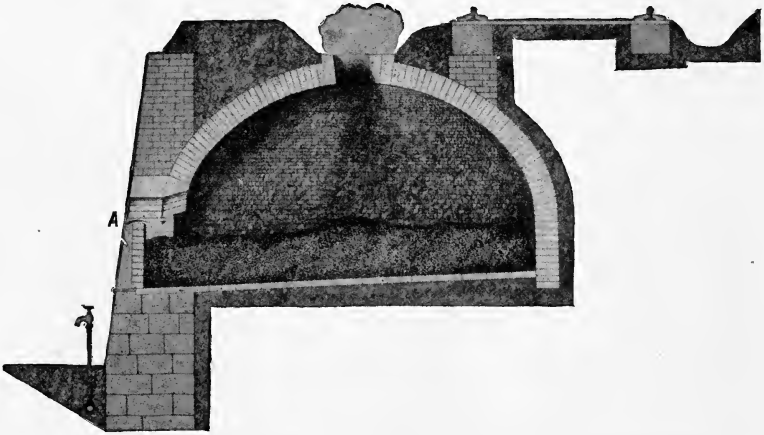

Fig. 110. — Cross-section of coke oven showing height of coal charged.

carbon in the fissures in the upper mass, already coked, giving the coke the silvery appearance[1] usually a property of high-grade coke. As the operation proceeds, the temperature rises and the flame becomes white and finally disappears. Toward the end, the air supply is gradually shut off, until none is admitted. The oven is permitted to stand for some time after the disappearance of all flame, and then water is turned in at the top by means of a hose, and the coke is quenched. The door is then removed and the coke withdrawn by long rakes. The standard time of coking for metallurgical coke is 48 and 72 hours.

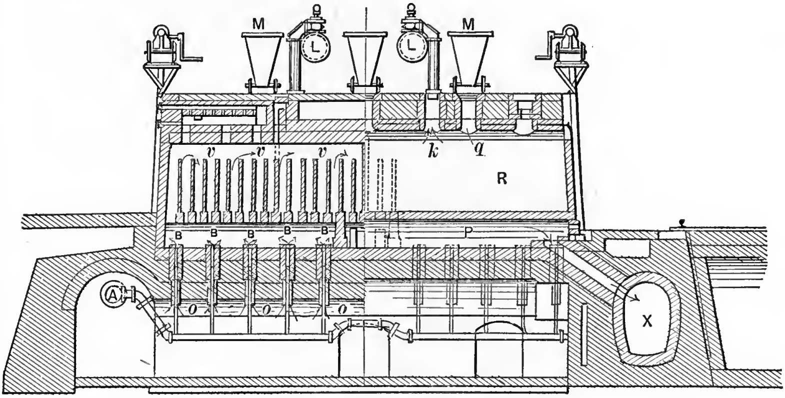

Fig. 111. — Longitudinal sections. The Otto-Hilgenstock by-product ovens.

After drawing the coke, the oven is recharged as rapidly as possible in order to avoid loss of heat, as the best coke is produced in hot ovens. Often the coke at the bottom of the oven is black and soft for several inches, due to insufficient heat; this black portion is known as *black ends*. Seventy-two hour coke is usually of a more cellular structure, of greater hardness of body, has less black ends than 48-hour coke, and makes a better metallurgical fuel, especially for iron blast furnace work. For lead and copper blast furnace smelting 48-hour coke may answer as well. The yield of coke from coal depends on the amount of volatile matter in the coal, and the amount of the fixed carbon consumed in the coking process, which depends upon the care used in coking. In the Connelsville

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[1] John Fulton, Treatise on Coke, 158.

district the yield of marketable coke is about 62 to 65 per cent. of the weight of the coal charged. The average temperature of the interior of the beehive oven during coking is 1402° C., and the highest temperature 1535° C.[1]

By-product coke ovens. Figs. 111 and 112 show a longitudinal and a cross-section respectively of the Otto-Hilgenstock[2] by-product retort oven. It consists essentially of the firebrick retorts *R*, about 33 ft. long, 6.5 ft. high, and 17 to 22 in. wide, holding a charge of 6 to 7 tons of coal. This coal is charged by larry cars *M* through the openings *q*, while the coke is discharged by special mechanical pushers through the doors *R′*. The gas given off from the coal during distillation escapes from the retort by the openings *k*, and is conducted to condensers which separate out ammonia liquor, tar, etc., and a certain proportion of the gas. The rest of the gas is returned to the main *A*, from which it enters the burners *B*, *B*, air for combustion being drawn in at *O*, *O*, from the foundation arches. The flame and products of combustion pass up the vertical flues

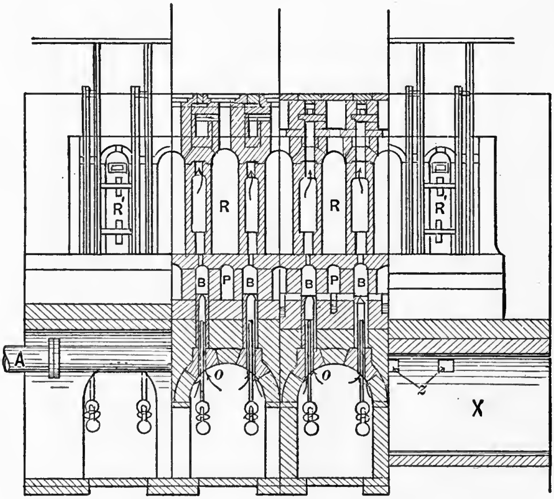

FIG. 112. — Transverse sections. The Otto-Hilgenstock by-product oven.

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[1] J. R. Campbell, E. and M. Jour., LXXXVII, 120 (1909).

[2] The United-Otto System of By-product Coke Ovens, by the United Coke and Gas Co., New York, 1906.

v, v, over the top of them, to the center of the chambers, thence down a channel in the wall to the flue P below the floor of the retorts, then to the flues z into the main flue X, from which they pass to boilers, giving up their remaining heat to form steam.

It will be noted that the coking retorts R are surrounded by flues in which the gas is burnt, thus uniformly heating the same from without to a high temperature. In some types of by-product retort ovens, the air for the combustion of the gas is preheated by a system of regenerating chambers, built of brick in checker-work fashion. The hot, waste products of combustion, in place of heating boilers, are conducted to one of these regenerators where they give up their heat to the brick work, thence passing to the stack. The other regenerator, which has been previously heated in this manner, has the air for combustion passed through it, thus absorbing the heat from the brick work, and by this preheating permitting a high temperature to be attained in the flues around the retort, with a smaller consumption of gas than would be possible without preheating the air. This permits more of the gas produced in coking to be used for the manufacture of illuminating or fuel gas. As the regenerators cool from the air passed through, they are reversed from time to time by a system of valves. Fig. 113 shows a general view of a United-Otto system by-product coke oven plant.

The physical properties of coke.[1] The following properties are discussed: (*a*) hardness of body, (*b*) cell structure, (*c*) purity, (*d*) uniform quality, (*e*) coherence in handling.

(*a*) *Hardness of body.* By this is meant the hardness of the cell walls of the coke, which is usually from 2 to 3.5, referred to the mineralogical scale. The property is important in that hard cokes (3 plus) are resistant to the solvent action of carbon dioxide gas in the blast furnace, — $CO_2 + C = 2CO$ — which takes place in the upper part of the furnace and is known as the "carbon transfer." This dissolution of the coke is undesirable since it should reach the "tuyeres" or blast openings of the furnace practically unaltered. The standard Connelsville coke produced in beehive ovens has a hardness of three.

(*b*) *Cell Structure.* Coke is cellular in structure. A piece

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[1] John Fulton, *ibid.*

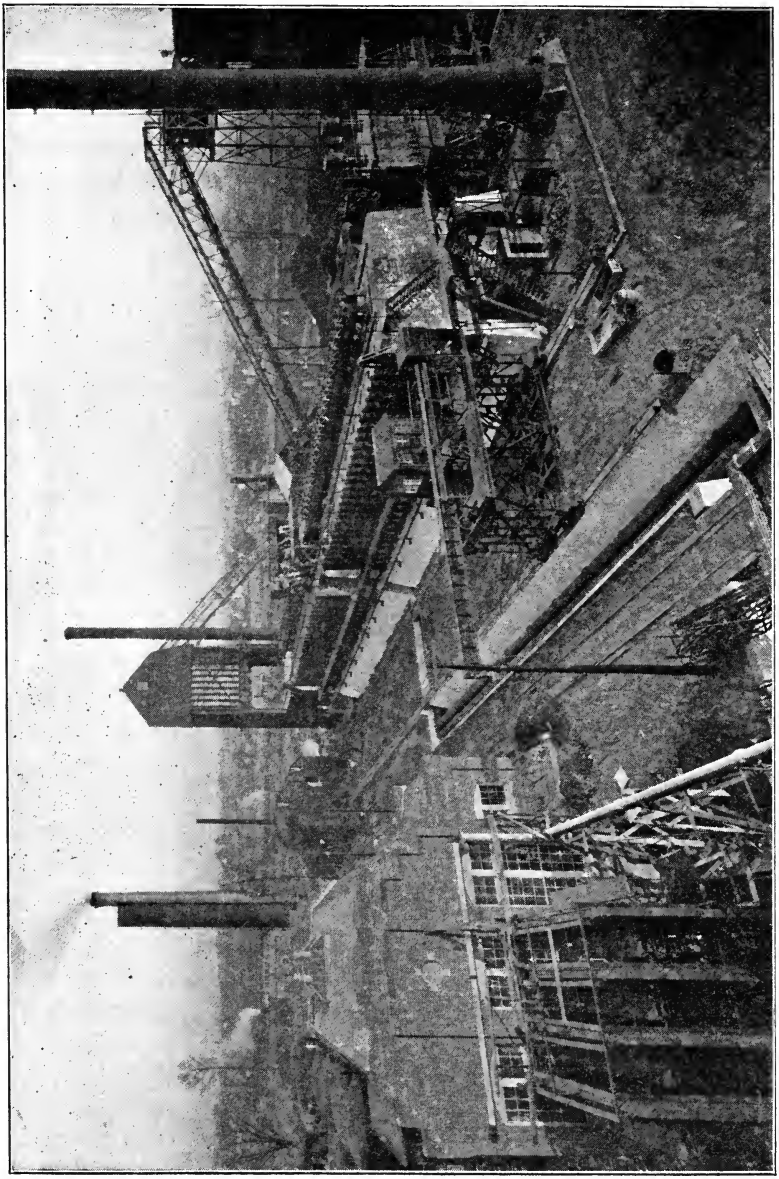

FIG. 113. — General view of the United-Otto system of by-product coke ovens.

of coke consists of walls of coke enclosing irregular spaces or cells. These cells intercommunicate with each other, for a piece of coke will readily absorb a great deal of water, about 70 per cent. of its dry weight. Standard Connelsville coke consists of about 44 per cent. coke and 56 per cent. cell space per unit volume. This cellular structure is important since it affords a large surface for combustion. This is essential, as the rapidity of combustion at the tuyeres of the furnace has a decided influence on the furnace capacity.

In the blast furnace the coke should pass to the zone of combustion practically unaltered, and then, when it comes into contact with the air blast, burn rapidly. There is a great deal of difference in the cell development of various cokes; in some instances it may be as low as 24 per cent.

(*c*) *Purity.* The term purity has reference to the absence of ash, sulphur, and phosphorus. Generally the ash contents of coke are not much below 10 per cent. Cokes with less than 5 to 7 per cent. are scarce. Table LXXII gives the composition of coke ash.

TABLE LXXII. COMPOSITION OF COKE ASH

Locality	Chemical Composition					
	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	S
Horr, Montana[1]	57.0	19.0	21.2	3.3	—	—
Belt, Montana[1]	51.6	10.0	33.6	—	—	—
Cardiff, Colorado[1]	48.9	18.9	23.9	5.8	1.4	0.8
Fairmount, West Virginia	43.2	25.0	23.1	8.87	—	—
Connelsville, Pennsylvania	50.3	14.9	21.88	13.10	—	—

The sulphur and phosphorus contents of coke are of importance in the metallurgy of iron. For iron blast furnace use coke should contain not more than 1 per cent. sulphur, though some cokes containing somewhat more than this are used. In lead and copper blast furnace smelting no particular limits are set. Phosphorus is usually low in cokes. In the metallurgy of iron this constituent should usually not exceed 0.05 per cent., though more is permissible when "basic" iron is made for the basic open-hearth steel process.

TABLE LXXIII. COMPOSITION OF COKES

Locality	Chemical Composition					
	Moisture	Volatile Matter	Fixed Carbon	Ash	Sulphur	Phosphorus
Connelsville, Pa., Standard coke[2]	0.80	1.31	86.88	11.54	0.695	0.05
Pocahontas, W. Va.[2]	0.345	0.341	92.69	5.82	0.738	0.0063
Alamo, Mexico[2]	—	1.35	83.80	14.85	1.08	0.005
Monongah, W. Va.[2]	0.23	0.80	89.77	9.80	0.976	0.039
Fairmount, W. Va.[3]	0.69	1.00	85.89	12.42	—	—
Cambria, Wyo.[3]	0.92	3.93	65.22	29.93	—	—
Colorado[3]	1.60	1.70	86.86	10.70	—	—
Lehigh, Pa.[1]	0.60	4.20	81.80	13.80	—	—
Horr, Montana[1]	0.50	4.00	75.70	19.9	—	—
Crows' Nest, B. C.[1]	0.50	4.10	85.8	9.9	—	—
Belt, Montana[1]	2.30	4.70	78.3	13.7	—	—
Cardiff, Colorado[1]	0.40	3.60	85.7	10.3	—	—
Castle Gate, Utah[1]	0.20	3.50	86.1	10.2	—	—
Raton Field, New Mex.[4]	0.58	1.77	79.96	16.99	0.698	—

(*e*) *Uniform quality.* Shipments of coke should be of uniform quality, and *black ends,* which are soft and do not resist the action of the furnace, should be absent. Cokes differ much in appearance, thus Connelsville coke is columnar in structure, usually of a bright silvery luster, in large, hard, massive pieces, and very coherent; while some West Virginia cokes resemble a conglomerate in structure, like pieces of charred coal cemented together, and do not possess any very prominent luster, but are rather dull. It is also more friable than the Connelsville coke, and large pieces break readily. Both kinds, however, make excellent blast-furnace coke.

(*f*) *Coherence in handling.* The hard, massive cokes stand railroad shipment much better than the softer friable kinds. Coke fines or *breeze* is very undesirable as a blast-furnace fuel, and in handling coke at the furnaces it is generally discarded, the coke being shoveled with coke forks which eliminate all pieces below a certain small size.

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[1] H. O. Hofman, T. A. I. M. E., XXXIV, 289 (1904).

[2] J. Fulton, Treatise on Coke, 334.

[3] C. H. Fulton and T. Knutzen, T. A. I. M. E., XXXV, 334 (1905).

[4] E. K. Judd, E. and M. Jour., LXXXIV, 8 (1907).

(*g*) *Crushing strength.* The crushing strength of coke varies with the coal from which it is made, and the process of coking. Coke made in beehive ovens has not the same strength as that made from the same coal in certain by-product ovens. Thus standard beehive oven coke from Connelsville coal has a crushing strength of about 300 lbs. per cu. in., while by-product coke from the same coal may attain a strength of 940 lbs. per cu. in. The crushing strength is of importance in reference to the load or burden the coke can withstand in the furnace without crushing. A strength of 300 lbs. per cu. in. is ample to resist the load in a 90-ft. iron blast furnace.

The crushing strength of various cokes made in beehive ovens will vary from 75 to 440 lbs. per inch. While the strength of cokes made in by-product ovens is usually much greater, and they also have a greater hardness of body, they are usually deficient in cell structure, which may be a serious defect for blast-furnace work. This last is often urged as an objection to by-product coke, but whether it is serious enough to carry weight is still to be determined by a wider experience.

(6) **Oil.** — Petroleum, or natural oil, or certain of its distillation products, are used extensively as a metallurgical fuel in localities in which it is abundant, as in Russia, or in the United States in California, and to some extent in Colorado. Its use is dependent upon economic considerations, such as (1) the nature of the oil; for while all oils make good fuel, certain kinds on distillation yield large quantities of gasolene, lighting, and lubricating oils, which sell at a high price, so that the use of the crude oil as a fuel is too costly. (2) The availability of large deposits of cheap coal may exclude the use of oil on account of the higher relative cost of the latter. While oil has a very high calorific power, and presents certain definite advantages as a metallurgical fuel for reverberatory furnaces, its use is restricted mainly to districts in which it is produced, or to such regions at long distances from coal supply where the freight costs on the latter warrant the shipping in of the oil. The calorific power of crude petroleum is about 21,000 B. T. U. per lb., while coals vary from about 9000 to 14,000. One pound of oil is equivalent to 2 to 2.25 lbs. of average coal, and perhaps more, as the efficiency in burning oil is greater than that in burning coal. Lima, Ohio, oil weighs 6.6 lbs. per gal., and a

barrel of 52 gals. weighs 355 lbs. An average weight of oil is 7.32 lbs. per gal. Taking into consideration the grade of coal, freight charges on oil and coal, the advantages of oil as fuel, *e.g.* in eliminating ash, thus reducing the cost of operation, the relative economy[1] of oil and coal may readily be calculated for any specific case.

Oil is used as fuel in California[2] for smelting copper ores in reverberatory furnaces; for copper-refining furnaces, ore-roasting furnaces, reverberatory furnaces for "softening" lead bullion, cupeling furnaces, and in retort furnaces for distilling zinc scums from the Parkes lead-desilverization process. In Colorado it is used at Colorado City in ore-roasting furnaces, and in Russia in open-hearth steel furnaces, and other metallurgical furnaces.

Petroleum or mineral oil consists essentially of hydrocarbons.[3] The oils usually belong in one of two groups: (1) the *methane* or paraffin group, represented by the general formula, C_nH_{2n+2}, as for example the Pennsylvania oils, and (2) *naphthenes*, represented by the general formula, $C_nH_{2n-6} + H_6$, which are isomers of the *ethylene* (C_nH_{2n}) or *olefine* groups, as for example the Russian oils. The color of the oils ranges from a straw color to almost black. The specific gravity, an indication of its viscosity, varies from 0.771 to 1.020. California oil has a gravity of from 0.827 to 0.88. Most mineral oils come in the range from 0.79 to 0.959.

When crude oil is subjected to distillation the following products are obtained.[4]

I. *Light oils:*

1. Petroleum ether, rhigolene, s. g. 0.65 to 0.66; boiling-point, 104 to 158° Fahr.
2. Gasolene, s. g. 0.64 to 0.667; boiling-point, 158 to 176° Fahr.
3. Petroleum naphtha C; benzine, s. g. 0.667 to 0.707; boiling-point, 176 to 212° Fahr.
4. Petroleum naphtha B; ligroine, s. g. 0.707 to 0.722; boiling-point, 176 to 248° Fahr.

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[1] Kent, Steam Boiler Economy, 141.

[2] A. von der Ropp, E. and M. Jour., LXXV, 81 (1903); E. and M. Jour., LXIX, 739 (1900).

[3] Boverton Redwood, Petroleum and its Products, 207 (1896).

[4] W. T. Brannt, Petroleum and its Products, 75 (1895).

5. Petroleum naphtha A; ligroine, s. g. 0.722 to 0.737; boiling-point, 258 to 302° Fahr.

II. *Illuminating oils:*

1. Kerosene, petroleum, s. g. 0.753 to 0.864; boiling-point, 302 to 572°.

III. *Residuum* (fuel oils — tar):

1. Lubricating oils, s. g. 0.745 to 0.8588.
2. Paraffin oils, s. g. 0.8588 to 0.959.
3. Coke residue.

Classified on this basis, Table LXXIV gives the approximate composition of American oils. It is to be noted that oils which yield high percentages of naphtha and kerosene are rarely used for fuel as they are more valuable for distillation. Frequently the residuum, or fuel oil only, of petroleum, is used as a fuel.

TABLE LXXIV. COMPOSITION OF AMERICAN OILS[1]

Products	Appalachian Field	Lima Indiana Field	Mid-Continental Field	Gulf Field	California Field	Corsicana, Texas	Colorado Field
	%	%	%	%	%	%	%
Naphthas, gasolene, benzine	12	11.5	11.0	3.0	6	7	3.5
Illuminating oil, kerosene..	67	43.0	41.0	15.0	18.0	50	35.0
Lubricating oils, inc. grease	12.5	15.0	—	6.0	1.5	—	3.0
Gas oil	—	—	25.0	45.0	—	—	—
Fuel oil, inc. acid oil, asphaltum oil, asphalt	4	25.0	20.0	28.0	72.0	40.0	55.0
Paraffin wax............	2	2.0	—	—	—	—	—

TABLE LXXV. ULTIMATE COMPOSITION OF OILS

Locality	Ultimate Chemical Composition			
	H	C	N	O
	%	%	%	%
Ohio, Mecca	13.071	86.316	0.23	—
California	11.819	86.934	1.1095	—
Pennsylvania, heavy oil	13.70	84.900	—	1.04
Pennsylvania, light oil	14.80	82.000	—	3.20
Ohio	13.1	84.2	—	2.70
Texas, Beaumont	13.2	86.8	—	—
Russia, Baku	12.3	86.6	—	1.10

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[1] Petroleum Review, Aug. 15, 1908.

Table LXXV gives the ultimate composition of oils.

The calorific power of oil varies from 9960 to 11,640 calories per kilogram, an average of 10,500 calories. The hydrocarbon bases of oil, methane, and ethylene have calorific powers of 13,065 and 11,850 calories respectively.

For metallurgical furnaces, it is best to use either crude petroleum or "residuum." The nature of the oil is of importance; some oils are thick and viscid, while others are rather fluid. It is usual to specify a certain specific gravity; in California, oil of 26 to 27° Baumé = 0.901 to 0.896 s. g. is used for metallurgical furnaces. The gravity, however, is not vital and almost any oil can be used, provided the apparatus for burning it is properly designed. Heavy oils are more difficult to force through small pipes and openings and are more apt to cause clogging, particularly if they contain grit and sediment. "Fuel oil" may be bought on the market, consisting of a mixture of heavy residuum from distillation with crude petroleum; this mixture is usually undesirable, as it may separate into its constituents in the storage tanks. The viscosity of oils increases rapidly with a lowering of the temperature, and in burning viscous oils it is common to jacket the oil pipes in the burners with steam, generally using this as the atomizing agent. Provision is also made to strain out sediment and grit from the oil before it enters the pumps which serve the burners, and to settle out any water that the oil contains.[1]

Oil as fuel presents several distinct advantages, when its use is economically warranted, as follows:

(*a*) A perfect control of flame, permitting of the establishment of oxidizing, neutral, or reducing conditions of furnace atmosphere in a very short space of time.

(*b*) A ready control of temperature, from high to low, in a short space of time.

(*c*) The attainment of high temperatures, as the calorific value of the oil is high.

(*d*) Cleanliness and neatness of operations, in that ash is absent. With no ash to dispose of, a considerable saving may be effected.

(*e*) The absence of fireplaces and grate bars, and avoidance of labor in cleaning grates.

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[1] G. W. Mellville, E. and M. Jour., LXXX, 625 (1905).

(7) **Gas.** — Gaseous fuel is of great importance in the metallurgical industry and is of wide application. It may be used in practically all types of metallurgical furnaces except the blast furnace, and it is the most scientific and practical method of utilizing fuel, at our command. Within recent years the use of gaseous fuel has greatly increased, as the difficulties of its application are being solved and the principles involved in its use are becoming better understood. Gaseous fuel is of two main types: (1) natural gas, and (2) artificial gas.

(1) *Natural gas,*[1] obtained from wells driven into certain rock strata in various districts where natural gas occurs, as in Pennsylvania, Ohio, West Virginia, Indiana, Kansas, etc. The natural gas supply, while formerly considered practically inexhaustible, is now looked upon in a different light and is being carefully husbanded. Some states, like Indiana, seem to have practically exhausted the supply. Natural gas is the highest grade fuel known and is used in open-hearth steel furnaces, particularly in the Pittsburg district, in zinc-smelting in Kansas and in the Portland cement industry in the latter state, as well as for other industrial purposes wherever it occurs. It is obtained from tight driven wells, from which it comes sometimes under great pressure. This "rock pressure," so called, is reduced by suitable regulating valves, and the gas is burnt at the furnaces under a pressure of not exceeding 4 to 6 oz. per square inch. It is frequently conveyed long distances by pipe lines to the place of utilization. Table LXXVI gives the composition of natural gases.

(2) *Artificial gas.* Artificial gas may be made from a number of different fuels, such as coke, anthracite coal, bituminous coal, lignite, wood, and also from oil. It is one of the great advantages of gaseous fuel that good gas may be made from a comparatively poor fuel, and in recent years *gas producers* have been adapted to poor coals for the production of very good gas. In some instances where not sufficient heat could be developed by the *direct firing* of certain coals on grates, the use of gas derived from these coals will answer all purposes for the development of heat and the proper temperature.

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[1] Consult, Production of Natural Gas in U. S., W. H. Hammon, Min. Ind., X, 464 (1901).

By these means low-grade bituminous coals and lignite become available for metallurgical purposes where otherwise they would be useless. Several kinds of artificial gas are used.

(*a*) *Producer gas,* known also as "air gas," Siemen's gas, and "fuel gas," is made by burning coke or coal in a thick bed in a gas producer, so that essentially all the carbon is burnt to CO. The gas theoretically consists of one volume of CO and two volumes of N_2, but in practice will also contain some CO_2. In modern producers some steam (H_2O) is invariably blown into the producer with the air, and the gas consists of a mixture of producer gas and "water gas" described below.

Table LXXVI. Composition of Natural Gas

Locality	Chemical Composition by Volume							
	H %	CH_4 %	C_2H_4 %	CO %	CO_2 %	O %	N %	H_2S %
Findlay, Ohio[1]	1.64	93.35	0.35	0.41	0.25	0.39	3.11	0.20
St. Mary's, Ohio[1]	1.74	93.85	0.20	0.44	0.23	0.35	2.98	0.21
Muncie, Ind.[1]	3.25	92.67	0.25	0.45	0.25	0.35	3.53	0.15
Kokomo, Ind.[1]	1.42	94.16	0.30	0.55	0.29	0.30	2.80	0.18
Liberty, Kansas[2]	1.64	93.35	0.35	0.41	0.45	0.39	3.41	—

(*b*) *Water gas.* This is the gas produced by blowing water vapor (steam) through incandescent carbon. The water vapor is decomposed with the production of H_2 and CO gas. Theoretically water gas is composed of one volume of CO and one volume of H_2, but as the above reaction is "endothermic," *i.e.* absorbs heat, the reaction would soon stop, unless external heat was applied. This is done by admitting air and burning some carbon with the consequent production of CO_2. Water gas, as such, is not a metallurgical fuel, but forms the basis of many illuminating gases used for lighting purposes.

(*c*) *Coal gas.* This is made by distilling bituminous gas coals in closed retorts. This furnishes a gas, practically solely for domestic use, chiefly for illuminating purposes.

(*d*) *Other gases.* Oil gas is made by vaporizing petroleum

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[1] C. C. Howard, Geol. Survey Ohio, VI, 137.

[2] D. Brittain, E. andM. Jour., LXXXVI, 568 (1908).

or other oils. Coke-oven gas is produced in by-product coke ovens by the distillation of coking coals. Neither is of much importance metallurgically. The chemistry of producer gas is fully discussed in the section on gas producers in Chapter XII.

Table LXXVII gives the composition by volume of the various types of gases.

TABLE LXXVII.[1] COMPOSITION OF ARTIFICIAL GAS

Type of Gas	Composition							Calorific Power B. T. U. per Cu. Ft.
	CO	H	CH_4	C_2H_4	CO_2	N	O	
Natural gas	0.50	2.18	92.6	0.31	0.26	3.61	0.34	1100.0
Producer gas — anthracite coal	27.0	12.0	1.2	—	2.50	57.00	0.30	137.4
Producer gas — bituminous coal	27.0	12.0	2.5	0.4	2.50	56.20	0.30	157.0
Producer gas — bituminous coal[2]	22.8	8.5	2.4	0.40	5.20	60.30	0.40	—
Water gas	45.0	45.0	2.0	—	4.00	2.0	0.50	322.0
Coal gas	6.0	46.0	40.0	4.00	0.50	1.5	0.50	735.0
Blast-furnace gas	25.56	—	—	—	12.68	61.76	—	87.85

The producer gases in the table contain rather less than the ordinary or usual amount of CO_2. It will generally contain from 5 to 10 per cent., with a corresponding decrease in the other constituents.

Table LXXVIII gives the composition of producer gas from American coals, with data of coal composition, calorific power, amount of gas obtained per pound of coal, etc. It is to be noted that lignite coals furnish a very good gas, though the quantity of gas produced per pound of coal is of course lower than for high-grade bituminous coals. All the coals in the table were burnt with the use of steam in the producer. It is very desirable to have hydrocarbon gases present in the fuel gas, as this gives rise to a luminous flame, due to the particles of carbon from the decomposition of the hydrocarbons becoming incandescent. The radiating effect of a luminous flame is much greater than that of a non-luminous flame, effecting a more

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[1] W. J. Taylor, T. A. I. M. E., XVIII, 868 (1890).

[2] H. H. Campbell, T. A. I. M. E., XXII, 374 (1893).

TABLE LXXVIII. COMPOSITION OF PRODUCER GAS

No.	Locality	Coal. Proximate Analysis				Calorific Power per Lb. of Air-dried Coal B.T.U.	Composition of Producer Gas (by volume)						Cu. Ft. of Gas obtained per Lb. of Dry Coal in Producer	Calorific Power of 1 Cu. Ft. of Gas B.T.U.	Calorific Power of 1 Lb. of Dry Coal in the Form of Gas B.T.U.
		% Moisture	% Fixed Carbon	% Volatile Matter	% Ash		% CO_2	% O_2	% CO	% H_2	% CH_4	% N_2			
1	Alabama	3.28	53.55	33.62	9.55	13,365	8.16	0.10	16.65	7.20	5.64	62.24	60.4	149.2	9000
2	Colorado	13.49	45.17	34.99	6.35	12,245	10.11	0.55	17.38	11.05	5.00	55.90	52.8	149.0	7860
3	Illinois	6.21	52.57	31.34	9.88	13,041	10.53	0.15	15.31	8.35	4.46	61.19	53.9	154.8	8330
4	Illinois	10.00	46.97	33.55	9.48	12,834	9.72	0.12	15.12	9.98	6.00	59.06	58.4	151.5	8840
5	Indiana	7.05	44.51	37.85	10.59	13,037	9.89	0.25	14.10	9.56	6.08	60.13	50.3	153.7	7730
6	Indiana	6.29	43.06	40.66	9.99	12,953	11.80	0.07	11.46	10.60	6.10	59.97	63.6	159.3	10,140
7	Indian Territory	3.85	50.59	36.95	8.61	13,455	8.25	0.11	19.39	7.69	4.92	59.65	54.1	159.2	8620
8	Indian Territory	9.00	40.68	33.06	16.36	11,392	7.29	0.236	17.636	10.427	6.30	58.109	61.9	161.1	9980
9	Iowa	2.10	36.66	36.92	24.32	10,489	10.06	0.17	12.57	9.53	7.67	60.00	58.1	160.2	9300
10	Kansas	1.09	54.22	33.06	11.63	13,421	10.27	0.13	12.40	9.05	7.42	60.73	62.8	167.2	10,500
11	Kentucky	6.25	45.66	39.00	9.09	13,226	10.87	0.29	12.45	10.92	6.52	58.95	55.1	155.9	8610
12	Missouri	9.05	39.38	36.30	15.27	11,882	12.07	0.20	10.53	7.63	6.33	63.23	63.0	140.0	8820
13	Montana	9.68	44.15	35.22	10.95	11,934	9.04	0.36	18.67	8.00	4.84	59.10	40.9	160.8	6580
14	North Dakota	16.17	36.48	38.53	8.82	11,255	8.69	0.23	20.90	14.33	4.85	51.02	41.5	188.5	7830
15	Texas	16.88	29.75	40.42	12.95	10,928	11.10	0.22	14.43	10.54	7.48	56.22	42.7	169.7	7260
16	Texas	10.66	40.11	39.42	9.81	11,086	9.60	0.20	18.22	9.63	4.81	57.53	51.6	156.2	8060
17	West Virginia	1.51	55.45	36.89	6.15	14,396	10.50	0.10	14.34	2.81	5.56	66.69	64.1	144.4	9260.
18	West Virginia	1.10	60.85	29.15	8.90	14,202	10.16	0.24	15.82	11.16	3.74	58.88	81.2	143.2	11,610
19	West Virginia	0.30	71.06	21.78	6.06	14,720	9.62	0.08	12.75	10.31	6.76	60.48	85.1	154.2	13,140
20	West Virginia	2.66	59.0	32.58	5.76	14,558	10.33	0.22	11.93	9.45	6.40	61.67	58.4	155.1	9070
21	West Virginia	0.57	60.90	32.68	5.85	14,580	10.40	0.20	13.70	9.55	6.60	59.55	54.0	151.0	8150
22	West Virginia	2.22	59.83	31.05	6.90	14,548	8.90	0.33	14.77	9.51	6.65	59.86	70.9	160.5	11,380
23	West Virginia	0.93	73.57	19.02	6.48	14,825	10.34	0.12	14.21	12.98	4.61	57.75	71.2	142.5	10,150
24	Wyoming, Cambria	2.73	37.40	37.61	22.26	10,656	10.21	0.59	15.46	10.79	5.52	57.43	40.9	151.0	6168

NOTE. From Report of Coal Testing Plant, Professional Paper 48, Part III, E. W. Parker. Coals were gasified in a Taylor Pressure Gas Producer.

thorough heat transfer in the furnace.[1] For the above reason, bituminous and lignite coals furnish a much better gas than anthracite or coke.

(8) **Other Fuels.** In metallurgy certain other fuels are used incidentally, which strictly cannot be considered fuels in the ordinary sense of the term. Thus in pyritic smelting the chief source of heat for the carrying on of the process is the combustion of pyrite (FeS_2) and pyrrhotite (Fe_7S_8) in the presence of silica (SiO_2). The equation expressing this reaction is:

$$(1)\quad 2FeS_2 + 3O_2 + 12N_2 + SiO_2 = 2FeO \cdot SiO_2 + 2S + 2SO_2 + 12N_2.$$

$$(2)\quad 2Fe_7S_8 + 13O_2 + 52N_2 + 7SiO_2 = 7(2FeO \cdot SiO_2) + 2S + 14SO_2 + 52N_2.$$

The heat is derived from the combustion of the iron to silicate, and part of the sulphur to sulphurous acid gas.

This subject is further discussed under thermal chemistry in Chapter XIV.

In the bessemerization of pig-iron, by blowing air through molten iron, the combustion of the silicon, carbon, and manganese contained in small quantities in the iron, to SiO_2, CO, and MnO respectively, furnish the heat necessary to carry on the operation.

In the bessemerization of copper matte, the oxidation of the iron sulphide to ferrous silicate and sulphurous acid gas furnish the heat necessary for the operation.

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[1] Geo. W. Goetz, T. A. I. M. E., XXII, 682 (1893).

CHAPTER XII

COMBUSTION

Combustion. — Combustion is that process whereby bodies unite with oxygen with the production of heat. The combination of oxygen and other substances is usually, but not invariably, an "exothermic reaction," *i.e.* one by which heat is evolved. It is essentially a chemical process. The materials used industrially for the production of heat by combustion have been fully discussed in the last chapter.

Calorific Power. — The calorific power of a substance is the quantity of heat evolved by the burning of a unit weight of the substance with oxygen. It is expressed in one of several units, the basis of which is the amount of heat required to raise a given quantity of water through a heat degree expressed in one of the conventional scales of temperature measurement. The heat units ordinarily used are the following:

(1) *Large Calorie.* This is the amount of heat required to raise one kilogram of pure water one degree C., the water being at 4° C.

(2) *Small Calorie.* This is the amount of heat required to raise one gram of pure water at 4° C. through one degree C.

(3) *British Thermal Unit or B.T.U.* This is the amount of heat required to raise one pound of pure water at 39.1° F. through one degree Fahrenheit.

(4) *Pound Calorie.* This is the amount of heat required to raise one pound of water at 4° C. through one degree C.

The relation between the different units is as follows:

1 large calorie = 3.96832 B.T.U.
1 B.T.U. = 0.251996 large calorie.
1 large calorie = 1000.00 small calories.
1 pound calorie = 2.2046 B.T.U.
1 pound calorie = 0.55556 large calories.

To convert calories per kilogram into B.T.U. per pound, multiply by 1.8; for 1 kg. = 2.2046 lbs. and 1 calorie = 3.96832 B.T.U., therefore the conversion factor is $\frac{3.96832}{2.2046} = 1.8$. To convert B.T.U. per pound into calories per kilogram multiply by 0.55555; for 1 kg. = 2.2046 lbs. and 1 B.T.U. = 0.2520 calories; therefore the conversion factor is $0.252 \times 2.2046 = 0.55555$.

One B.T.U. is equivalent to 778 ft. lbs. of energy, and 1 horse-power = 33,000 ft. lbs. per minute = 42.416 B.T.U. per minute.

Heat of Formation. — Every chemical reaction has a heat balance, *i.e.* it either gives out or requires a certain definite amount of heat to complete itself. Thus,

$$\underset{(12)}{C} + \underset{(32)}{O_2} = \underset{(44)}{CO_2} + 97{,}200 \text{ calories.} \qquad (1)$$

When 12 grams of carbon unite with 32 grams of oxygen to produce 44 grams of carbon dioxide, 97,200 gram calories of heat are liberated. If the kilogram be the unit of weight used, the heat is expressed in large calories. The figure 97,200 in this instance expresses the *molecular heat of formation* of the compound CO_2. In the same manner all compounds have a heat of formation. When heat is evolved during the formation of the compound, the heat of formation is designated by *plus* (+); and when heat is absorbed, by *minus* (−). Most compounds evolve heat when formed from their elements, or from their chemical radicals. Elementary substances have no heat of formation. It will be noted that the heat of formation is expressed for one *mole* of the substance, *i.e.* the molecular weight in grams. Equation (1) above may also be expressed as follows: Since 12 grams of carbon in burning to CO_2 give rise to 97,200 calories, one gram of carbon in burning to CO_2 evolves $\frac{97{,}200}{12} = 8100$ calories, or the *calorific power* of carbon in burning to CO_2. Or, 32 grams of oxygen in uniting with 12 grams of carbon of form CO_2 give rise to 97,200 calories, and one gram of oxygen uniting with carbon gives rise to $\frac{97{,}200}{32} =$ 3037.5 calories. That is, the heat evolved or absorbed may be expressed in terms of a unit of any of the substances entering into the reaction. The heats of formation for compounds are determined experimentally by means of the bomb calorimeter and unless otherwise stated are expressed for room temperature, viz., about 15° C. This means that in the heat of formation is included the heat given out by the products of the reaction, in cooling from the temperature reached by the reaction to the temperature of the water in the calorimeter. For example, when hydrogen is burnt with oxygen the following reaction takes place if the final product of combustion is water in the liquid form:

$$\begin{array}{ccccccc} H_2 & + & O & = & H_2O & + & 69{,}000 \text{ calories.} \\ (2) & & (16) & & (18) & & \end{array} \qquad (2)$$

One gram of hydrogen in burning to water evolves 34,500 calories, which is the calorific power of hydrogen.

In burning coal containing hydrogen, the water formed is in the form of vapor or steam, and escapes with the other products of combustion at a temperature of say 300 to 400° C. Therefore, this steam carries off heat in the form of latent heat and specific heat (sensible heat), which must be subtracted from the above figure. Thus, when hydrogen is burnt with oxygen and the product is steam at 100° C, the equation is as follows:

$$H_2 + O = H_2O + 58{,}060 \text{ calories.} \qquad (3)$$

One gram of hydrogen evolves 29,030 calories, or the calorific power of hydrogen under these conditions.

As stated above, if the products of combustion escape above 100° C., a further deduction must be made equivalent to the amount of heat required to raise the steam from 100° C. to the temperature of the escaping products of combustion. This is equivalent to the weight of the steam, times the mean specific heat between 100° C. and the temperature of the escaping products of combustion, times the number of degrees expressing the difference between the temperature of the escaping products of combustion and 100° C. This method applies generally to all similar calculations.

The heat balance of a reaction is expressed as follows:

$$\begin{array}{lllllllllll} 2\,FeS & + & 3\,SiO_2 & + & CaCO_3 & + & 3\,O_2 & + & 12\,N_2 & = \\ 2(88) & & 3(60) & & 100 & & 96 & & 24(14) & \\ \multicolumn{11}{l}{2(24{,}000) + 3(180{,}000) + 273{,}850} \\ \multicolumn{11}{l}{\qquad \text{sum} = 861{,}850 \text{ cal.}} \end{array}$$

$$\begin{array}{ccccc} 2\,FeSiO_3 & + \; CaSiO_3 \; + & 2\,SO_2 & + \; CO_2 & + \; 12\,N_2 \\ 2(132) & 116 & 2(64) & 44 & 24(14) \end{array}$$

$$2(254{,}600) + 329{,}350 + 2(69{,}260) + 97{,}200$$

$$\text{sum} = 1{,}074{,}270 \text{ cal.}$$

Therefore the heat evolved from the reaction proceeding from left to right is 1,074,270 − 861,850 = 212,420 calories. The first row of figures below the chemical symbols indicates the molecular weights involved; the second row, the molecular heats of formation. Where more than one molecule is involved, the heat of formation must be multiplied by the number of molecules. In making the summation the algebraic sum of the heats of formation is taken, *i.e.* plus and minus heats of formation are given their proper sign, and the addition made. (In the above equation only plus heats of formation are involved.) The sum on each side of the equation is then obtained. If the number of calories on the right is greater than that on the left, heat is evolved by the reaction in the quantity indicated by the difference between the sums; if the alternate is true, heat is required for the reaction in the amount indicated. In the above equation the number of calories evolved may be expressed, as before, per unit weight of any of the substances entering into the reaction; thus, 176 parts of iron sulphide (FeS) burning in air in the presence of silica and lime carbonate as indicated in the equation evolve $\frac{212{,}420}{176} = 1206$ calories per gram of iron sulphide.

When the heat evolved by a certain reaction is known, then the heats of formation, if unknown, may be calculated for certain compounds. By experiment it is known that the following reaction is true:

$$\begin{array}{l} CO + O = CO_2 + 68{,}040 \text{ calories.} \\ (28) + (16) = (44) \end{array} \tag{5}$$

It is also known that the heat of formation of CO_2 is 97,200 calories; therefore we have the following:

$$\begin{array}{l} CO + O = CO_2 + 68{,}040 \text{ calories.} \\ x \qquad\qquad\quad 97{,}200 \end{array}$$

Therefore, $x = 97{,}200 - 68{,}040 = 29{,}160$ calories, heat of formation of CO. One gram of C burning to CO according to the reaction, —

$$\begin{array}{rcl} C + O & = & CO \\ (12) + (16) & = & (28) \\ & & (29160) \end{array} \qquad (6)$$

evolves $\frac{29,160}{12} = 2430$ calories. Therefore, one gram of carbon burning to CO gives rise to 2430 calories, and one gram C produces $\frac{28}{12} = 2\frac{1}{3}$ grams of CO, and one gram of

TABLE LXXIX.[1] MOLECULAR HEATS OF FORMATION AND CALORIFIC POWERS OF CERTAIN SUBSTANCES

Substance	Reaction	Molecular Heat of Formation Calories	Calorific Power per gm. of Substance Calories
C	$C + O_2 = CO_2$	97,200	8100
C	$C + O = CO$	29,160	2430
CO	$CO + O = CO_2$	68,040	2430
H	$H_2 + O = H_2O$ vapor	58,060	29,030
H	$H_2 + O = H_2O$ liquid	69,000	34,500
P	$2P + 5O = P_2O_5$	365,300	5892
Fe	$Fe + O = FeO$	65,700	1173
Fe	$Fe_3 + O_4 = Fe_3O_4$	270,800	1612
Fe	$Fe_2 + O_3 = Fe_2O_3$	195,600	1746
Si	$Si + O_2 = SiO_2$	180,000	6428
S	$S + O_2 = SO_2$	69,260	2164
FeS	$Fe + S = FeS$	24,000	To $FeO + SO_2$ 1261
Mn	$Mn + O = MnO$	90,900	1653
CH_4	$C + H_4 = CH_4$	22,250	To $CO_2 + H_2O$ 13,309[2] 11,942[3]

CO burning to CO_2 gives rise to $\frac{68,040}{28} = 2430$ calories. Then one gram of carbon in the form of CO burning to CO_2 gives rise to $2430 \times 2\frac{1}{3} = 5670$ calories, and the total heat of one gram of carbon burning first to CO and then to CO_2 is $2430 + 5670 = 8100$ calories. If carbon, therefore, is converted into carbon monoxide gas, viz., producer gas, which losing

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[1] For further data consult Richards, Metallurgical Calculations, Part I.

[2] The water as liquid.

[3] The water as vapor.

its sensible heat in passing from the producer to the place of its use, which is usually the case, the loss is $\frac{2430 \times 100}{8100} = 30$ per cent. The efficiency of coal in the form of typical producer gas therefore theoretically cannot exceed 70 per cent. It is also apparent that imperfect combustion of the carbon, viz., to CO instead of CO_2, when burnt on grates, as in reverberatory furnaces or under boilers, will cause heavy losses.

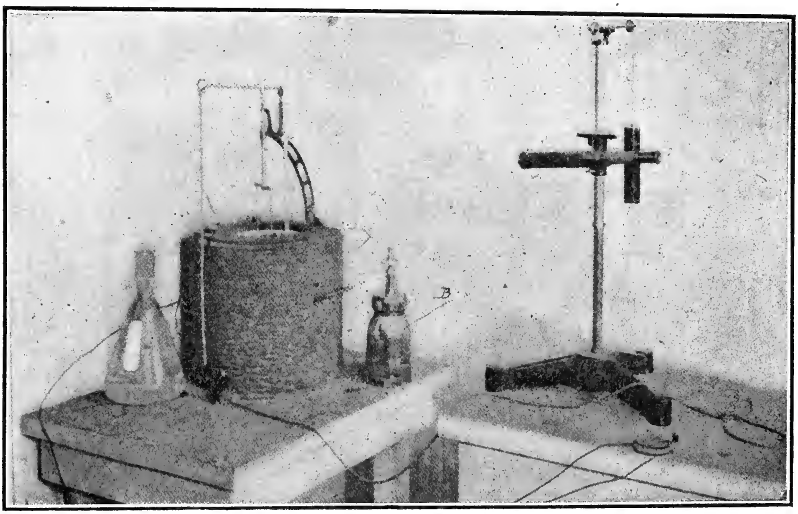

FIG. 114. — Mahler bomb calorimeter. B is the bomb.

METHODS OF DETERMINING THE CALORIFIC POWER OF FUELS. The calorific power of a fuel, viz., coke, coal, or gas, may be determined in two ways: (1) By actual combustion in a calorimeter; (2) by calculation from the ultimate analysis. An approximate determination for solid fuels may be made by fusion with litharge, PbO, the amount of lead reduced indicating the calorific power of the fuel.

I. Method by the Calorimeter. (*A*) **The Mahler Bomb Calorimeter.**[1] — This is an instrument for determining the calorific power, or the heat of formation of substances, and

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[1] Practically all the data on the Mahler Bomb Calorimeter is taken from a paper on this subject, by G. A. Burrell, West. Chem. and Met., IV, 6 (1908).

is shown in Figs. 114 and 115 (cross-section). It consists of the following essential parts:

(1) *The calorimeter jacket, AA.* This is a double-walled, felt-covered (on top and outside) water-jacket filled to the top with water. Its use is necessary in order to minimize heat radiation as much as possible.

(2) *The bomb proper, B.* This is a heavy, cylindrical, nickel steel receptacle about 5 in. high, and 3 in. wide at the bottom. The interior is lined with enamel, and all fittings on the inside are made of platinum. The bomb is provided with a well-threaded screw top, through which the platinum electrodes pass and to which is attached the platinum stay for holding the tray. The bomb is firmly clamped into a lead-lined vise, and by means of a long, heavy wrench the top can be firmly screwed in place. This is necessary both on account of the oxygen pressure inside, and because of the heavy pressure exerted when combustion of the coal takes place. The oxygen tank is supplied with a valve, another valve is placed between the pressure gage and the oxygen tank, and the top of the bomb is provided with an easy working needle valve.

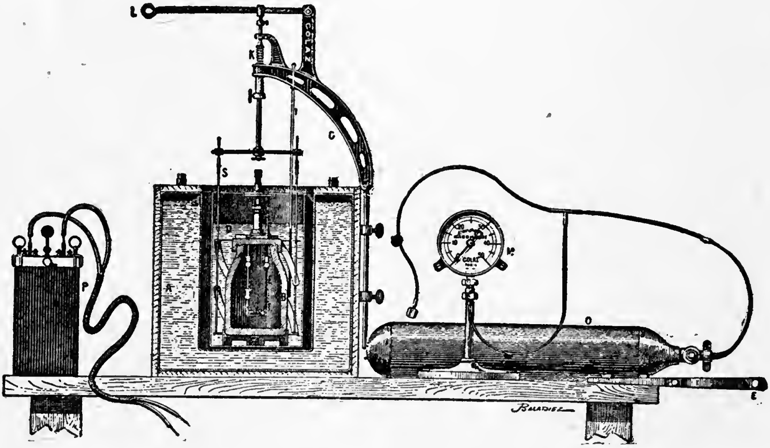

FIG. 115. — Cross-section of bomb calorimeter.

(3) *The support, C, for holding the water stirrer and thermometer.* This support clamps to the outside of the water-

jacket and bends up over the bucket. The water stirrer is semicircular, sets around the bomb, and by means of a spring and drill movement is made to revolve about the bomb and keep the water in constant agitation. The operator works the stirrer continually by means of a cord while the determination is in progress.

(4) *The water bucket, D.* This is a copper bucket with a capacity of about 4 liters of water.

(5) *A manometer, M, or pressure gage, for measuring the pressure of the oxygen used.* A pressure of 18 atmospheres of oxygen is sufficient. Some coals can be burned with as little as 15 or 16 atmospheres, but it is best practice to use 18.

(6) *A tank of oxygen, O.* This must be tested for hydrocarbon impurities by passing 3 or 4 liters through a combustion train over hot cupric oxide, and weighing the absorption bulbs for an increase in weight. (Either CO_2 or H_2O.) The absorption reagents must show no perceptible increase in weight.

(7) *A small press for briquetting the coal.* — This is made by boring a hole about ½ in. in diameter through a solid casting about 3 in. long, 2 in. wide, and 1 in. deep. A pestle is turned to just fit this hole, and an ordinary office screw press completes the apparatus. The coal (60-mesh) is placed in the hole, the pestle inserted and enough pressure applied by means of the screw press to give a briquette of enough cohesion to hold together well, but not one pressed together too tightly. This briquette is broken into small pieces about ⅛ in. in size and weighed into the platinum tray. Better results are obtained in the calorimeter when the coal is thus treated than when left in the loose condition, due to the coal's flying off the tray at times and thus escaping complete combustion. The amount of pressure required for a briquette of the best cohesion depends upon the nature of the coal. Coals high in volatile matter require less pressure than those containing a low percentage.

(8) *The stand for holding a telescope.* This is provided with a counterbalance by means of which the telescope is made to slide up and down, and thus follow the mercury as it fluctuates in the thermometer. The operator sits about 5 feet back from the instrument and reads the thermometer, *T*, through the telescope. Each degree on the thermometer is divided into 50 divisions and with a little practice it may easily be read to 0.001 of 1°.

(9) *A storage battery, P, connected to furnish the current necessary to burn the iron fuse.* Where lighting current is available in the building, however, it is more convenient to connect with that current through a rheostat.

The above items, with several small-necked 3-liter flasks, complete the apparatus. An accurate balance to weigh the coal is also needed.

The principle of the calorimeter is as follows: The coal (about 1 gram) is placed in the platinum tray about $\frac{3}{4}$ in. in diameter. This tray is fastened to a platinum rod attached to the inside of the cover of the metallic bomb. This platinum rod serves as one electrode of the instrument, while the other electrode is another platinum rod also suspended from the inside of the cover. A fine iron wire is then fastened between these electrodes and laid directly across the coal in the tray. The cover is screwed down tight on the bomb, which is then charged with about 18 atmospheres of oxygen and immersed in water. Electrical connections are then made, the thermometer placed in position alongside of the bomb, the water is agitated by means of the stirrer, *S*, for several minutes, and the electric current turned on. The iron wire burns, the coal undergoes complete combustion, thus heating the bomb, which in turn heats the water, whose rise in temperature is measured by the thermometer.

If the calorimeter system is so calibrated that each degree rise in temperature corresponds to 3000 calories, and the thermometer is so graduated as to read to 0.001° C., we have a ready and accurate means of determining the heating value of the coal. Each 0.001° will correspond to 3 calories. A *water equivalent* of 3000 is to be recommended in order to simplify the multiplication. With this instrument it is possible to get calorimetric values checking as closely as 0.2 per cent on the same sample, so that a variation of 0.4 per cent. always requires another determination. Corrections have to be made for radiation, for combustion of the iron fuse, for the formation of nitric acid, and for the formation of sulphuric acid instead of sulphur dioxide. The Mahler bomb calorimeter is one of the best, combining simplicity with accuracy and speed. One determination requires about 35 or 40 minutes. Ten determinations may be made in a day of 8 hours.

Determination of the water equivalent of the apparatus. The thermal capacity of a body of water is numerically equal to its mass in grams, but the case is different with the materials of construction of the calorimeter. These substances, in this case steel, brass, platinum, enamel, etc., have different thermal capacities than water, and the heat given to these parts must be taken into account. The thermal capacity of the calorimeter is expressed in terms of the quantity of water which the number of heat units expressing that capacity would heat one degree. This is called the water equivalent. The gain of heat by the calorimeter and its fittings must be added to that gained by the water.

The water equivalent of the apparatus may be obtained by three methods:

(1) By making a calorific determination in the bomb, on some substance of known heating value, as napthalene, which has a value of 9692 calories.

Supposing that 2500 grams of water were used in the calorimeter bucket, and the heat of the naphthalene raised the temperature of the water 3° C. Since a calorie is the amount of heat required to raise one gram of water 1° C., it would take a substance having a heating value of 7500 calories to raise 2500 grams of water 3° C. That is, the heating value of the naphthalene is 7500 calories. But we have neglected the water equivalent of the apparatus. Knowing the heating value of naphthalene to be 9692 calories, the water equivalent of the apparatus may be readily obtained by dividing 9692 by 3 and subtracting 2500 from the quotient. In this particular case we obtain a water equivalent of 731 calories. Several determinations should be made in this way and the average of the results taken.

(2) Since the thermal capacity of a body is equal to the product of its specific heat and mass, we may determine the water equivalent of the apparatus by multiplying the weight of each part by its specific heat; that is, the weight of the steel, brass, lead, and enamel lining, multiplied by their respective specific heats. This method, however, is only approximately correct, as the weight of the enamel lining can only be estimated, and because all of the parts are not immersed in water.

(3) Determinations of the water equivalent of the apparatus

may also be made by adding definite weights of warm water to definite weights of water in the calorimeter.

The water is measured, not weighed. A large measuring flask has to be calibrated by weighing at a definite temperature. A curve is then drawn on coördinate paper giving, for different temperatures, the number of cubic centimeters of water to be added, in order to make the 2500 grams, or whatever the amount is being used. That is, the temperature of the water used will of course fluctuate from time to time owing to weather conditions; hence one temperature, 15° C., is used and small amounts of water are added for each temperature, in order that the same amount of water may be present in the calorimeter each time a determination is made. In pouring the water from the measuring flask into the calorimeter bucket, the time of draining must always be the same.

Very unsatisfactory results will be obtained in calorimetry work if the greatest care is not taken to guard against too large radiation transfers of heat. That is, the temperatures of the water in the calorimeter bucket, in the calorimeter jacket, and of the air in the room have to be so related to each other that the transfers of heat by radiation from the water in the bucket, and to the water in the bucket, will be as small as possible, and that these negative and positive transfers of heat will very nearly balance each other.

This transfer of heat depends upon several factors over which the operator has control, and which must be closely watched in order to get the best results.

When the water equivalent of the system is such that one degree rise in temperature corresponds to about 3000 calories, and where the character of the coal is known, viz., whether lignite, bituminous, etc., the operator can very nearly tell beforehand about how much the temperature of the water in the bucket is going to rise, and when several calorific determinations are being made on coals from the same locality, one may be run, and serve as a gage for the others. A typical example will illustrate this point.

Assume that we have a bituminous coal which has a heating value of 6900 calories. If the water equivalent of the system is 3000 calories, we will have a rise in temperature of the water in the bucket of about 2.3° C. Say the water in the calorimeter jacket stands at 21° C., and the room temperature is 23° C. Now, if the temperature of the water which is going to be poured into the bucket is given an initial temperature of 19° (managed by putting the flask full of water under the tap, and in hot weather by using a refrigerator), its final temperature will be 21.3° C. During the first part of the determination there will be a small transfer of heat from the water in the jacket to the water in the bucket, a gain or positive change. During the latter part of the operation there will be a small transfer of heat from the water in the bucket to the water in the jacket, a loss or negative change. These transfers in opposite directions will partly neutralize each other and the result will be a radiation gain or loss which has been reduced to a minimum. This adjustment gives a larger rate before the combustion period and a small rate after it.

On the other hand, if the temperature of the water in the bucket is given an initial temperature of say 17° C., the final temperature will be 19.3° C., and there will not only have been a decided gain of heat by the water in the bucket during the first part of the operation, but there will also have been another large gain in the latter part, and the result would have been a large positive change that would go far toward making an unsatisfactory result. By far the largest radiation changes take place between the bucket water and the jacket water, but where the room temperature is 4 or 5 degrees higher than the jacket temperature, it has its influence and should be taken into consideration. The jacket-water temperature can be adjusted within two or three degrees of the room temperature, however, by adding a little warm water when necessary. By working under the first named conditions the greatest rate of change occurs before combustion, and the rate of change in temperature after the combustion period is small. The larger the final rate of change, the greater the possible error. The effects of the large rate, within reasonable limits, before the combustion period is small, while the final rate is carried back and operates through an interval of several minutes; hence the desirability of having the larger rate before the combustion, rather than after it, is evident. Care must be taken to keep the jacket water not too near the dew point, and in damp weather that temperature has to be kept on this account several degrees above the room temperature. Records should be kept of the room temperature, jacket-water temperature, bucket-water temperature, pressure of oxygen in the bomb, and humidity of the atmosphere.

Method of making a determination. Mix the sample of coal in the bottle with a spatula. Make a small briquette of the sample as already described. Break this briquette into small lumps about $\frac{1}{8}$ in. in size. Weigh one gram into the platinum tray. Anthracite coals, cinders, cokes, etc., can only be satisfactorily burned by putting a thin sheet of asbestos on the bottom of the tray, and weighing the coal onto this; the variety called paper asbestos is the best. The heat is in this way not conducted away as rapidly as when the bare platinum is used, and the material will be completely burned. Anthracites, cokes, cinders, etc., of course cannot be briquetted. Fasten this tray to the platinum support (which also serves as one electrode) attached to the inside of the cover of the bomb. Connect the fine iron wire between the two platinum electrodes, and rest it across the coal.

Place the bomb in the lead-lined vise and screw the lid on very firmly. A lead gasket sets into a groove on the top of the bomb, and a projection on the cover sets firmly against this lead, insuring a tight connection. Connect the copper tube leading from the oxygen tank, by way of the pressure gage, to the bomb. Open the bomb valve. Have the valve leading to the pressure gage closed. Open the valve on the oxygen tank. Then very slowly run in 18 atmospheres of oxygen. If the oxygen is run in too fast there is danger of the fine coal being blown off the tray. After the required amount of oxygen has been run in, shut off the manometer valve, bomb valve, and oxygen valve, in the order named. Detach the bomb from the copper tube, adjust the water temperature as previously described, and carefully pour in the exact amount, letting drain about 12 seconds, and place the bucket containing this water inside the calorimeter jacket. Place the bomb in its small steel support and set it in the bucket. The bucket rests on a small wooden triangle and is of such size that a space of about 1 in. is left all around it next the inside of the water jacket. This felt-covered water jacket is about 15 in. high and 12 in. in diameter. Adjust the stirrer. Adjust the thermometer so that it rests about midway between the bomb and side of the bucket, and its bottom about 4 cm. from the bottom of the bucket. Two thermometers are required, each having a range of about 5°. Focus the telescope so that it reads the thermometer very distinctly. The operator then sits down back of the telescope, watch on table, agitates the stirrer, and after two or three minutes' time commences to take minute readings of the thermometer. Minute readings are taken until a regular rate of change is established. That is, the water in the jacket being at a higher temperature than the water in the bucket, a constant slight transfer of heat takes place from the jacket to the bucket. This transfer amounts to about 0.01° C. per minute. This figure may be taken as a typical rate, but it often varies more or less from this.

When the rate of transfer of heat becomes constant, which is almost always the case after six or seven minutes, the electric current is thrown in circuit, the temperature readings having been carefully recorded. The wire fuse burns, the coal then ignites, the bomb becomes warm, and the temperature of the water in the bucket begins to rise. The telescope is moved up the slide, following the mercury, and on the first half-minute after combustion was started another temperature reading is taken. Then another reading on the second half-minute, and after that every minute, until the temperature has attained a maximum, and for seven or eight minutes after that, until the rate of fall of the temperature of the bucket water has attained a regular decrease. The maximum temperature is usually attained at the fourth or fifth reading after the electric current has been turned on, but some slow, hard-burning coals do not reach a maximum until the sixth or seventh reading. During all this time the stirrer must have been worked regularly and constantly. A jerky or irregular movement influences the rate, after the final rate has been established and the temperature has fallen from the maximum, about the same amount each minute. About 0.003° C. may be taken as a typical rate of decrease, although, as stated before, the rates depend upon the heating value of the coal, the water equivalent of the system, and the adjustment of the bucket- and jacket-water temperatures. The apparatus is then disconnected, and the gaseous products of combustion and excess of oxygen let out of the bomb by opening the needle valve. The cover is then taken off and the interior of the bomb examined for unburned coal. Any unburned coal may be seen lying in the solution in the bottom of the bomb.

If not over 0.01 of a gram in weight, this unburned coal may be dried and weighed, and this weight subtracted from the original weight taken, to obtain the true weight. However, this practice cannot be relied upon, for some of the coal will burn and leave a black cinder, consisting of coal and some ash, and there is no way of telling how much has burned.

The solution in the bottom of the bomb is then washed out, and the acids titrated by means of a standard solution of ammonia. The sulphur may then be determined in this solution by acidifying with HCl, filtering from the ash, and precipitating the sulphur with $BaCl_2$.

The ends of the electrodes are examined for traces of unburnt wire, and if present are allowed for. Corrections have to be made for radiation changes, for the combustion of the iron wire, for the formation of aqueous nitric acid, and for the combustion of sulphur to sulphuric acid instead of sulphur dioxide.

Corrections. — The temperature taken for the beginning of the combustion is the reading taken at the time of burning of the wire fuse. For the end of the combustion period the first temperature reading is taken which falls well within the established final rate. The radiation corrections applied to the combustion period are obtained by taking into account the fact that the changes in the rate of gain or loss in temperature are proportional to the changes in temperature. From this proportion the rate of gain or loss at the beginning and end of each interval of time is found. The temperature correction for each interval during the combustion period is obtained by adding the rates at the beginning and end of the interval and dividing the algebraic sum by 2 for the minute intervals and by four for the half-minute intervals. The sum of these corrections added to the difference between the readings at the beginning and end of the combustion period is the true temperature change due to the combustion. This multiplied by the water equivalent of the system gives the total calories of heat produced by the combustion.

A definite length of iron wire corresponding to a weight of 12.1 mgs. is used as a fuse to start the combustion of the sample. Any unburned portion is measured, and the corresponding weight subtracted from the weight of the fuse used. Knowing the heat of formation of Fe_2O_3 per gram of Fe, the correction in calories for the heat produced by the burning of the iron wire can be ascertained.

In making the correction for nitric acid and sulphuric acid, the bomb is thoroughly washed out and these washings titrated with a standard solution of ammonia. This standard solution is made so that one cubic centimeter is equivalent to 0.0025 gram nitrogen as nitric acid. The heat of formation of aqueous nitric acid is 1058 calories per gram of nitrogen, and when the solution is made up as above, each cubic centimeter of ammonia stands for a correction of 2.65 calories.

In the bomb, oxidation is complete, and the sulphur burns to aqueous sulphuric acid, instead of to sulphur dioxide, as is the case in ordinary combustion. Consequently part of the acidity in the bomb washings is due to sulphuric acid, and a further correction is necessary. For each gram of sulphur present in the coal, the heat developed in the bomb is in excess 2230 calories, which is 22.3 for each per cent of sulphur. One c.c. of the standard ammonia solution is equivalent to 0.00286 gram of sulphur as sulphuric acid, or to $0.286 \times 22.3 = 6.38$ calories. After multiplying the number of cubic centimeters of ammonia used in the titration by the heat factor for nitric acid (2.65), it is necessary to make a further correction of $6.38 - 2.65 = 3.73$ for each c.c. used in titrating sulphuric instead of nitric acid.

This is a correction of 3.73 divided by $0.286 = 13$ units for each 0.01 gram of sulphur present in the coal. This correction is accordingly made by multiplying the ammonia by 2.65 and adding 13 units for each 0.01 gram sulphur in the coal.

The accompanying table shows one of the determinations worked out, the method of putting down the data, calculations, etc.:

TABLE LXXX. CALORIMETER DATA

Sample No. 5

Jacket-water temperature = 21°
Wet and dry bulb temp. = 17° and 25°

Tray and coal = 9.4623 g.
Tray = 8.4623 g.
Coal = 1000 g.

Time	*Readings*			
1.45	19.300° C.	5)0.050		
1.46	19.310° C	+ .010 = initial rate.		
1.47	19.320° C.			
1.48	18.330° C.			
1.49	19.340° C.			
1.50	19.350° C.[1]	+ 0.0100	+ 0.0041	
1.50½	20.020° C.	+ 0.0066		
1.51	21.460° C.	− 0.0007	+ 0.0015	
1.52	21.965° C.		− 0.0020	
1.53	21.975° C.[2]			
1.54	21.972° C.	− 0.0033	− 0.0034	
1.55	21.969° C.	− 0.0034		
1.56	21.968° C.		+ 0.0002	
1.57	21.964° C.			+ 0.0100
1.58	21.960° C.			− 0.0034
1.59	21.955° C.			+ 0.0134 = total change in rate.
2.00	21.952° C.			
2.01	21.949° C.			
2.02	21.944° C.			
2.03	21.941° C.	11) 0.037		
2.04	21.938° C.	.0034	= final rate.	

Combustion period = 21.975° − 19.350° = 2.625°
Correction for radiation = + 0.0002°
2.6248°
Water equivalent = 3000
Total calories = 3000 × 2.6248 = 7874.4
Wire fuse and acid corrections = 45.69
Net calories, or true heating value = 7828.21
Corrections made up as follows:
Wire fuse corrections = 15.47 calories.
Nitric acid correction 6.5 c.c. NH_3 sol. × 2.65 cal = 17.22 calories.
Sulphuric acid correction 0.01 g. sulphur = 13.00 calories.
Total .... 45.69 calories.

(*B*) **The Parr Calorimeter.**[3] — This is a simpler instrument than the bomb calorimeter, and for technical work has

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[1] Beginning of combustion.

[2] Maximum temperature.

[3] S. W. Parr, Jour. Am. Chem. Soc., XXII, 646; XXIX, 1606.

the advantage that its use requires no oxygen supply. It is well adapted to determining the heating power of soft coals. Its factor of error is within 0.5 per cent.

Description. Fig. 116 shows the general view of the instrument and Fig. 117 a cross-section, to which the accompanying description applies. *A* is a copper vessel of a little over 2 liters capacity insulated by two outer vessels of indurated fiber, *B* and *C*, so placed as to afford the air spaces *b* and *c* for additional insulation. The cover is double with corresponding air spaces. The cartridge *D* has an inside capacity of 25 c.c. It rests on a pivot below and extends through the covers above, and has a small removable pulley *P* at the end. Turbine wings fastened to spring clips are placed on the cartridge and a short cylinder *E*, open at both ends, is provided for directing the current set up by rotation of the vanes attached to the cartridge. *T* is an accurate thermometer. The stem *G* of the cartridge is so arranged as to permit the passage of a short piece of No. 12 copper wire (Fig. 118). It is also provided with the valve *M* at the lower end which prevents the escape of the enclosed air when heated by the combustion of the charge. The two ends of the cartridge, *E*, *D*, and *F*, screw on.

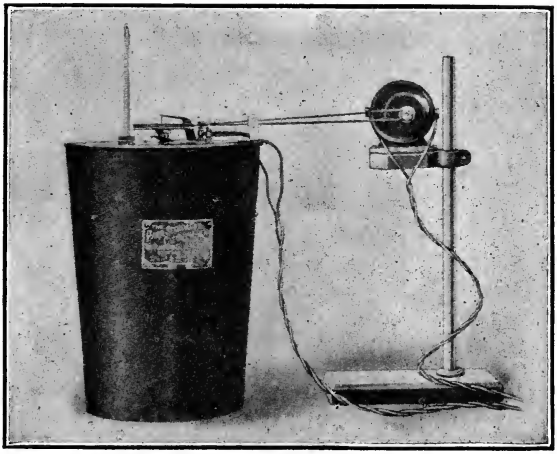

Fig. 116. — The Parr calorimeter.

Operation. One gram of coal, ground to pass a 100-mesh screen, is dried in an air oven at 105° to 110° C. and then roughly mixed with 16 to 18 grams of sodium peroxide which is fine enough to pass a 25-mesh screen. The mixture is placed in the cartridge, the top of which is screwed on, and then shaken thoroughly to mix the contents. After tapping the cartridge to settle the contents to the bottom it is placed in the copper vessel *A* and two liters of water added, the temperature of which is 3° to 4° C. lower than the temperature of the room. The pulley *P* on the cartridge is then connected with a small motor by means of a string, giving 50 to 100 r.p.m. to the cartridge. When the water in the vessel *A* attains a con-

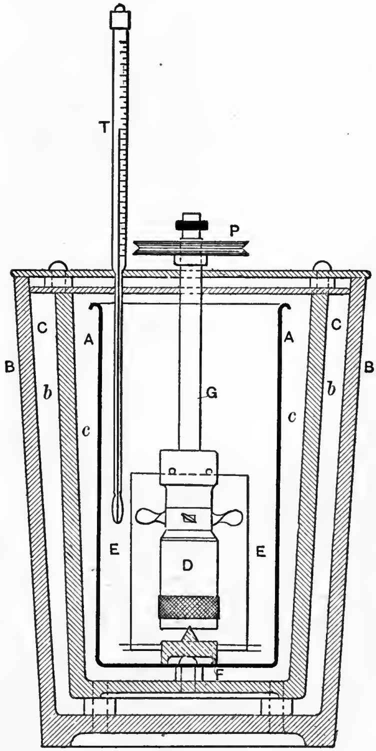

Fig. 117. — Cross-section of the Parr Calorimeter.

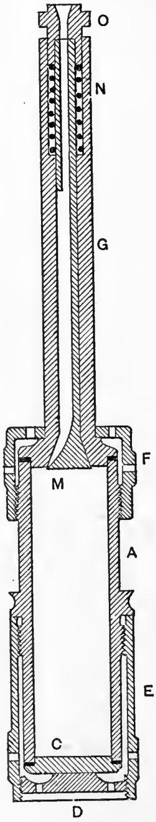

Fig. 118. — Cross-section, cartridge of Parr calorimeter.

stant temperature as determined by the thermometer, this is recorded and a half-inch piece of hot No. 12 copper wire is dropped through the valve into the charge, which is at once ignited and burns completely in two to three seconds. The extraction of the heat is effected in about five minutes. The reading of the maximum temperature is taken and the calculations made as follows:

(1) *Correction factor for the hot wire.* From many determinations this is 0.012° C. = 0.021° F. for $\frac{1}{2}$ in. of No. 12 copper wire. For $\frac{1}{4}$ and $\frac{3}{8}$ in. lengths proportionate figures are used.

(2) *Correction factor for the heat resulting from the combination of the products of combustion,* CO_2 *and* H_2O, *with the sodium peroxide used.* This heat of combination causes an excess over and above the actual heat of combustion, amounting to 27 per cent. of the total indicated heat. This data is the result of many tests on different coals. The calculation for heating power then is as follows: C' = total indicated calories; C = actual calories due to combustion, *i.e.* calorific power of the fuel; t = degrees rise in temperature; w = weight of the water employed in grams.

Then $$C' = (t - 0.012°) \times w,$$

and $$C = C' - \frac{C' \times 27}{100}$$

$$C = (t - 0.012° \times w \times 0.73)$$

The sodium peroxide used must be free from absorbed moisture. In some instances it will be preferable to use 0.5 gram coal in place of 1 gram. For very accurate work the following additional correction factors are applicable:

For sulphur in coal, 0.006° C. for every 1 per cent. in 0.5 g. coal.

For ash in coal, 0.001° C. for every 1 per cent. in 0.5 g. coal.

For combined water in coal, *i.e.* in lignites, 0.0033° C. for every 1 per cent. in 0.5 g. coal.

When potassium chlorate is used in addition to the sodium peroxide to act as an accelerator of combustion a correction of 0.040° C. is applied for every 0.5 g. used. When the ignition in the cartridge is accomplished by an electric fuse, as it may be in one form of the Parr calorimeter, a correction of 0.008° C.

for every 10 mg. of fuse consumed is applied. The sum of these corrections are to be subtracted from t as in the above formulas.

II. Calculation of Calorific Power from the Ultimate Analysis. — This method is due to Dulong, who states that the heat generated by a fuel during combustion is equal to the sum of the possible heats generated by its component elements, less that portion of the hydrogen which will form water with the oxygen of the fuel. His formula is:

$$\text{Calorific power in calories} = 8080\ C + 34500\ (H - \frac{O}{8})$$

The formula is based on the assumption that in a coal the elements C, H, O, S, etc., exist to all intents and purposes uncombined, and on combustion with oxygen form the compounds CO_2, H_2O, etc., liberating the full heat of formation of these compounds. This is in effect true for the carbonaceous fuels, as coal, coke, wood, etc., the calorific power of which can be readily calculated from their ultimate analysis, but it is not true for many compounds. Thus, the calorific power of pyrite (FeS_2) cannot be calculated from its constituents, since the calorific power of a compound is the calorific effect of its constituents in burning to certain products, minus the heat which was required to form the compound from its elemental constituents, *i.e.* its heat of formation, and which is not known for pyrite. When the heats of formation of the compounds are known the calorific power may readily be calculated.

The best form of Dulong's formula for the calculation of calorific powers of fuel is that of the "Verein Deutscher Ingenieure" in which allowance is made for the combustion of sulphur and for the heat absorbed by the water in the coal, and which uses a figure for hydrogen, which takes into account the water generated by the burning of the coal, as escaping in the form of vapor, which is the case under industrial conditions.

Modified Dulong's formula:

$$X = 8100\,C + 29{,}000\ (H - \frac{O}{8}) + 2500\,S - 600\,E$$

X = calorific power in large calories.
C = amount of carbon present in one kg. of coal.
H = amount of hydrogen present in one kg. of coal.
O = amount of oxygen present in one kg. of coal.

S = amount of sulphur present in one kg. of coal.
E = amount of water present as such in one kg. of coal.

For example: what is the calorific power of an air-dried coal of the following ultimate analysis: Ash, 4.79 per cent.; hydrogen, 6.09 per cent.; nitrogen, 1.09 per cent.; carbon, 58.41 per cent.; oxygen, 28.99 per cent.; and sulphur, 0.63 per cent? On combustion this coal gives rise to 0.5484 g. of water vapor, of which 0.2223 g. is formed by the combustion of the available hydrogen ($H - O$) with the oxygen of the air, and 0.3261 g. due to the combined oxygen and hydrogen in the coal; *i.e.*, it is assumed that all oxygen in the coal is combined with hydrogen, the rest of the hydrogen being the *available hydrogen.*

$$X = (8100 \times 0.5841) + 29{,}000 \left\{ 0.0609 - \frac{0.2899}{8} \right\} + (2500 \times 0.0063) - (600 \times 0.3261) = 5267.60 \text{ calories.}$$

This coal yielded 5753 calories by a bomb calorimeter test, in which the water is condensed and the heat in it recovered. The calculation by Dulong's formula in the form of, calorific power $= 8080\,C + 34{,}500\,(H - \frac{O}{8}) + 2250\,S$, are usually within 2 per cent. of the results of the calorimeter test,[1] providing the analysis on which the calculations are based is accurate.

III. **Berthier's Method of Determining Calorific Power.** — This is based on the amount of lead reduced by the coal from litharge (PbO). The reduction is according to the following reaction:

$$\overset{446}{2PbO} + \overset{12}{C} = \overset{414}{2Pb} + CO_2$$

One gram of carbon reduces $\frac{414}{12} = 34.5$ grams of lead. Since the calorific power of carbon is 8080 calories, one gram of lead reduced represents $\frac{8080}{34.5} = 234$ calories. This factor will serve well for anthracite coals, but it is too low for bituminous coals on account of the hydrogen contained in them, which has a much greater reducing power than carbon. By experi-

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[1] N. W. Lord and F. Haas, T. A. I. M. E., XXVII, 259 (1897).

ment[1] the proper factor for bituminous coals is 268.3 calories for every gram of lead reduced per gram of coal.

The method is carried out as follows: One gram of fine dry coal is mixed with 40 grams litharge (PbO) free from PbO_2, placed in a 20-gram crucible, or one equivalent in size. The mixture is covered with 15 grams of litharge and the crucible covered with its clay cover and placed in a muffle furnace at a bright red heat. The fusion should be complete in 10 to 15 minutes or there is danger of the litharge eating through the crucible. The muffle used should have a good draft through it, so that there is no danger of lead being reduced by the presence of reducing gases from the fire. Just as soon as the fusion is quiet, the crucible is taken from the furnace, tapped, and its contents poured into an iron mold. When cold the button is separated from the excess litharge, by hammering, and then weighed. The weight multiplied by the proper factor gives the calorific power in calories. The method serves well as a rapid approximate determination of the calorific power and is usually within 2 to 5 per cent. of the calorimeter determination.

Temperature of Combustion. — The temperature of combustion, termed also the *pyrometric effect,* is the temperature attained by the flame from the combustion of a fuel under constant pressure. If we consider a unit mass of fuel in contact with the required amount of air for complete combustion in a space insulated against radiation, and burn the same under constant pressure, the calories of heat liberated by the combustion will be absorbed by the products of combustion and raise these to a certain temperature. This temperature is the temperature of combustion and can readily be calculated.

Let C = the calorific power of the fuel in calories.
C_1 = the latent heat absorbed at $t°$ by the products of combustion, *e.g.* water in passing from the liquid to the vapor state.
M = the mass of the products of combustion, made up of the individual masses, P_1, P_2, P_3, P_4, etc., of the gases and ash present.
Sm = the mean specific heat of the products of combustion,

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[1] W. A. Noyes, McTaggert, and Craver, Jour. Am. Chem. Soc., XVII, 843 (1895).

made up of the mean specific heats of the various products of combustion, Sm_1, Sm_2, Sm_3, Sm_4.

T = the final temperature of the products of combustion, viz., the *temperature of combustion*, above $t°$.

Then it follows from the above that

$$C_2 = (C - C_1) = MTSm, \text{ or}$$

$$C_2 = (C - C_1) = T\ (P_1Sm_1 + P_2Sm_2 + P_3Sm_3 + P_4\,Sm_4, \text{etc.})$$

$$\text{and } T = \frac{C - C_1}{P_1Sm_1 + P_2Sm_2 + P_3Sm_3 + P_4Sm_4, \text{ etc.}}$$

which is the formula for the calculation of the temperature of combustion.

The temperature of combustion hence is the theoretical temperature attainable by the flame on the assumption of the complete combustion of the fuel to such products as form. The formula is general in its nature and is applicable to all combustion reactions, with either oxygen or air, in the exact amount required or in excess, if the correct masses and specific heats are used. At the present time there is much data available on the specific heat of gases at high temperatures, which was formerly lacking. The older calculations of combustion temperatures were invariably much too high, due to the use of incorrect values of specific heats. Table LXXXI gives the values of the specific heats of gases commonly in use.

Calculation of the temperature of combustion of a coal. The composition of the coal is as follows: Ash, 4.79 per cent.; hydrogen, 6.09 per cent.; nitrogen, 1.09 per cent.; carbon, 58.41 per cent.; oxygen, 28.99 per cent.; and sulphur, 0.63 per cent.

(*a*) The available hydrogen in one gram of coal is $0.0609 - \frac{0.2899}{8} = 0.0247$ grams.

(*b*) The amount of water is, $0.2899 + 0.0362 = 0.3261$ g.; *i.e.* the amount of oxygen plus its combining weight of hydrogen.

(*c*) The amount of water formed by the burning of the available hydrogen is, $0.0247 + 8\ (0.0247) = 0.2223$ g.

Air consists of 3 parts oxygen and 10 parts nitrogen by weight, or 23.1 and 76.9 per cent. respectively; and 21 parts oxygen and 80 parts nitrogen by volume, or 20.8 and 79.2 per cent. respectively. The carbon burns to CO_2 according to the following reaction:

TABLE LXXXI. SPECIFIC HEAT OF GASES[1]

Gas	Specific Heat S at 0° C.		Specific Heat, S_t at t° C.		Mean Specific Heat, Sm between 0° and t° C.	
	Per Kg.	Per Cu. M.	Per Kg.	Per Cu. M.	Per Kg.	Per Cu. M.
[2] Nitrogen	0.235	—	$0.235 + 0.000038\,t^\circ$	—	$0.235 + 0.000019\,t^\circ$	—
[3] Nitrogen	0.2405	0.303	$0.2405 + 0.0000428\,t^\circ$	$0.303 + 0.000054\,t^\circ$	$0.2405 + 0.0000214\,t^\circ$	$0.303 + 0.000027\,t^\circ$
[3] Oxygen	0.2104	0.303	$0.2104 + 0.0000374\,t^\circ$	$0.303 + 0.000054\,t^\circ$	$0.2104 + 0.0000187\,t^\circ$	$0.303 + 0.000027\,t^\circ$
[3] Carbon monoxide	0.2405	0.303	$0.2405 + 0.0000428\,t^\circ$	$0.303 + 0.000054\,t^\circ$	$0.2405 + 0.0000214\,t^\circ$	$0.303 + 0.000027\,t^\circ$
[3] Carbon dioxide	0.19	0.370	$0.19 + 0.00022\,t^\circ$	$0.37 + 0.00044\,t^\circ$	$0.19 + 0.00011\,t^\circ$	$0.37 + 0.00022\,t^\circ$
[3] Hydrogen	3.70	0.303	$3.70 + 0.0006\,t^\circ$	$0.303 + 0.000054\,t^\circ$	$3.70 + 0.003\,t^\circ$	$0.303 + 0.000027\,t^\circ$
[3] Water vapor	0.42	0.340	$0.42 + 0.00037\,t^\circ$	$0.34 + 0.00030\,t^\circ$	$0.42 + 0.000185\,t^\circ$	$0.34 + 0.00015\,t^\circ$
[3] Sulphur dioxide	0.125	0.360	$0.125 + 0.0002\,t^\circ$	$0.36 + 0.0006\,t^\circ$	$0.125 + 0.00010\,t^\circ$	$0.36 + 0.0003\,t^\circ$
[4] Sulphur dioxide	0.1450	0.4164	$0.1450 + 0.00020\,t^\circ$	—	$0.1450 + 0.00019\,t^\circ$	—
[4] Methane	0.5930	0.4256	$0.593 + 0.000148\,t^\circ$	—	$0.593 + 0.0000741\,t^\circ$	—

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[1] The data holds up to temperature of 2000° C.

[2] Holborn and Henning, Metallurgie, V, 240 (1908).

[3] Chiefly the data of Mallard and Le Chatelier, taken from J. W. Richards, Metallurgical Calculations, Part I.

[4] J. v. Ehrenwerth, Metallurgie, VI, 306 (1909).

$$\begin{array}{ccc} C + O_2 & = & CO_2 \\ 12 \quad 32 & & 44 \end{array}$$

One part carbon requires $2\frac{2}{3}$ parts oxygen to produce $3\frac{2}{3}$ parts of CO_2. This amount of oxygen carries with it as an inert gas, $2\frac{2}{3} \times 3\frac{1}{3} = 8\frac{8}{9}$ g. nitrogen. Therefore, 1 part of carbon required $11\frac{5}{9}$ g. of air ($2\frac{2}{3}$ g. O_2 + $8\frac{8}{9}$ g. N_2).

(*d*) 0.5841 g. carbon in the coal produce, $0.5841 \times 3\frac{2}{3} = 2.1417$ g. CO_2. The total products of combustion therefore are:

Nitrogen = $P_1 = 0.5841 \times 8\frac{8}{9} = 5.192$ g. To this must be added the 0.0109 g. in the coal and the 0.6586 g. accompanying the O_2 required to burn the available hydrogen, making a total of 5.8615 g.

Carbon dioxide = P_2 = 2.1417 g.
Water = P_3 = 0.3261 g. + 0.2223 g. = 0.5484 g.
Ash = P_4 = 0.0479 g.

The calorific power of this coal as calculated from Dulong's formula (modified to take into account the latent heat of water and its escape as steam) is 5267.60 calories. In the calculation which follows the small amount of sulphur in this coal is neglected.

In the equation,

$$T = \frac{C - C_1}{P_1Sm_1 + P_2Sm_2 + P_3Sm_3 + P_4Sm_4}$$

$C - C_1 = 5267.60$ (since the latent heat of water has already been deducted); $P_1 = N_2 = 5.8615$ g.; $P_2 = CO_2 = 2.1417$ g.; $P_3 = H_2O = 0.5484$ g.; P_4 = ash = 0.0479 g.

The specific heats are as follows:

for nitrogen, $Sm_1^{(0^\circ - T^\circ)} = 0.235 + 0.000019\ T^\circ$;
for carbon dioxide, $Sm_2^{(0^\circ - T^\circ)} = 0.190 + 0.00011\ T^\circ$;
for water vapor, $Sm_3^{(100^\circ - T^\circ)} = 0.42 + 0.000185\ (100 + T^\circ)$;
for ash, $\mathrm{Sm}_4^{(0^\circ - T^\circ)} = 0.27$;

Therefore,

$$T = \frac{5267.60}{5.8615\ (0.235 + 0.000019T) + 2.1417\ (0.19 + 0.00011T) + 0.5484\ (0.42 + 0.000185\ \{100 + T\}) + (0.0479 \times 0.027)}$$

or, $$0.004484095\ T^2 + 20.377819\ T - 52676 = 0$$
$$T = 1840^\circ\ C.$$

The graphical method. Another method is available, the graphical method, by means of the thermal capacities of the gases of combustion.[1]

The thermal capacity of a gas is the number of calories absorbed by a unit weight or volume of a gas in passing from any temperature T to any other temperature T_1, at constant pressure. In the same manner the calories of heat set free in cooling from T_1 to T is the thermal capacity. Mallard and LeChatelier express the thermal capacity of gases in absolute temperature by the following equation:

$$Q = \text{thermal capacity in cal.} = a\frac{T}{1000} + b\frac{T^2}{1000^2}$$

in which a is a constant = 6.5, common to all gases, and b is a constant, variable for different gases. Its values are for O_2, N_2, H_2, CO, 0.6; for H_2O, 2.9; for CO_2, 3.7; for CH_4, 6.0.

The specific heat of a gas at any temperature is obtained by taking the first derivative of the formula for the thermal capacity of the gas at that temperature, but when thermal capacities are available, specific heats are not required for the calculations to follow.

The equation for the temperature of combustion, on the basis already outlined, that the heat liberated during combustion is to be found in the products of combustion, viz., is equal to the thermal capacity of the products of combustion, is as follows:

$$\Sigma L = \Sigma a \ (T - T_0) + \Sigma b \ (T^2 - T_0^2)$$

from which T can be calculated. The value for T, however, may be found graphically in a much shorter time. Fig. 119 shows the plotting of the equation. It is required to find the intersection of the line ΣL with the curve, the temperature indicated by the intersection being the temperature of combustion. In the figure the ordinates *bk, cl, dm, en,* indicate the sum of the thermal capacities of the products of combustion at the corresponding indicated temperatures. Tables LXXXII and LXXXIII give the thermal capacities of the various gases at temperatures up to 2000° C. per molecular volume and per kg. which are used in the calculations.

As an example, calculate the temperature of combustion of the same coal when burnt with the proper amount of cold

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[1] E. Damour and A. L. Queneau, Industrial Furnaces, 1906, p. 10, etc.

air, and also with the same amount of air preheated to 400° C. The composition of the coal is, ash, 4.79 per cent.; hydrogen, 6.09 per cent.; nitrogen, 1.09 per cent.; carbon, 58.41 per cent.; oxygen, 28.99 per cent.; and sulphur, 0.63 per cent. The calorific power of this coal = ΣL = 5267.60 calories, with the water in the form of vapor at 100° C. The products of combustion are:

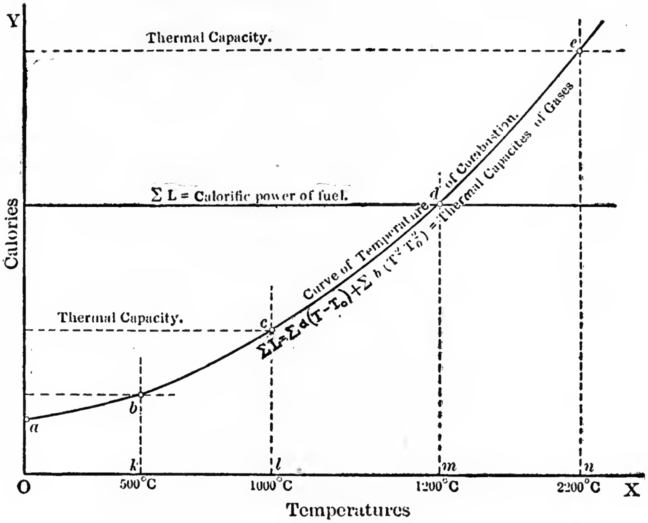

FIG. 119. — Graphic method for the determination of the temperature of combustion.

CO_2 = 2.1417 g.
H_2O = 0.3261 + 0.2223 = 0.5484 g.
N_2 = 5.8615 g., made up as follows: from combustion of carbon, 5.19 g.; from combustion of hydrogen, 0.6586 g.; and from the coal, 0.0109 g.

The thermal capacities of these gases are:

	For 600° C.	For 1000° C.	For 2000° C.
CO^2	2.1417×145 = 310.30	2.1417×277 = 592.78	2.1417× 728 = 1557.92
H^2O	0.5484×326 = 178.78	0.5484×609 = 333.97	0.5484×1542 = 798.60
N^2	5.8615×154 = 902.44	5.8615×264 = 1547.04	5.8615× 575 = 3369.50
Totals ..	1391.52	2473.79	5726.02

TABLE LXXXII. THERMAL CAPACITIES OF GASES PER MOLECULAR VOLUME

Temperatures	O_2, N_2, H_2, CO	H_2O	CO_2	CH_4	$=0.002t$
0° C.	0	0	0	0	0
200° C.	1.39	1.73	1.85	2.19	0.4
400° C.	2.82	3.69	3.99	4.85	0.8
600° C.	4.31	5.87	6.44	8.02	1.2
800° C.	5.82	8.23	9.18	11.46	1.6
1000° C.	7.43	10.98	12.22	15.77	2.0
1200° C.	9.05	13.87	15.55	20.37	2.4
1400° C.	10.73	17.00	19.18	25.44	2.8
1600° C.	12.46	20.35	23.10	30.99	3.2
1800° C.	14.21	23.86	27.21	36.86	3.6
2000° C.	16.05	27.76	31.84	43.55	4.0
2200° C.	17.91	31.82	36.65	50.54	4.4
2400° C.	19.84	36.10	41.76	58.02	4.8
2600° C.	21.81	40.62	47.16	66.04	5.2
2800° C.	23.82	45.64	52.84	74.42	5.6
3000° C.	25.89	50.64	58.86	83.34	6.0

TABLE LXXXIII. THERMAL CAPACITIES OF GASES PER KILOGRAM

Temperatures	O_2	N_2, CO	H_2	H_2O	CO_2	CH_4	$=.09t$
0° C.	0	0	0	0	0	0	0
200° C.	47.3	50	700	100	43.1	136.6	18
400° C.	88.0	100	1400	203	91.0	303.0	36
600° C.	134.0	154	2150	326	145.0	499.0	54
800° C.	181.0	207	2900	461	208.0	726.0	72
1000° C.	232.0	264	3700	609	277.0	982.0	90
1200° C.	284.0	325	4550	770	354.0	1269.0	108
1400° C.	334.0	383	5350	943	435.0	1584.0	126
1600° C.	391.0	445	6250	1130	523.0	1931.0	144
1800° C.	444.0	508	7100	1330	618.0	2307.0	162
2000° C.	503.0	575	8050	1542	728.0	2712.0	180
2200° C.	558.0	637	8950	1751	840.0	3148.0	198
2400° C.	620.0	708	9900	1985	950.0	3614.0	216
2600° C.	681.0	777	10,900	2241	1070.0	4109.0	234
2800° C.	735.0	850	11,900	2520	1200.0	4635.0	252
3000° C.	810.0	921	12,950	2799	1355.0	5190.0	270

In Fig. 120 is plotted this data, which gives rise to the curve *bcde*. This curve is intersected at the point *d* by $\Sigma L = 5267.60$ calories, the calorific power of the coal, and projecting the point *d* to the basal line it corresponds to a temperature of 1866° C., the temperature of combustion. Considering the fact that the graphic method is necessarily approximate to a certain degree, this is a good agreement with the calculated result.

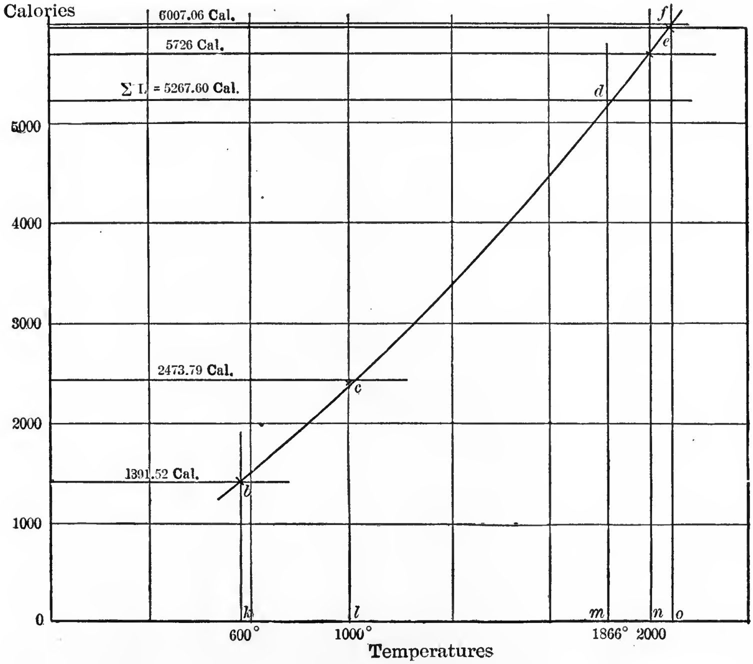

Fig. 120. — Graphic method showing the data for the determination of the temperature of combustion of a coal.

In calculating the temperature of combustion of this same coal with the air preheated to 400° C., the method of procedure is similar. The effect of preheating the air will be to add to the calorific power of the coal the calories in the preheated air used, *i.e.* its thermal capacity at 400° C. The amount of air used to burn one gram of coal as already determined is, 7.6058 g. made up of 5.8506 g. N_2 and 1.7552 g. O_2, and the thermal capacity of this at 400° C. is

$$\begin{array}{rcl}
5.8506 \times 100 & = & 585.00 \text{ calories.} \\
1.7552 \times 88 & = & \underline{154.46} \text{ calories.} \\
 & & 739.46 \text{ calories.}
\end{array}$$

Adding this to the calorific power of the coal, we get 5267.60 + 729.46 = 6007.06 calories = $\Sigma L'$. If this is plotted as shown in Fig. 120, $\Sigma L'$ intersects the curve in the point *f*, which projected to the basal line indicates a temperature of combustion of 2070° C.

Preheating the air or fuel is practised extensively in burning gas in regenerative furnaces, and the example indicates the method of calculation for obtaining the temperature of combustion. When both gas and air are preheated, the calories in both, at the temperature of preheating, are added to the calorific power of the fuel to get the term ΣL.

Table LXXXII gives the thermal capacities of the gases in molecular volumes, which is in convenient form for the calculations, when combustible gases are dealt with. The method of solving by the graphic method is then the same as when the calculation is made for weights. In a gaseous body the molecular weight in kilograms corresponds to a volume, alike for all gases of 22.22 cu. meters. This is called the kilogram molecular volume. By a coincidence,[1] if the molecular weight be expressed in ounces, each molecule of gas, or molecular volume, is 22.22 cu. ft.

Table LXXXIV gives data on the combustible gases and carbon, such as weight per cu. m., calorific power per molecular volume, etc.

Dissociation of the Gaseous Products of Combustion.—It was formerly assumed that the dissociation of carbon dioxide into carbon and oxygen, and of water vapor into hydrogen and oxygen, at temperatures of 1200° to 2500° C., was very appreciable, and that on this account the complete combustion of carbon and hydrogen was practically impossible, thus limiting the attainable temperature of combustion. With only the old data on specific heats available, the calculated temperature of combustion was invariably double and triple that attainable in practice and the discrepancy was explained on the basis of dissociation of the gases of combustion. It is now known

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[1] J. W. Richards, Metallurgical Calculations, Part I, 4.

that the error was due to the use of incorrect values for the specific heats and the thermal capacities of the gases of combustion, and that the dissociation of CO_2 and H_2O for temperatures not exceeding 2500° C. is very small. Thus the dissociation of CO_2 at 1500° C. is only 0.08 per cent., and at 2000° C. 4 per cent. Fig. 121 shows the dissociation curves[1] of carbon dioxide and water vapor, the latter resembling the former very much. The dissociation of carbon monoxide is of a different nature and is discussed under the section on gas producers.

TABLE LXXXIV. DATA ON COMBUSTIBLE GASES

Substance	Reaction of Combustion gram. mol. vol.	Large Calories Liberated per g. mol. vol. 22.22 liters	Density referred to Hydrogen	Weight of 1 c. m. of gas
Hydrogen	$H_2 + \frac{1}{2}O_2 = H_2O$	69.0[2]	1	0.09 kg.
Hydrogen	$H_2 + \frac{1}{2}O_2 = H_2O$	58.2	—	—
Carbon Monoxide ..	$CO + \frac{1}{2}O_2 = CO_2$	68.2	14	1.26
Methane	$CH_4 + 2O_2 = CO_2 + 2H_2O$	213.5[2]	8	0.72
Methane	$CH_4 + 2O_2 = CO_2 + 2H_2O$	195.2	—	—
Carbon	$\frac{1}{2}C_2 + O_2 = CO_2$	97.6	—	—
Carbon	$\frac{1}{2}C_2 + \frac{1}{2}O_2 = CO$	29.4	—	—
Water vapor	—	—	9	0.81
Nitrogen	—	—	14	1.26
Oxygen	—	—	16	1.44
Carbon dioxide	—	—	22	1.98

Amount of Air Required for Combustion. — The highest temperatures in burning a fuel are obtainable when the theoretic amount of air is used. This condition is, however, not realizable in practice, and usually an excess of air is needed to attain approximately a complete combustion of the fuel. In ordinary direct firing of coal on grates in boiler practice, the amount of air burnt per pound of carbon varies from 16 to 40.7 lbs.,[3] while the theoretic amount is 11.52 lbs. The excess of air used depends upon the fire-box construction, type of grate, the draft, and the thickness of the fuel bed; or if forced fan draft is used. It is probably always 50 to 100 per cent. in direct firing, as otherwise incomplete combustion takes place and an excessive amount

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[1] Nernst und von Wartenberg, Zeit. für Phys. Chemie., 56, No. 5 (1906).

[2] J. W. Richards, Metallurgical Calculations, Part I, 4.

[3] Donkin and Kennedy, in W. R. Ingalls, Metallurgy of Zinc, 264 (1903).

of carbon monoxide is produced, aside from an appreciable percentage of unburnt fuel. In burning gas the percentage of excess air is much less on account of the greater ease with which the air and gas can be intimately mixed. The excess of air decreases with the temperature of preheating of the air and gas. Thus, with gas at 600° C. and air at 50° C. from 20 to 100 per cent of excess air is required for complete combustion, but with air and gas preheated to 1000° C. only 5 per cent. of excess air is required.[1]

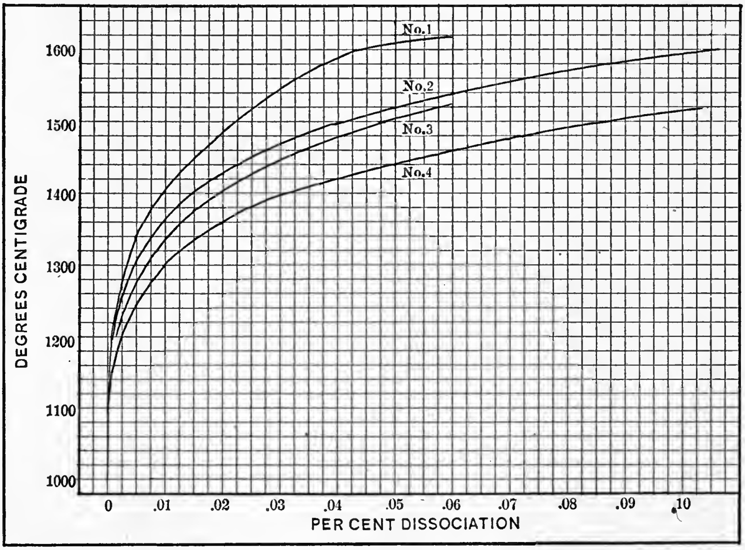

FIG. 121. — Dissociation curves of water vapor and carbon dioxide: Curve No. 1, H_2O at atmospheric pressure; No. 2, CO_2 at atmospheric pressure; No 3, H_2O at 0.1 atmospheric pressure; No. 4, CO_2 at 0.1 atmospheric pressure.

The following data gives the calculated temperatures of combustion of Kansas natural gas with different quantities of air:[2]

	Cold air	Air preheated to 500°C.	Air preheated to 1000°C.
Theoretic amount of air	1885° C.	2135° C.	2400° C.
25 per cent. excess of air	1640° C.	1930° C.	2220° C.
5 per cent. of unburnt gas	1875° C.	2130° C.	2385° C.

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[1] H. H. Campbell, T. A. I. M. E., XIX, 151 (1890).

[2] Queneau, Industrial Furnaces, 28 (1906).

The conclusions to be drawn as to the effect of excess or deficiency of air in combustion are evident from the data.

Table LXXXV gives the theoretic amount of air required for the combustion of various fuels.

Table LXXXV. Theoretic Amount of Air Required for Combustion

Fuel	Products of Combustion	Wt. or volume	Amount of Air			Products of Combustion. Amt.				
			O_2	N_2	Air	CO	CO_2	H_2O	N_2	Total
Carbon....	CO	Kg.	1.33	4.46	5.79	2.33	—	—	4.46	6.79
"	CO	Lb.	1.33	4.46	5.79	2.33	—	—	4.46	6.79
"	CO	Cu.m.	0.93	3.55	4.48	1.86	—	—	3.55	5.41
"	CO_2	Kg.	2.67	8.93	11.6	—	3.67	—	8.93	12.60
"	CO_2	Cu.m.	1.87	7.15	9.02	—	1.87	—	7.12	8.90
Hydrogen .	H_2O	Kg.	8.00	26.72	34.72	—	—	9.00	26.72	35.72
" .	H_2O	Cu.m.	5.59	21.29	26.88	—	—	11.19	21.29	32.48
Methane ..	$CO_2 + H_2O$	Kg.	4.00	13.36	17.36	—	2.75	2.25	13.36	18.36
"	$CO_2 + H_2O$	Cu.m.	2.80	10.64	13.44	—	1.40	2.79	10.65	14.84

Flame. — When fuel ignites and burns with air it gives rise to a highly heated mass of the products of combustion, which, if they contain small particles of incandescent solid matter, usually carbon, so as to be visible, is termed "flame." When a fuel burns completely to carbon dioxide and water vapor, these products of combustion, although highly heated, are not visible, and hence there is no flame. When CO is formed, which later burns to CO_2, its combustion gives rise to a blue, faintly luminous flame. Flame is also the combustible gas arising from fuel in the process of combustion with air. Thus, when a bituminous coal is burnt in a deep bed, part of the coal passes into combustible hydrocarbon gases and CO, which, passing into the hot furnace chamber, meet air, with which they burn as flame, some of the hydrocarbons being dissociated with the liberation of finely divided solid carbon. The length of flame is largely dependent upon the amount of the combustible gases thus liberated, which mixing with air burn through a certain distance. If enough air is admitted immediately for complete combustion the length of flame may be short, but if the air be admitted at different points along the path of the flame, or the thorough mixing of air and gas requires some time, the flame will be long. In burning gaseous fuel in a furnace the air and gas mix at the air and gas ports entering the furnace and burn over considerable distance as flame. When heating by means of flame, as in reverberatory furnaces, it is essential to give the flame ample space for its free development. It should not be deflected or come in contact with the roof or walls of furnaces. A much higher heating effect is thus obtained. The hot products of combustion which are non-luminous, *i.e.* which are not flame, can heat by contact only, and but very little by radiation. On the other hand, the luminous flame heats by radiation and is thus much more efficient in the furnace. For these reasons coals such as anthracite or coke are not suitable for firing reverberatory furnaces since they produce a nearly non-luminous flame. As already stated, the luminosity of the flame is due to the particles of incandescent solid carbon present which are derived from the dissociation of hydrocarbon gases.[1]

TABLE LXXXVI.[2] IGNITION TEMPERATURE OF GAS MIXTURES

T_2 = absolute	Mixture	T_2 = absolute	Mixture
878° C.	$4H_2 + O_2$	914° C.	$H_2 + 2O_2 + 4N_2$
813° C.	$2H_2 + O_2$	910° C.	$H_2 + O_2 + 4N_2$
844° C.	$H_2 + 4O_2$	958° C.	$2CO + O_2 + 2N_2$
994° C.	$6CO + O_2$	940° C.	$4CO + O_2 + 2N_2$
874° C.	$2CO + O_2$	877° C.	$2H_2 + O_2 + 2CO$
904° C.	$CO + O_2$	825° C.	$2H_2 + 3O_2 + 2CO$
922° C.	$2H_2 + O_2 + 4N_2$	—	—

Ignition Temperature of Fuels. — Before combustion begins, it is necessary to heat the fuel to a temperature called the *ignition temperature.* Thus, pine wood will ignite at 295° C.; average bituminous coal at about 325° C.; while coke and anthracite require about 500 to 600° C. Combustible gases must also be preheated to a certain temperature before they will ignite. The accompanying table gives the ignition temperatures of a number of gas mixtures.

Chimney and Grate Design for Furnaces. —The chimney

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[1] Friedrich Siemens, by G. W. Goetz, T. A. I. M. E., XXII, 682 (1893).

[2] Geo. K. Falk, Jour. Am. Chem. Soc., XXIX, 1536.

of a furnace is an essential part for creating a draft which will give the necessary amount of air to burn the required amount of coal on the grate of the furnace. The draught produced by a chimney is a function of three factors:

(1) The difference in temperature between the hot products of combustion entering the chimney and the temperature of the outside air.

(2) The height of the chimney.

(3) The acceleration due to gravity.

The quantity of gas discharged by a chimney may be represented by the equation

$$Q = A\ V$$

in which Q = cubic feet discharged per second.
A = the area of the top of the chimney in square feet.
V = the velocity in feet per second.

This last may be calculated from the formula

$$V = 8\sqrt{h\left(1 - \frac{t'}{t''}\right)}$$

in which h is the height of the chimney in feet, t' = the absolute temperature of the outside air, t'' = the absolute temperature of the hot products of combustion.

The velocity of the gases, therefore, varies as the square root of the height of the chimney. Therefore, if the velocity is to be doubled, the height must be increased four times. Since the friction increases very rapidly with the height, in effect it would be necessary to increase the height of the chimney by much more than four times in order to double the velocity, *i.e.*, the draft. It follows from this that very high chimneys are useless and they are rarely made more than 150 ft. high. In general, a chimney for metallurgical furnaces should not be less than 35 ft. high. Ordinary chimneys are most frequently 60 to 70 ft. high, unless it is necessary to disperse the products of combustion into a higher stratum of the atmosphere for hygienic or economic reasons. The actual velocity of gases in a chimney is about 0.33 of the theoretical velocity. In practice, the velocity of gases rising through a chimney is generally from 10 to 23 ft. per second, though it may attain 33 ft. to 40 ft. per second when the products of combustion enter the chimney at an unusually high temperature.

In order to obtain as much of the calorific power of the coal as possible it is of course essential that the products of combustion should give up their contained heat to the furnace charge as completely as possible and enter the chimney at only such a temperature as is necessary with the height of the chimney to obtain the necessary draft. In this connection it may also be pointed out that since the density of the escaping gases decreases quite rapidly for an increasing temperature a point is soon reached where the mass of the products of combustion discharged by the chimney cannot be increased by a further rise in temperature of the gases entering the chimney at the bottom. By calculation it may be determined that the maximum capacity of the chimney is reached when the difference in temperature between the gases entering the same and the outside air is 273° C. As already stated, the quantity of gas discharged by a chimney, other factors being equal, varies directly as the cross-sectional area. The amount of gas depends of course on the amount of coal burned in a unit of time. One square foot of chimney area should be supplied for every 75 to 125 lbs. of coal burnt per hour on the grates. Sometimes this ratio is as low as one square foot for 50 lbs. The amount of grate area required to burn coal is as follows: For rapid combustion, which is employed when high temperatures are desired, there should be one square foot of grate area for every 30 to 60 lbs. of coal. This applies to copper-smelting furnaces; for roasting sulphide ores, 1 square foot of grate for every 8 to 15 lbs. of coal; for boilers, 1 sq. ft. of grate for from 10 to 20 lbs. of coal. When the coal has coking properties, less coal can be burnt per one square foot of grate area than when it is non-coking. These data establish the ratio between grate area and chimney area. Thus, if 1 sq. ft. of chimney area will discharge the products of combustion from 125 lbs. of coal per hour, and this is burnt on a grate whose area is 5 sq. ft., equivalent to 25 lbs. of coal per square foot of grate area, the ratio of grate area to chimney area is 5 to 1. Generally stated, for metallurgical furnaces, the ratio of grate area to chimney area varies between 5 : 1 and 2 : 1; for steam boilers, where combustion is necessarily slower, the ratio varies between 8 : 1 and 6 : 1. The area of the flue leading from the hearth of the furnace to the chimney is usually somewhat smaller than the chimney area, as the gases leaving the hearth have a high temperature and hence a high velocity. The relation between the grate area and the area of the hearth of the reverberatory furnace is dependent upon the temperature which it is desired to obtain in the hearth. If this be high, the ratio of hearth to grate should be small; if low, it can be larger. The large reverberatory copper-smelting furnaces at the Anaconda smelter in Montana have a hearth area of 2200 sq. ft. and a grate area of 112 sq. ft., making a ratio of hearth to grate of 19.6 : 1. The ratio of flue to grate area is 1 : 7, which is low, but is due to the high temperature of the discharging gases and other factors of construction. The amount of coal burnt per square foot of grate surface per hour is from 40 to 45 lbs.[1] In older and smaller Montana reverberatory furnaces the ratio of hearth to grate area varied from 15.5 and 16.5 : 1. The ratio of flue to grate is 1 to 5.4. The ratio of chimney to grate area is 1 to 3.2. The amount of coal burnt per square foot of grate surface per hour is from 35 to 60 lbs.[2]

Mechanical Draft[3] and Mechanical Stokers. — In place of high chimneys in boiler practice mechanical draft may be installed. This is done by placing large exhaust fans between the furnace and a low chimney, drawing the products of combustion through what is called an economizer, an apparatus consisting of a large number of pipes through which the boiler feed-water circulates, while the hot gases in passing round about them give up their heat to the water and are drawn into the fan and then discharged through the chimney. This system does away with high chimneys and makes it possible to control the air supply for the fuel, and in this way the rate of combustion, much more closely than with chimneys. The system has not been applied to metallurgy to any extent except in the condensation of fume from lead blast furnaces in bag houses where the gases from the furnace are drawn through long iron flues to cool them before being passed through the bags by the fan and thence on to the chimney. Where in metallurgical operations hot or warm blast can be economically applied, such a

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[1] L. S. Austin, T. A. I. M. E., XXXVII, 468 (1906).

[2] H. O. Hofman, T. A. I. M. E., XXXIV, 292 (1904).

[3] W. W. Christie, Eng. Magazine, XXI, 81 (1901); also, Mechanical Draught, W. B. Snow, The B. F. Sturtevant Co., Boston.

system may be advantageously used, the "economizer" being replaced by a *U*-pipe stove (see page 509, or a set of checkerwork stoves similar to that described on page 508).

Mechanical stokers[1] which automatically feed fuel at a steady rate to the grates are largely used in boiler practice. They have been applied to some extent to metallurgical furnaces, particularly to puddling furnaces for making wrought-iron, and reverberatory roasting furnaces, with some success, effecting an economy of fuel.

Burning Powdered Coal. — The burning of pulverized fuel is of great importance in the Portland cement industry, the rotary clinkering kilns being fired with this kind of fuel. The system[2] used is clearly shown in Fig. 122, in which *H* is a hopper filled with very finely crushed coal that feeds into an injector *I*, in which it is blown by blast from the blower *B*, through the pipe *P* into the furnace *R*. Fig. 123, *A*, shows a detail section of the injector which is self-explanatory.

This method of burning coal presents several advantages: (1) It is possible to burn the coal with almost the exact amount of air required for complete combustion, which means the attaining of nearly the theoretic temperature of combustion. (2) The coal is completely burnt, no carbon remaining unconsumed in the ash. (3) The air can be closely controlled and almost any length of flame up to 60 ft. produced.

A disadvantage is the settling of the ash of the burnt coal upon the furnace charge, and in the flues leading to the stack. In cement kilns the length is so great that the ash all settles upon the charge, where it does no harm, becoming incorporated with the "clinker," or burnt cement, as the kiln revolves, but in other types of furnaces it may settle on the charge and choke the flues with a hard semi-fused crust and interfere with the draft in a short time. The best results with powdered coal are obtained when the coal and air are blown into a highly heated space, as is afforded by the ordinary furnace. The stream should not come in contact with cold surfaces, since this will reduce the temperature of the coal and air below the ignition

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[1] W. W. Christie, Eng. Magazine, XXIII, 528 and 717 (1902).

[2] R. K. Meade, paper read before the first meeting of the Am. Inst. Chem. Eng., Pittsburg, Dec. 28, 1908, from the Elec. Chem. and Met. Ind., VII, 57 (1909).

point and result in incomplete combustion. Coal-dust firing for this reason has not been successfully applied to boilers.

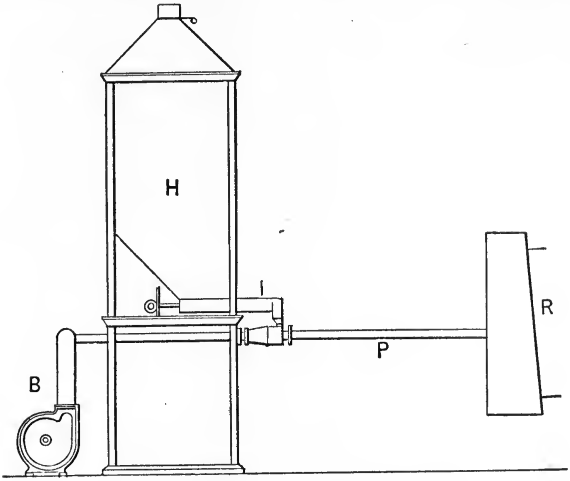
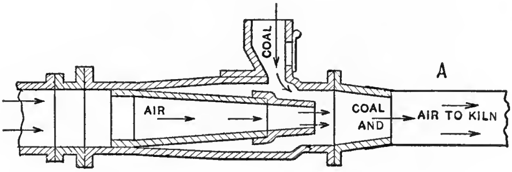


FIG. 122. — Burning powdered coal.



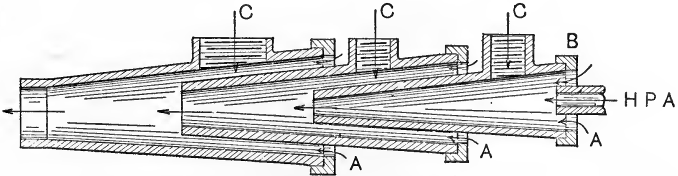


FIG. 123. — Injectors for burning powdered coal.

It has been experimentally tried in reverberatory copper-smelting furnaces with promise of success.[1]

For burning coal in this manner it is crushed in toothed

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[1] S. S. Soerens, E. and M. Jour., LXXXI, 274 (1906). C. F. Shelby, E. and M. Jour., LXXXV, 540 (1908), Eng. and Min. Jour., LXXXV, 121, 1017 (1908).

rolls and pulverizers so that practically all of it passes a 100-mesh screen. If the coal contains any appreciable moisture it is necessary to first pass it through rotary dryers. The powdered coal is fed into the hopper of the injector by means of a screw conveyor so that the coal feed can be closely regulated. The air pressure from the blower in the low-pressure system is usually from 8 to 10 oz. per square inch. In the high-pressure system air is furnished by a compressor at 80 lbs. per square inch. The form of injector for this system is shown in *B*, Fig. 123, in which the coal dust is fed through the opening *cc*, the high-pressure air at *HPA* and extra air at the points *AA*. In both systems the air blown into the injector need be only a fraction of that required for the combustion of the coal, the rest of the air being drawn into the furnace by draft. Where the feed pipe enters the furnace a nozzle of suitable shape is attached so that almost any shaped flame may be obtained.

Burning oil. — A form of oil burner[1] suitable for metallurgical furnaces is shown in Fig. 124. The oil enters the burner through the pipe *A;* steam enters through the pipe *B* and escapes into the nozzle *C* through a small opening, at which it meets the oil, vaporizing the same. The valve *D* serves to open or close the small openings *x* by means of which the nozzle is cleaned by steam. The use of steam in the burners has the advantage of heating and vaporizing the oil, so that when it escapes at the nozzle and enters the heated interior of the furnace to be burnt by air it is already largely gasified. The nozzle of the burner may take a variety of forms dependent upon the shape of flame that is desired. Other data on oil is to be found in Chapter XI.

Gas Producers. — The number of different types of gas producer are many and no attempt is made in this work to describe different forms of apparatus; it is merely desired to outline the principles of the production of fuel gas from solid carbonaceous fuel. A typical example of a gas producer suitable for bituminous and lignite coals is the form of Taylor producer shown in Fig. 125. The gas producer consists essentially of a comparatively deep shaft lined with fire brick, provided in the bottom with a suitable grate upon which rests a bed of ashes,

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[1] L. D. Ricketts, Trans. Inst. Min. and Met., Bul. 64, 28 (1910), Bul. 62, 29 (1909).

upon which in turn rests a deep bed of coal. The bottom of the producer is tightly enclosed and air is admitted through a suitable opening in carefully regulated quantity. The top is also tightly closed to prevent the escape of gas, the fuel being fed usually by means of a special automatic feed. In Fig. 125

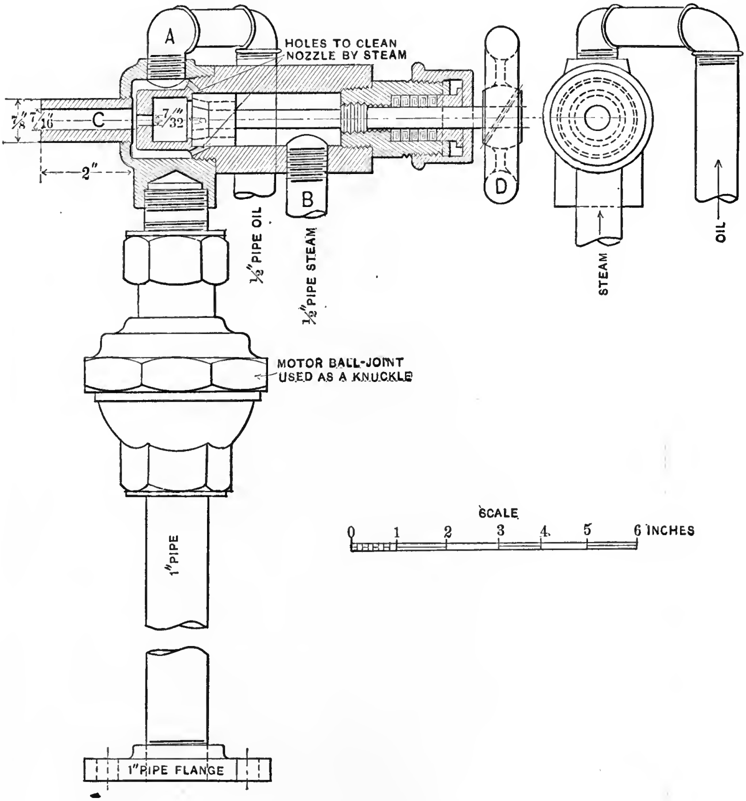

Fig. 124. — Shelby oil burner.

the hopper *A* holds the coal and feeds to the secondary hopper *B*, from which the coal is discharged into the producer by means of the revolving distributor *C*. *F* is a revolving grate upon which rests a bed of ashes reaching usually to the level *zz*, or a little below it. On this rests the bed of coal extending to the level *cc*. *E* is the pipe opening by means of which air and steam is blown into the producer, the air being to a considerable

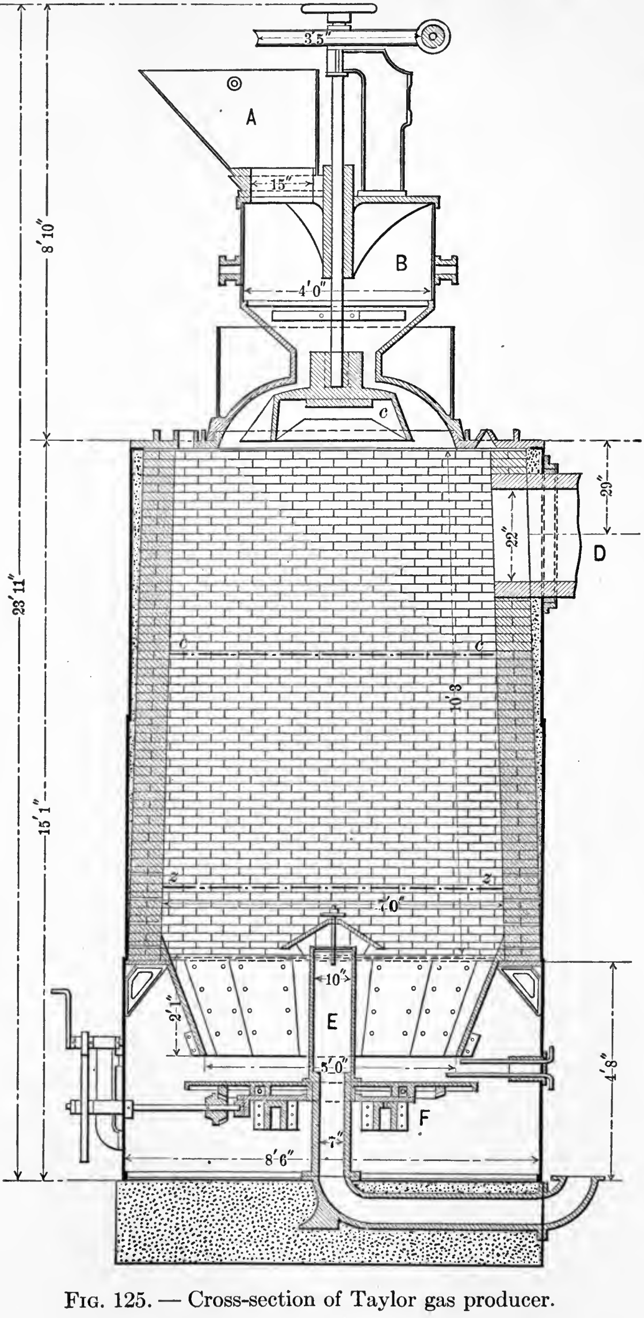

FIG. 125. — Cross-section of Taylor gas producer.

extent preheated, since the pipe is surrounded by hot ashes. The gas is discharged through the opening *D*, from whence it passes either directly to the furnaces or to gasometers for storage. Under certain circumstances, as when gas is made from lignitic coals or wood, it may pass first through condensers and scrubbers which take out the tarry products that might otherwise clog the gas flues. From time to time the grate is revolved to discharge ashes and to settle down the coal bed, and thus stop up fissures and channels that have formed in the coal and which tend to permit the formation of poor gas by allowing the formation of an undue amount of CO_2 gas. The automatic feed at the top of the producer feeds coal continuously.

The chemistry of the production of gas. When a limited supply of air is blown into the bottom of a deep bed of incandescent carbon, which, however, is at a comparatively low temperature, 500 to 700° C., there is produced both CO and CO_2. The CO_2 rising through the incandescent carbon is reduced practically entirely to CO, so that the final gaseous product is CO and N_2. In the upper part of the coal bed, if this be bituminous or lignite coal, distillation takes place with the production of hydrocarbon gases such as heavy carbureted hydrogen, C_4H_4, and smaller amounts of other hydrocarbons, which in turn are decomposed into the lighter hydrocarbon gases C_2H_4 and CH_4. With air alone, the gas therefore consists of CO, N_2, and some hydrocarbons, mixed with a certain amount of CO_2 gas which escapes reduction. The thermo-chemistry of this reaction is essentially as follows:

$$\begin{array}{ll} (1) & \underset{12}{C} + \underset{32}{O_2} = \underset{44}{CO_2} + 97{,}200 \text{ calories.} \\ (2) & \underset{97200}{CO_2} + C = \underset{2(29160)}{2CO} - 38{,}880 \text{ calories.} \end{array}$$

The heat liberated in burning 24 parts of carbon to CO gas is $97{,}200 - 38{,}880 = 58{,}400$ calories or $\frac{58400}{24} = 2433$ calories per kilogram of carbon burnt to CO. Since the heat liberated by burning one kilogram of carbon to CO_2 is 8100 calories, the fuel value of 1 kg. carbon in the form of CO is $8100 - 2430 = 5670$ calories. If the heat evolved in the burning to CO could be kept in the gas as sensible heat until it is burnt there would be little loss, but practically all of this sensible heat in the gas is lost by radiation between the producer and the furnace. Theoretically, this loss of heat is $\frac{2430}{8100} \times 100 = 30$ per cent., and the efficiency of producer gas cannot be more than 70 per cent. of the fuel value of the coal. In the production of producer gas from coal by means of air only, the temperature of the producer is apt to rise and the gas be discharged at an increasing temperature which will increase the loss. If steam be now blown into the producer, an *endothermic* reaction, one that requires heat to proceed from left to right, takes place as follows:

$$\underset{58060}{H_2O + C} = \underset{29160}{H_2 + CO} - 28{,}900 \text{ calories.}$$

Eighteen parts of water vapor are decomposed by 12 parts of carbon, with the absorption of 28,900 calories or 2408 calories per gram of carbon converted in this way to CO. This reaction has a chilling effect on the producer and offsets the heating effect of the carbon-oxygen reaction. It is evident that while the decomposition of water vapor by carbon requires heat, this is again recovered when the gas, $CO + H_2$, produced by the reaction is burnt later on. It is true, therefore, that if a mixture of air and steam be blown into the producer in the proper ratio, the effect would be that the heat necessary for the reaction between water vapor and carbon is furnished by the sensible heat liberated from the carbon-oxygen reaction, and this converted into potential heat in the gas, to be recovered on burning the gas. Thus, instead of a possible efficiency of only 70 per cent., the efficiency may be materially increased by the use of steam, in conserving the sensible heat in the gas.

Most modern producers are blown by a mixture of air and steam, and it is usually figured that 20 to 25 per cent. of the carbon in the fuel can be oxidized by steam and 80 to 75 per cent. by air. The use of a certain quantity of steam has also the advantage that, as the air is decreased, the amount of inert nitrogen in the gas is also decreased, resulting in the production of a richer gas. It is to be noted, however, that there can be no final gain of energy obtained by the use of steam, for the production of steam in the first instance required heat energy. Its function is to transfer part of the sensible heat liberated in the producer, to latent or potential heat in the gas. The efficiency of the ordinary producer is about 65 to 75 per cent., *i.e.* the calories in the gas produced are 65 to 75 per cent. of those present in the original coal. The losses are due chiefly to (1) loss of sensible heat in gas; (2) loss by radiation and conduction; (3) loss by unconsumed fuel; (4) loss due to driving out moisture from coal, and that due to the heat required to vaporize the hydrocarbons in the coal.

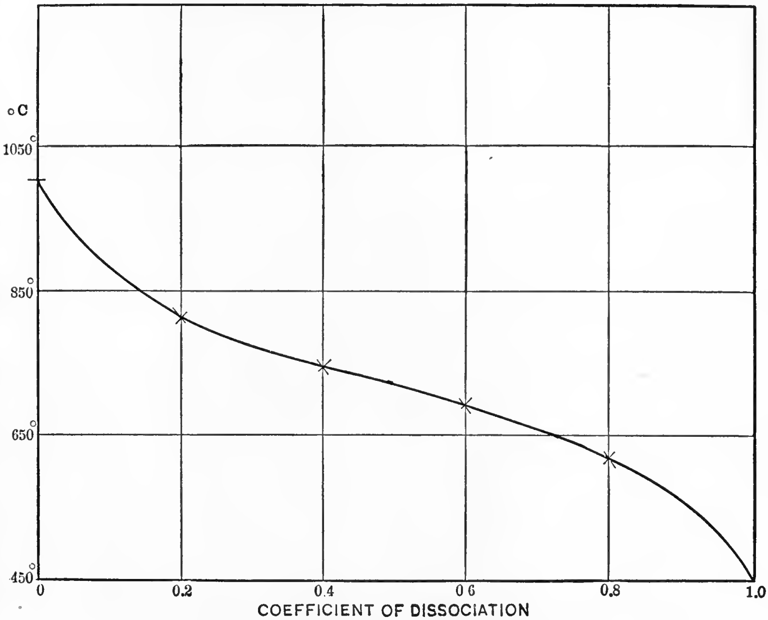

Fig. 126 — Dissociation of carbon monoxide.

The temperature at which the producer is operated has an influence on the amount of CO_2 present in the gas. Fig. 126 shows the dissociation curve of carbon monoxide, from which it is apparent that the dissociation of the gas is complete at 450° C. Essentially, this means that carbon will burn entirely to CO_2 if the temperature of combustion be below 450° C. also that above 1000° C. no CO_2 is formed in burning carbon, but practically only CO. This, of course, has reference to a system in which the three entities, carbon, carbon monoxide, and carbon dioxide are in contact at atmospheric pressure.

It follows, therefore, that for producers operated between 1000° and 450° C. carbon dioxide is always present, and in large amount at the lower temperatures. Since the use of steam has the effect of lowering the temperature of the producer, its use increases the amount of CO_2 present in the producer gas. " Mond " gas is a producer gas made with a large amount of steam so that it contains a higher percentage of hydrogen than ordinary producer gas, but also a greater percentage of carbon dioxide, which lowers its heat-producing value. When coal is used which clinkers badly at comparatively low temperatures, and thus gives trouble in the producer, it may be desirable to make " Mond " gas, on account of the low temperature at which the producer is worked.

CHAPTER XIII

FURNACES. THE PRODUCTION AND HEATING OF BLAST

Definition and Classification. — No commercial metal is produced for the market without the aid of high temperatures generated in some type of *furnace*. Some metals, like iron, copper, and lead, are brought from their ores to the state of finished product practically solely by furnace operations. Some metals, like gold and silver, may be produced in large part by hydro-metallurgical operations, but before the finished product is obtained some type of furnace is used. Furnaces, therefore, are the most important apparatus employed in the winning of metals from their ores. A furnace is a structure in which any substance such as an ore, metal, glass, etc., may be submitted to a high temperature. There are many different kinds of furnaces and a complete and accurate classification of them is difficult, but that based on the relation of fuel to the furnace charge is the most convenient and satisfactory. This classification is as follows:

I. Furnaces in which the charge of ore or metal is in direct contact with the fuel, which is usually coke, charcoal, or coal.

a. Hearths; shallow receptacles, of greater diameter than depth, in which the combustion of the fuel is carried on by either natural or forced draft.

b. Shaft furnaces. The height is greater than the diameter.

(1) Kilns, in which the combustion of fuel is carried on by natural draft.

(2) Blast furnaces, in which the combustion of the fuel is carried on by forced draft.

II. Furnaces which essentially consist of a *hearth* or smelting space, which is separate and distinct from the grate upon which the fuel is burnt, or from the gas producer in which the fuel is gasified, the heating effect being accomplished by radiation from the flame or the products of combustion which pass over the charge on the hearth.

a. Direct-fired reverberatory furnaces.

b. Gas-fired regenerative reverberatory furnaces.

III. Furnaces in which the charge to be heated is in a space or vessel insulated from any contact with the fuel or the products of combustion.

a. Retort furnaces for distillation.

b. Muffle furnaces.

c. Vessel furnaces, kettles, crucible furnaces.

IV. Electric furnaces.

a. Electric furnaces in which the heating effect of the electric current is used to obtain the requisite temperature.

b. Electric furnaces in which the current is used chiefly for the purpose of electrolysis.

I.–*a.* **Hearths.** — Hearths are at the present day but little used in metallurgy. The hearth represents the most primitive type of furnace, and, though perfected and modernized for certain operations, is comparatively little used. The ordinary blacksmith's forge is a typical hearth. Lead smelting by the roast-reaction method is carried out in hearths in some districts.[1]

b. (1) **Kilns.** — Draft kilns, similar to the lime kiln, have been used for the calcination of carbonate iron ores, the roasting of oxidized iron ore containing some sulphur, and for the roasting of pyrites for sulphurous acid gas. For this latter purpose the kilns are about 5 × 8 ft. in cross-section, inside measurement, and 12 to 15 ft. high. The coarse lump ore rests on iron grate bars. A flue leads out from near the top and conducts away the gases. The kiln is covered and the ore is charged through a hopper. The pyrites furnish the fuel for their roasting, the air for combustion being drawn in below the grate.[2] The kiln is built of common brick, lined with fire brick and tied together by angle bars and rods.

Fig. 127 shows a typical lime kiln. The lime rock, in pieces up to 12 in. diameter, is charged through the open top of the kiln into the shaft *A*, lined with fire brick, and is discharged at intervals in the calcined state by the chutes *B*. The kiln is

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[1] K. W. M. Middleton, Engineering and Mining Journal, July 6, 1905.

[2] Schnabel, Handbook of Metallurgy, I, 51 (1898). Translated by Henry Louis.

fired from the grates *C* by means of wood or coal. Fig. 128 shows the Davis-Colby gas-fired kiln for roasting hematite or magnetite iron ores containing 2 to 3 per cent. sulphur, the larger part of which must be eliminated before smelting. It consists of two concentric shafts of brickwork, enclosing the annular space *E*, 18 to 24 in. wide, into which is charged the ore to be roasted, at the cone-shaped top *L*. The roasted ore is discharged at *C*. Gas from a producer, carried by the mains *A*, enters the openings *X*, where it meets air at the openings *B*, burning in the annular space *E*, the products of combustion being discharged through the openings *D* into the central shaft *F*, and thence down through the flue *F* to the stack.[1] Kilns of this type, 16 ft. in diameter and 28 ft. high, roast 75 to 100 tons iron ore per day. The ore contains 2 to 3 per cent. sulphur and is roasted down to 0.1 to 0.2 per cent. sulphur.

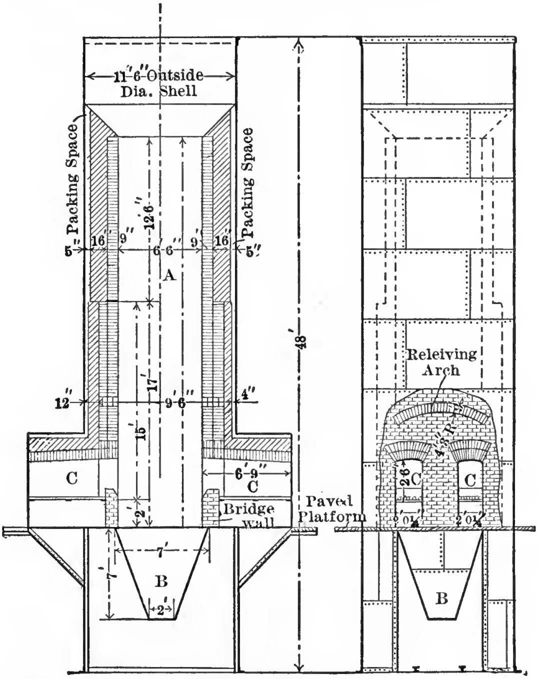

Fig. 127. — Lime kiln.

The Gjers kiln for roasting iron ores is extensively used in the

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[1] S. G. Valentine, T. A. I. M. E., XVIII, 303 (1889).

Cleveland district in England. It is a cylindrical kiln, about 25 ft. in diameter and 30 ft. high, built of fire brick and held together by iron plates and rods. The ore and fuel are charged together continuously at the top in the ratio of 1 ton of coal to 25 of ore, while the calcined ore is discharged at the bottom. Draft doors for air are provided around the circumference near the bottom of the kiln. The capacity of the kilns is about 35 tons of ore per day.[1]

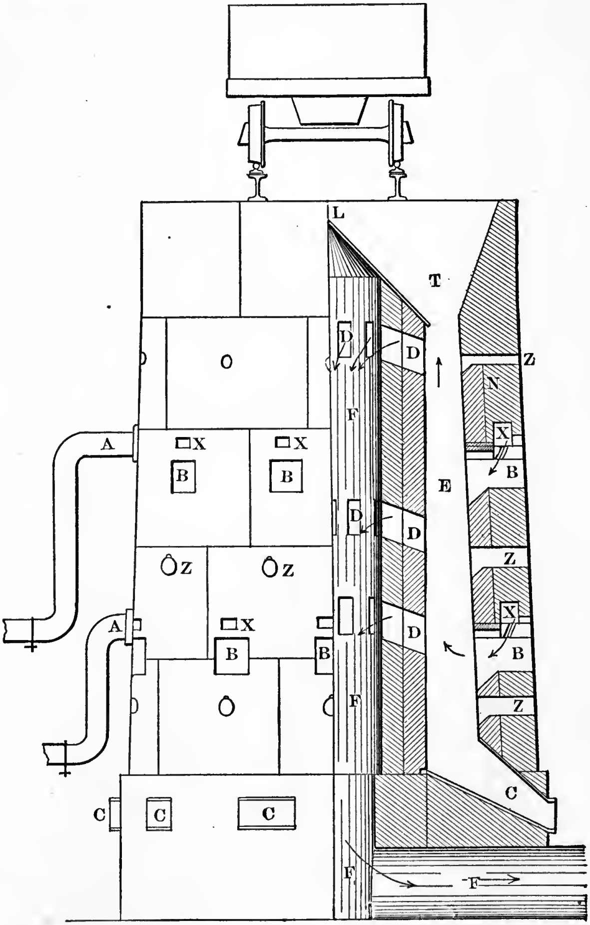

Fig. 128. — The Davis-Colby ore-roasting kiln.

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[1] Roberts–Austen, An Introduction to the Study of Metallurgy, 287 (1902).

(2) **Blast Furnaces.** — The blast furnace represents a very important type in the metallurgy of iron, copper, and lead. By the use of forced draft or blast, rapid combustion of fuel is obtained with the consequent production of high temperature and relatively great capacity of furnace.

Practically all blast furnaces consist of a vertical shaft of different heights for different purposes, lined either with refractory brick or built of a series of *water jackets,* rectangular cast-iron or steel boxes, in which water constantly circulates. The cross-section of the furnace may be circular, elliptical, or rectangular, dependent upon the size of the furnace and the pressure of the blast necessary to force the gases through the furnace at the proper speed. The ore, fluxes, and fuel are charged at the top of the furnace in alternate layers, *e.g.* coke first, followed by ore and then by limestone, all in the proper proportion to give a suitable smelting mixture, the total weight of the substances constituting the *charge.* The size of the charge depends on the nature of the smelting; thus, in smelting iron ore, a typical charge is 24,000 lbs. iron ore, 6000 lbs. limestone, 10,200 lbs. coke, the relative weights in this particular instance being obtained by careful calculation based on the chemical composition of the substances entering into the charge. A typical charge for a 48 × 180 in. furnace in a case of copper matte smelting is 2700 lbs. copper-bearing pyrites, 1300 lbs. siliceous gold ore, 150 lbs. limestone, 200 lbs. slag, 150 lbs. first matte, 140 lbs. coke, a total of 4640 lbs. When one charge has been fed its constitutents are repeated in the same order as that of the first one, when the descent of the furnace contents warrants the addition. The charge is considered to be made up of *burden* and *fuel;* the latter is usually coke, while the former is made up of all the other constituents of the charge. The fuel is calculated in percentage on the basis of burden; thus, if the burden be 10,000 lbs. and the fuel 1000 lbs., the charge is 11,000 lbs. and the per cent. of fuel is 10. It is usually desirable to use the minimum percentage of fuel that will furnish the required heat units to carry on the furnace operations.

The charge may either be shoveled into the furnace by hand, from the *charge floor,* or charged by means of mechanical devices which dump it directly into the furnace without the intervention of hand labor.[1] Iron blast furnaces are invariably charged by mechanical means such as are shown in Fig. 129. This device is known as the *bell and hopper feed.* The hopper *A* is charged directly from a self-dumping skip which raises the ore, flux, and coke from bins, where it is filled automatically. The lever *C*, operated by compressed air, lowers the bell *B* at the will of the operator, and the charge passes into the furnace. The design of the bell and hopper is important as it must distribute the furnace charge in the proper manner, the fine material usually to the side and the coarse to the center, so as to make a furnace column that will offer a uniform resistance throughout its cross-section to the passage of the rising gases. Usually the frictional resistance to the gases is less along the walls of the furnace than through the tortuous interstices beween the pieces of the charge, so that if fine material predominated in the center of the charge column, the larger part of the gases would pass up along the walls at a high velocity and but little gas pass through the central part of the charge. Since in the blast furnace these gases have important functions, such as preheating the charge and reducing certain constituents to the metallic state, it is at once apparent that, for the proper working of the furnace, the gas current should rise as uniformly as possible through the charge. These principles apply to all types of blast furnaces, *i.e.* it is essential that the rising gas current pass uniformly through all parts of the charge, in as far as this is possible. This condition is obtained mainly by a proper distribution of the furnace charge as regards the fine and coarse pieces. What the proper distribution is, depends on the shape of the furnace to some extent, but generally speaking the fines should pass to the walls, while the coarse material should go to the center. In shoveling ore, the fine material, particularly if damp, acts more sluggishly than the coarse, and hence will fall short, or almost directly from the shovel, while the coarse will fall from the shovel in a long arch and pass on further than the fine. In charging a rather wide furnace, by hand labor, from either side, the coarse and fine will tend to take their proper relative position, but if the same furnace were charged from the center, as by an ordinary bell and hopper device, or by shoveling through a

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[1] O. Baker, T. A. I. M. E., XXXV, 553 (1905). T. F. Witherbee, T. A. I. M. E., XXXV, 575 (1905). A. S. Dwight, T. A. I. M. E., XXXII, 353 (1902).

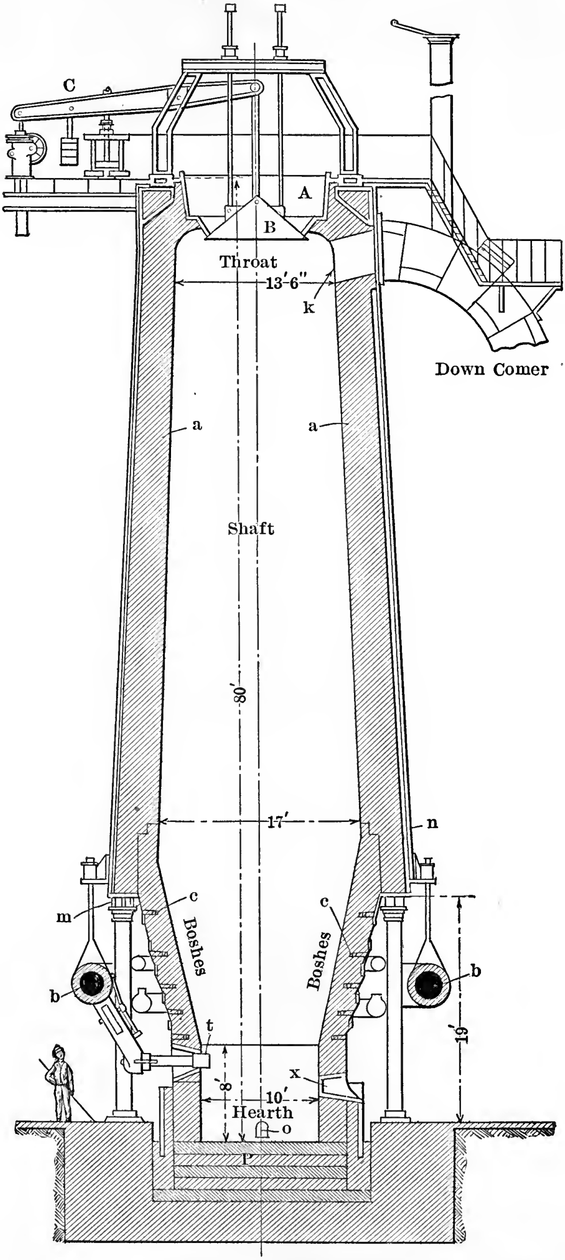

FIG. 129. — Longitudinal section of iron blast furnace.

centrally located feed opening, the distribution of the coarse and fine would be the opposite to that desired. It is essential for any mechanical device, that the design be such as to get the desired distribution. In the iron blast furnace it is usual in modern practice to use a double bell in which the upper one is always closed, when the lower one discharges into the furnace, in this manner acting as a gas seal. In the iron blast furnace the gases are discharged at the throat and escape through the downcomer.

The charge for the furnace consists of pieces of ore and flux ranging in size from very fine material to pieces 5 and 6 inches in diameter in lead smelting, and pieces of 10 and 12 inches in diameter for iron and copper smelting. During the descent of the charge the individual pieces of ore and flux split and break up into small pieces under the influence of heat, and become more or less thoroughly mixed by the time they arrive in the zone of slag formation, where they fuse together into slag and other fluid furnace products. The coke, in large part, descends unaltered and not much broken to near the tuyeres of the furnace, where it is rapidly burnt by the stream of air.

Fig. 129 shows a vertical longitudinal section of an iron blast furnace. The cross-section of the furnace is circular. The furnace is filled to a short distance below the gas flue *k* and is constantly charged as already described. The walls of the shaft of an 85 ft. furnace are usually 5.25 ft. thick when new, and built of a high grade of fire brick. The bosh walls are 2.25 to 3 ft. thick, of fire brick, and have built into them hollow bronze Gayley cooling plates, *c c*, in which water continually circulates. This device is necessary to cool the bosh walls and preserve them, for the corrosion in this part of the furnace is very great. The hot air blast is conveyed to the furnace through the blast or bustle pipe *b*, which is lined with a non-conducting substance, usually fire brick, and into the furnace through the tuyeres *t*, which are shown in detail in Fig. 130. The tuyeres, of which there are usually 8 to 16 from 5 to 8 in. in diameter at the nozzle, are water-cooled, *i.e.* water circulates through both the tuyere proper and the *cooler* as shown in the illustration. The *hearth* and *crucible* is the furnace space below the tuyeres and serves to collect the molten products of the furnace, the slag and iron, allowing also for their separation by gravity. From time to time slag is withdrawn through the *cinder notch* x, and run into large ladle cars, while the iron is tapped at O and run into sand molds to form *pigs*, or into large ladle cars to be conveyed to the steel plant where it is stored for the steel furnaces in a large receptacle called the *mixer*. The bottom of the hearth P is made of special fire-brick furnace bottom blocks.

The weight of the shaft walls a is carried by the mantle ring m, which is supported by columns. In this way only little weight is carried by the bosh walls. The shaft walls are enclosed by steel plates, called the mantle, which binds the whole structure firmly together. The interior of the furnace is made up of (1) the *throat* or opening at the top; (2) the *shaft*, extending from the throat down to the widest part of the furnace; (3) the *boshes*, extending from the widest part of the furnace to the beginning of the cylindrical part just above the tuyeres; (4) the *hearth* or *crucible*, the cylindrical part below the tuyeres. The shape of the iron blast furnace is that of a pair of truncated cones set end to end, the upper one upright and very acute, the lower one inverted and relatively obtuse.[1] In the modern

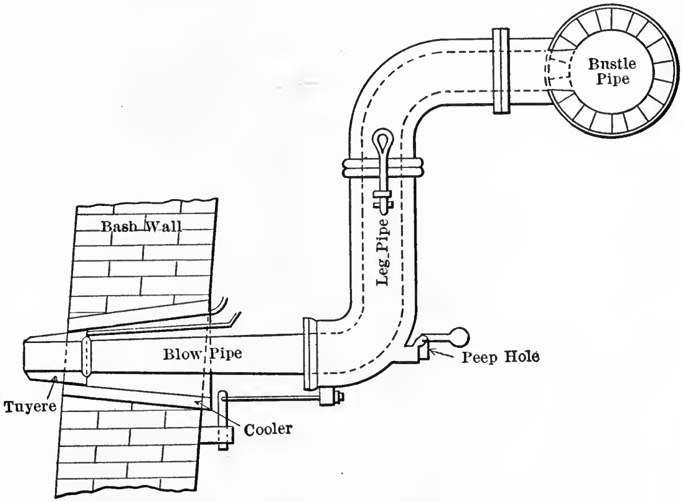

FIG. 130. — Detail of blast-furnace tuyere.

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[1] H. M. Howe, Mineral Industry, XVII, 548 (1908).

furnace the total height is from 80 to 100 ft. measured from the bottom of the hearth to the throat. The hearth diameter is usually 12½ ft., but may be as large as 17 ft. The diameter is limited by the penetrating power of the blast, which must be able to reach the center. The usual blast pressure in the blast pipe is 10 to 15 lbs. per square inch, although higher pressures are sometimes obtained when the frictional resistance of the furnace is very great, due to untoward conditions. Some approximate experiments[1] give the following data as regards the air pressure in the bustle pipe and that at the orifice of the tuyere and in the interior of the furnace at the tuyere level about 2½ ft. in from the tuyere. With a pressure of 10 lbs. per square inch in the bustle pipe, the pressure at the nose of the tuyere was 7.6 lbs. and in the furnace 7.5 lbs. per square inch. The depth of the hearth, from the bottom of the furnace to where the boshes begin, is usually 8 to 10 ft. The angle the bosh walls make with the horizontal varies from 73 to 76 degrees. If the bosh walls are made flatter than this, the furnace charge is apt to hang up and descend irregularly, since the pasty, somewhat soft coke, which is the only solid material left in the boshes, will not slide readily over the wall as that below it is burnt at the tuyeres. If the angle be made too steep, the volume of the furnace will not increase rapidly enough above the tuyeres to provide for the expansion of the furnace gases, as these ascend from the tuyeres where they are formed. This increase in volume above the tuyeres is very necessary to provide room for the greater volume of the gases of combustion, due to their high temperature; otherwise their velocity would be too great, causing such frictional resistance as to hang up or *scaffold* the solid charge. The shaft increases in volume downward, to provide for the swelling or increase in volume of the furnace charge. This swelling is very considerable and is due in part to the absorption of carbon by the iron ore during its reduction. The bosh walls serve to arch the charge and thus sustain its weight, while in a furnace with vertical walls the great weight of the charge would rest, at least in part, directly on the molten material in the hearth, a very undesirable condition. With a bosh wall slope of 76° the height of the boshes is usually made 12 ft., which gives a greatest width of furnace at the beginning of the bosh of 18 ft.

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[1] R. H. Sweetser, T. A. I. M. E., Bul. 27, 285; March (1909).

At this point the shaft commences, the slope of its walls being best 6 to 9 degrees from the vertical. The diameter at the top is usually not less than 16 ft. so as to insure a uniform distribution of the charge. In the furnace we have to consider a rather slowly descending solid and liquid charge, and a rapidly ascending gas current. This latter, passing through the interstices of the pieces of the charge has a very high velocity, probably 2000 to 4000 ft. per minute,[1] so that its lifting and sustaining power is very considerable.

The height of the furnace is an important dimension. (1) It must be sufficient to give the necessary time to the rising gases to give most of their heat to the descending ore charge, and thus preheat it to the degree necessary for the various chemical reactions to take place. (2) It must be sufficient to give ample time in the descent of the charge for the iron oxides to be reduced to metallic iron before they reach a zone in the furnace in which the temperature is such as to cause their union with silica and thus to enter the slag. By experience the best height is about 80 to 90 ft. Furnaces of a given hearth area have the greatest capacity with this height, showing the best preparation of the furnace charge during its descent in the furnace.

An increased height does no good, but rather harm, as with every foot of height the resistance to the passage of the gases is increased, requiring a higher velocity, which entails greater expenditure of power in the blowing engines; a greater production of flue dust, due to this higher velocity; and poor working, induced by an irregular descent of the charge, due to the retarding effect of the high velocityof the gas current.

It is to be noted that the pressure of air and gases in the furnace is incidental only, and is due to the frictional resistance offered to the gas flow by the furnace. The criterion is always the amount, viz., volume of air which is blown into the furnace, and not its pressure. For the production of one ton of iron there is required a certain amount of fuel, and to burn this fuel requires a certain quantity of air. The air going into the furnace is measured by the number of revolutions of the blowing engine, which with a given cylinder displacement furnishes a given number of cubic feet of air per minute. The pressure of the air blast measures the frictional resistance of the furnace.

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[1] H. M. Howe, *ibid.*

(See page 516.) In general, the lower this is for a given volume of air blown into the furnace, the better the condition of the furnace. It is evident that it takes less power to blow 64,000 cu. ft. of air per minute into a 100-ft. furnace (cubic content 32,000 cu. ft.) under 12 lbs. pressure, than under 20 lbs. pressure.

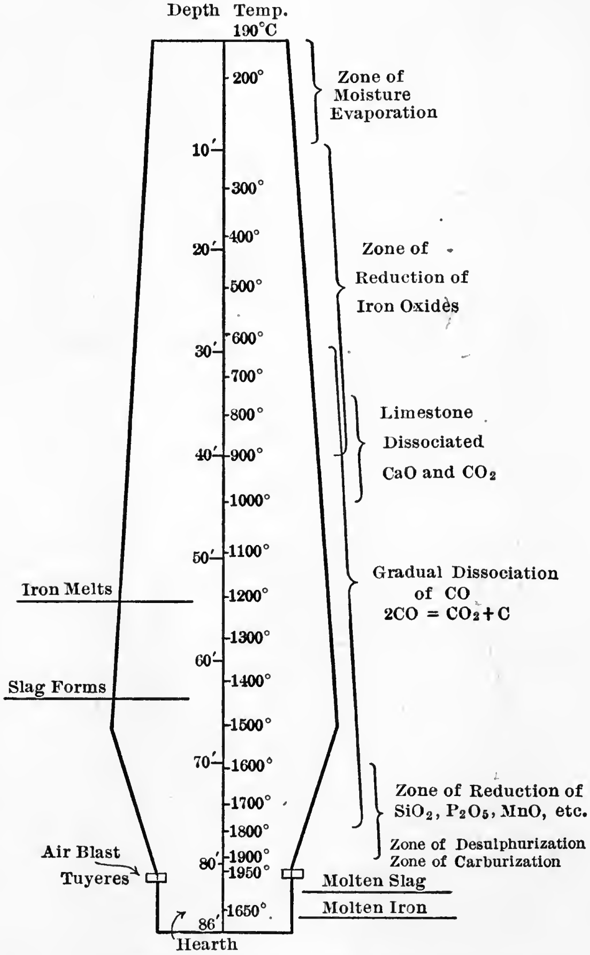
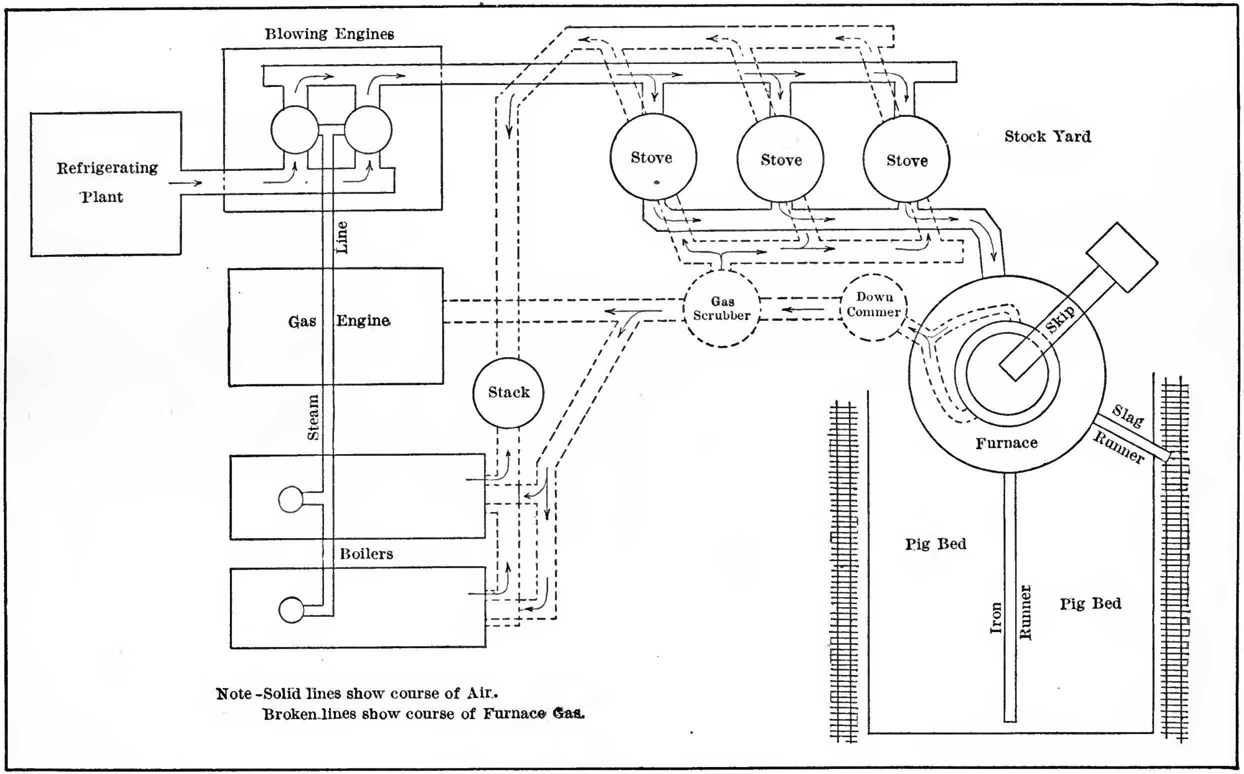


Fig. 131. — Section of blast furnace, showing temperature.

The cross-sectional area just above the tuyeres in the furnace is the smelting area of the furnace, and it is this area which



Note -Solid lines show course of Air.
Broken lines show course of Furnace Gas.

FIG. 132. — Plan of blast-furnace plant.

primarily determines the capacity of the furnace, on the assumption that the quantity of air blown in is such as to give the maximum possible rate of combustion of fuel over this area. This maximum rate is dependent on the velocity of reaction between carbon and oxygen in the formation of carbon monoxide, under the conditions prevailing.

The separation of iron and slag takes place by gravity inside of the hearth. This is called an *inside* separation, in distinction to an *outside separation* which is practised in copper matte smelting, and in which case both slag and matte flow from the furnace into an outside receptacle called a *forehearth,* in which the separation takes place.

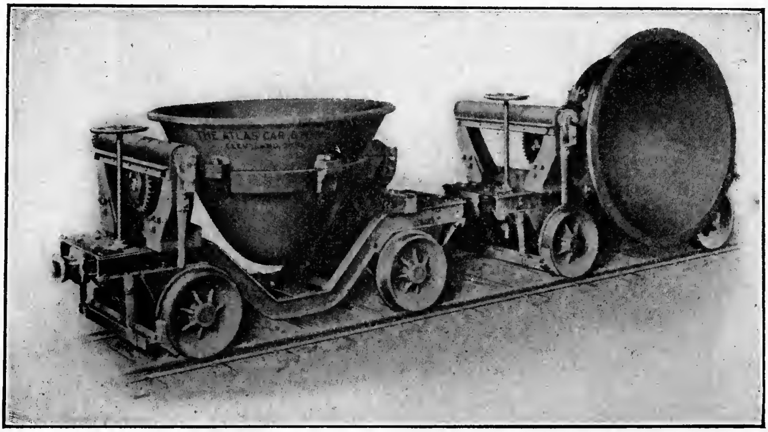


FIG. 133. — Slag cars.

Fig. 131 shows the longitudinal outline section of a blast furnace in which are given the temperatures that prevail at different depths and the location of the several important zones. The figure is approximate only. For the chemical reactions in the iron blast furnaces see pages 204, 230.

Fig. 132 shows the plan of a blast-furnace plant which is self-explanatory. This should be consulted in connection with the scheme on page 202. The hot blast stoves are shown in detail in Fig. 184. The refrigerating plant, for taking moisture out of the air, is described on page 498. The blowing engines are shown in Figs. 182, 183. Fig. 133 shows slag cars for the conveyance of slag from the furnace to the slag dump. The capacity of a 90-ft. furnace with a hearth 14 ft. in diameter is approximately 450 tons of iron per 24 hours.

The copper matting blast furnace. The copper blast furnace is shown in perspective in Fig. 134, and in section in Figs. 135 and 136. The shaft, instead of being built of fire brick, is made of steel or cast-iron water jackets which are shown in detail in Fig. 137. In the copper furnace the whole shaft is usually built of water jackets, Fig. 137 showing the lower set, an additional set making up the height of the furnace to the feed floor.

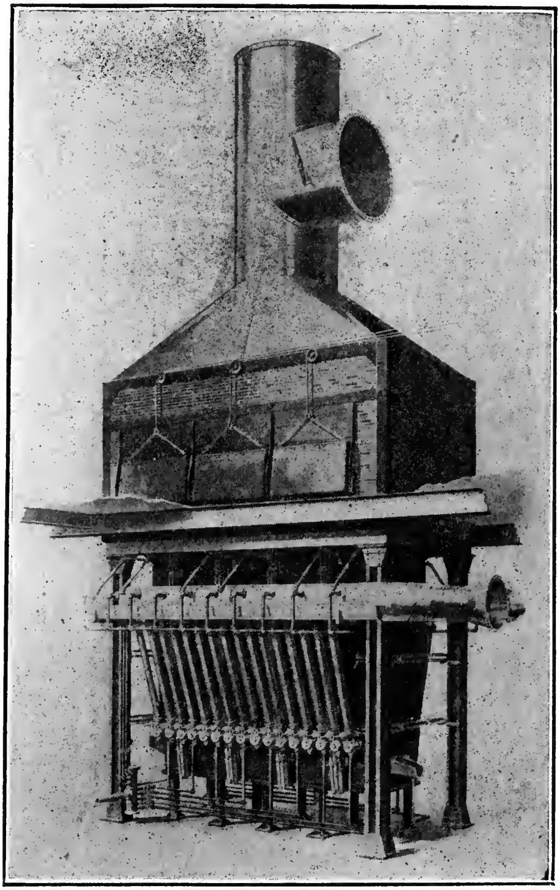


Fig. 134. — General view copper matting furnace.

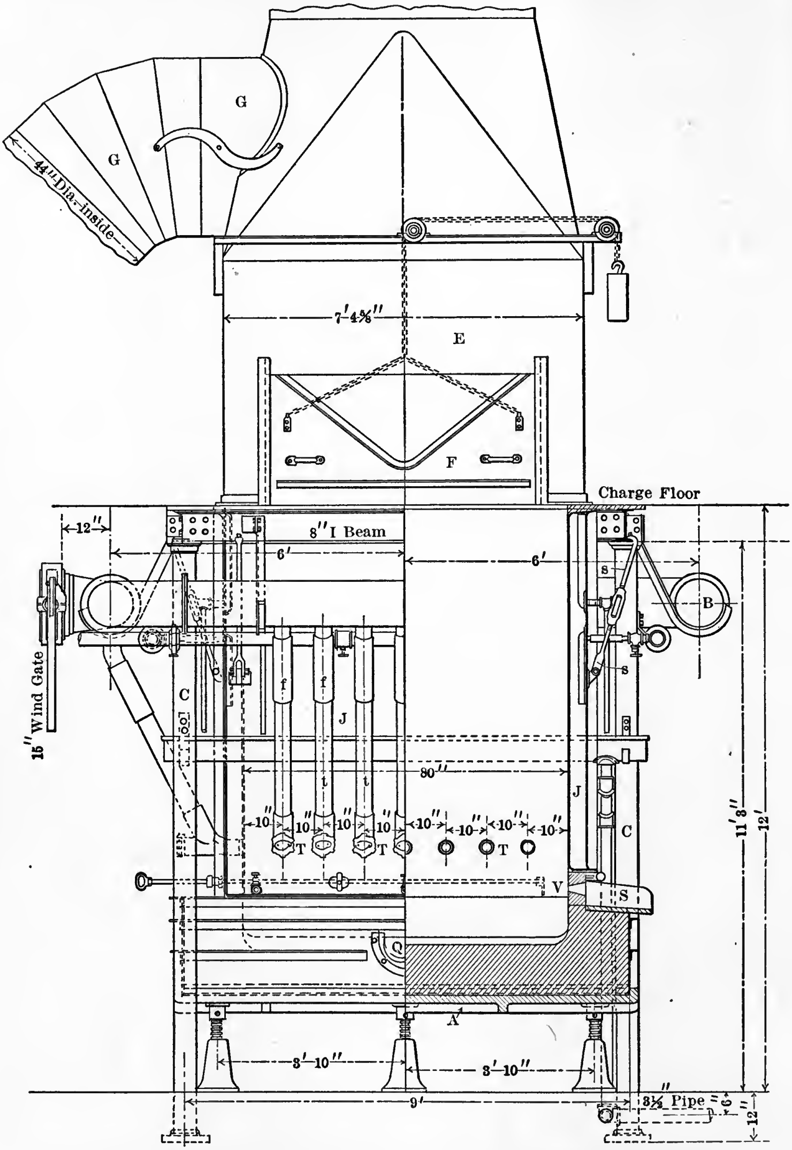


Fig. 135. — Elevation and longitudinal section of copper blast furnace.

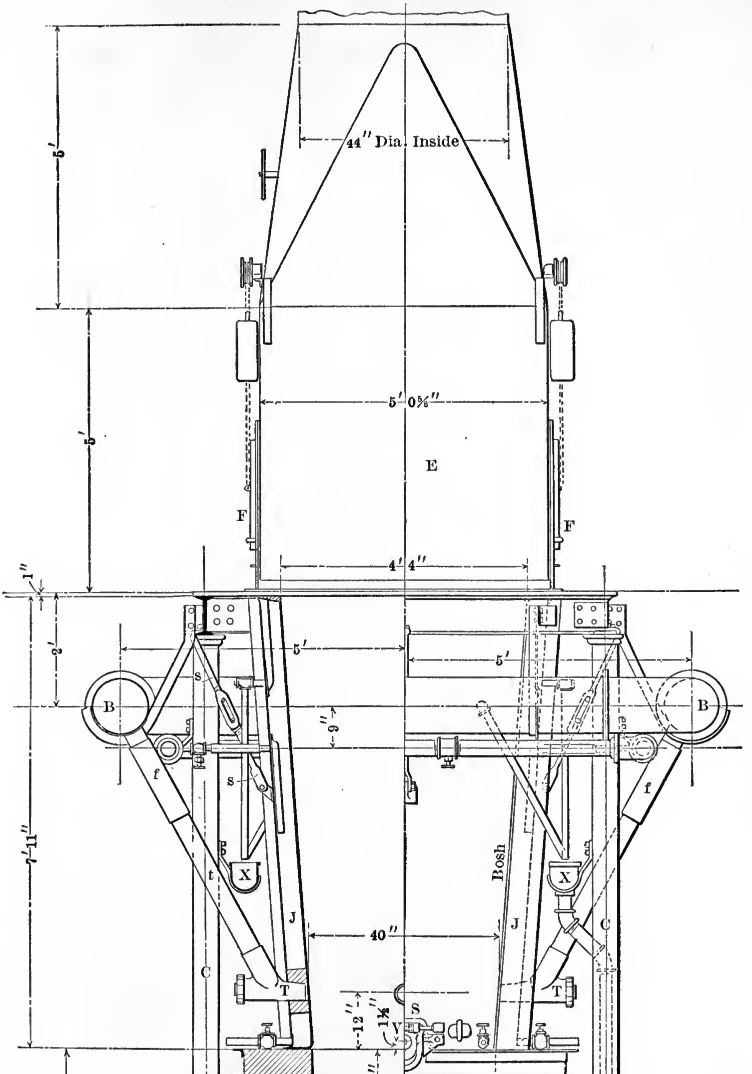


Fig. 136. — Elevation and end section of copper blast furnace.

The space *A* is for the insertion of the tap jacket which contains the discharge spout of the furnace. In the main jackets the feed-water pipes connect at *d d*, and the discharge or overflow pipes at *c c*, and discharge into a trough shown at *X* in Fig. 136. In smelting with water jackets a crust of slag soon builds up on the inside of the jacket, forming the actual smelting surface and protecting the iron plate. In blowing in a furnace it always takes more water to keep the jackets at the proper temperature than is used after the inside crust has formed. The use of water jackets is very convenient in that it does away with the corrosion of the lining of the furnace and the consequent expense of repair. The loss in heat, however, by the use of water jackets is much higher than if the comparatively non-conducting fire-brick lining were used. In a 36 × 120 inch lead furnace, with two sets of end jackets and two sets of side jackets, 2000 gallons of water per hour were used, the feed water entering at 22° C. and leaving at 67° C., thus absorbing 750,000 pounds calories per hour. The coke consumption in the furnace was 1000 lbs. per hour, capable of furnishing 7,000,000 calories. The loss of heat by the jacket water was therefore 10.7 per cent.[1] The general convenience obtained, however, very much outweighs this disadvantage. Water jackets for copper furnaces are most frequently made of steel, either welded or riveted together, though if the cooling water be acid as is sometimes

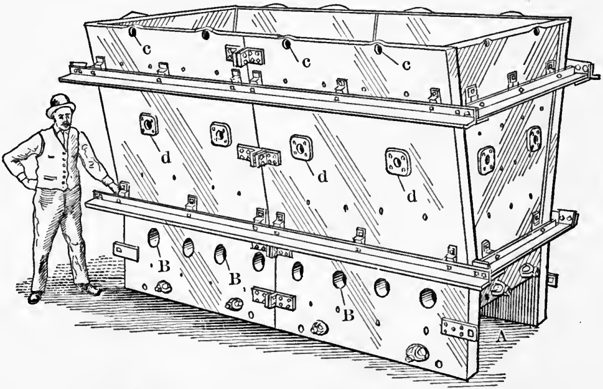


Fig. 137. — Welded steel water jackets for a copper furnace.

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[1] L. S. Austin, Mining and Scientific Press, XCVII, 525 (1908).

the case, cast-iron jackets are preferred on account of their greater non-corrodibility. In Figs. 135 and 136, *A* shows the cast-iron base plate supported on screw jacks, which rest either directly on the floor block or on a truck. On this plate normally rest the jackets, though in the furnace shown in the figures a crucible of fire brick is built up on which the jackets rest. The weight of the jackets *J* is carried by the steel columns *C* through the suspension bars *s*. The illustration shows a small

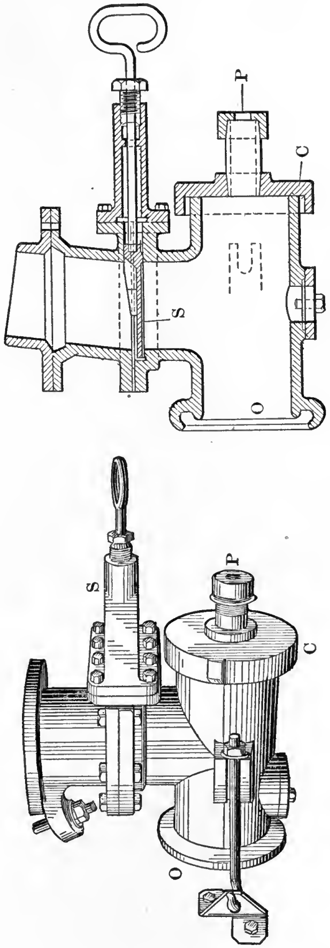

FIG. 138. — Copper and lead blast-furnace tuyeres.

furnace 40 in. wide and 80 in. long at the cross-section of the tuyeres, and the number of jackets is but four, in one set only. Fig. 134 shows a large furnace, with a set of upper and lower jackets, 8 side jackets, 4 end jackets, and 1 tap jacket, a total of thirteen. In longer furnaces there may be as many as sixteen jackets and more. In Fig. 136 the side jackets are *boshed* with a slope of 7.5 in. in 8 ft., while the end jackets are vertical. In copper furnaces with a double tier of jackets, the lower side jackets only are boshed, while the upper side jackets are vertical.

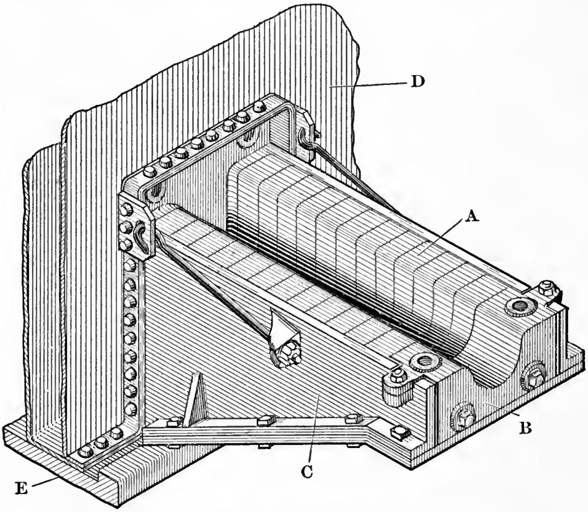

Fig. 139. — Trap spout for copper furnace.
E, base plate; A, magnesite brick; B, copper water-cooled tip; D, tap jacket; C, cast-iron plate.

All the end jackets are vertical. The boshes in copper and lead furnaces, while not so pronounced as in the iron blast furnace, have the same general functions. The tuyeres are shown in *T* and in detail in Fig. 138. The air comes from the blower through the bustle pipe *B*, to the tuyere pipe *t*, which has a flexible connection at *f* for the removal of the tuyere in case of necessity. In larger furnaces the tuyere connection is rigid. The furnace is discharged through the tap hole *V* and the spout *S* into a *forehearth*. The spout *Q* is provided to drain the furnace when desirable. In small furnaces intermittent tapping is resorted to, *i.e.* the clay plug at *V* is punched in when the liquid contents of the furnace approach the level of the tuyeres, and the matte and slag are run into the forehearth where their separation takes place by gravity. When the blast commences to blow out through the tap hole this is stopped by a fresh clay plug. Large furnaces are tapped continuously by means of a trap spout as shown in Fig. 139. This tap has the intake from the furnace

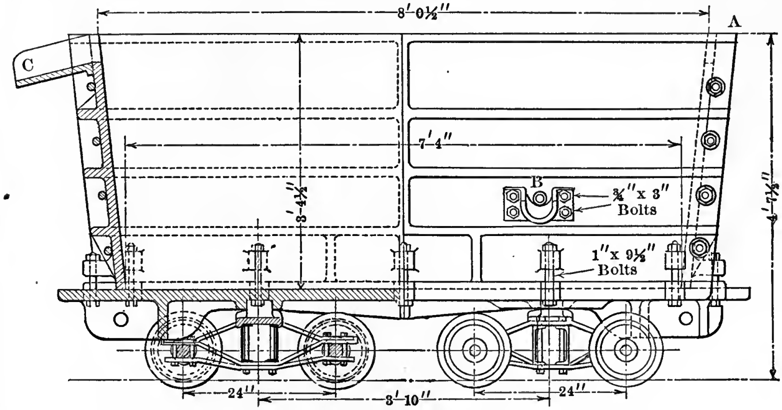

FIG. 140. — Elevation and part section of forehearth.

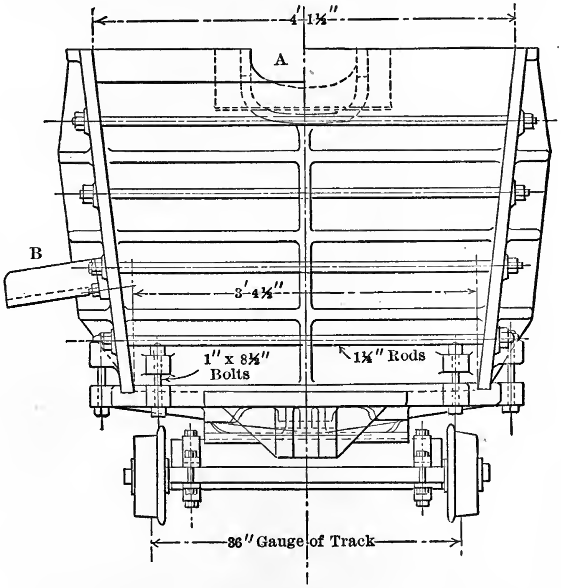

FIG. 141. — End elevation of forehearth.

lower than the discharge from the tip, in this manner trapping the blast, since the slag and matte will always stand several inches high over the discharge orifice in the furnace. The difference in level between the intake and the discharge, viz., the height of the spout, will be governed in any given furnace by the blast pressure carried. Taps of this type are used only when the furnace has a large capacity, *i.e.* the flow of slag and matte is large and constant.

Above the charging floor is the hood *E* which passes into the flue *G*, which enters the dust chambers in connection with the chimney. The flue dust which is entrained by the gases escaping under pressure passes with them through the flue *G* and is settled out in the dust chambers. The charge is shoveled into the furnace through the doors *F*, special scales being generally provided on the charge floor to weigh the constituents of the charge in order to conform to the calculations made for the purpose of obtaining the proper smelting mixture.

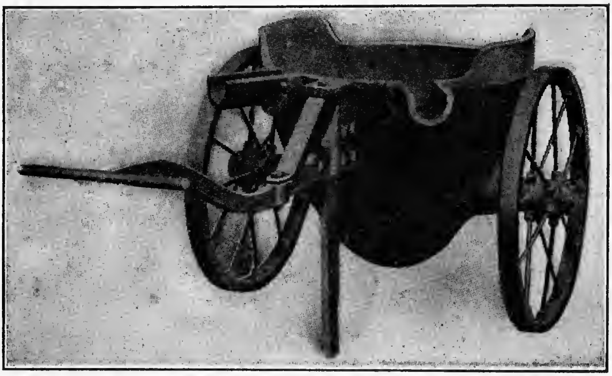

FIG. 142. — Settling pot.

Figs. 140 and 141 show a large movable forehearth. This is made of heavy ribbed cast-iron plates tied together by rods and set on a truck. It is lined with fire brick, either fire-clay or magnesia brick. The slag and matte flow from the furnace tap into the forehearth at *A*. When once the forehearth has filled, a crust is allowed to form on its contents, as high up as possible, and a hole maintained open at *A*, for the entrance of freshly molten material from the furnace. Likewise an opening is maintained at *C*, where the slag overflows into a settling pot shown in Fig.

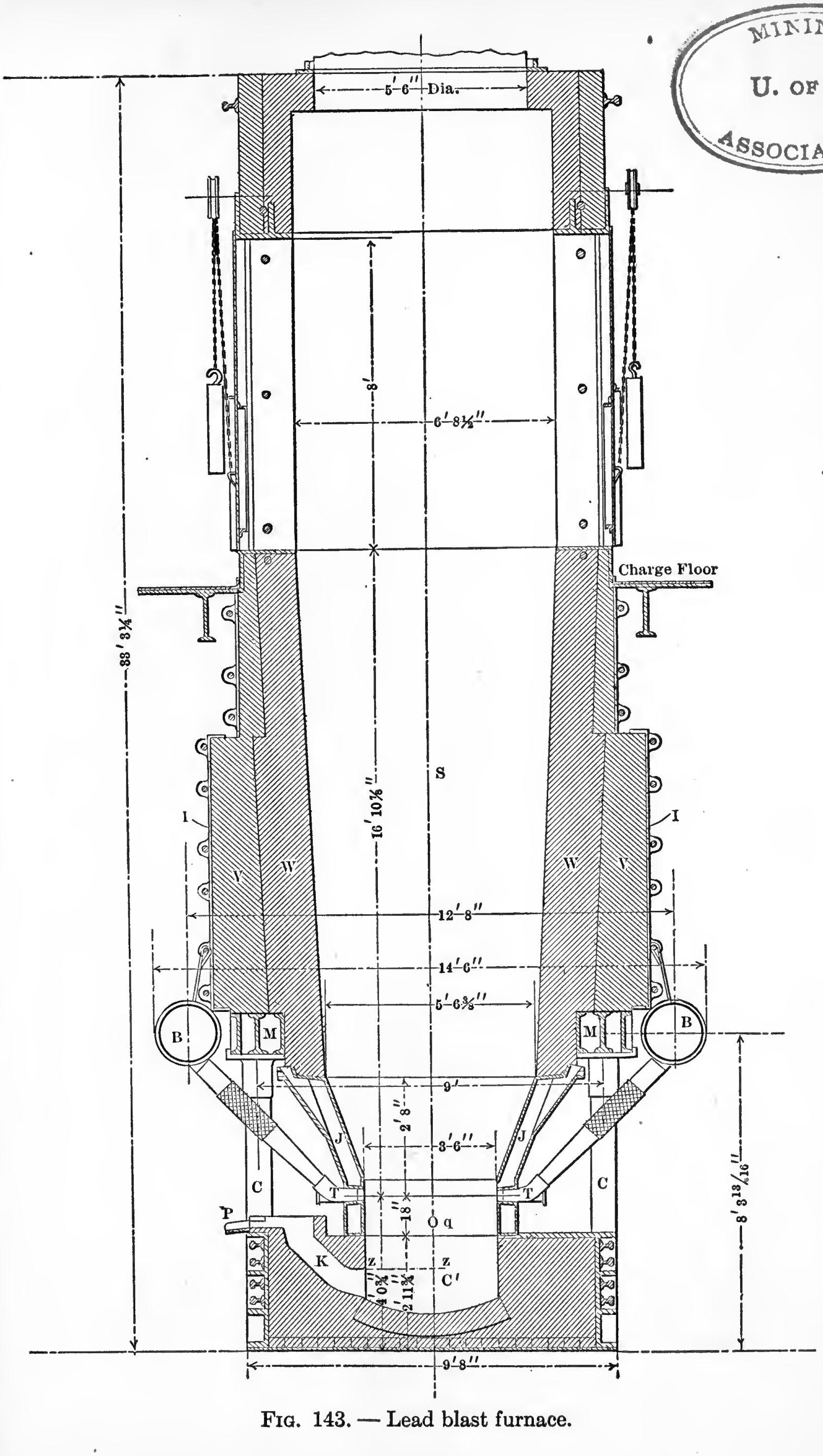

FIG. 143. — Lead blast furnace.

142 which acts as a secondary forehearth. The overflow slag from this is often directly granulated by flowing water, or handled in slag pots. The matte in the forehearth continuously settles by virtue of its superior gravity and is tapped into pots from time to time from the spout *B*. The forehearth is kept *open*, *i.e.* its contents are kept molten, by the continually inflowing stream of molten material. Its size is determined by the size of the furnace; if the quantity of slag and matte is great, large forehearths are used; if it be small, small ones must be used, as otherwise the quantity of molten material entering it will not be sufficient to keep it from chilling and freezing. When movable forehearths are used, they are easily replaced by a new one in case of accident, and furnace operations are not stopped.

The lead blast furnace. Fig. 143 shows the vertical end section of a lead blast furnace. In general construction the lead blast furnace resembles the copper blast furnace very much. The lead furnace, however, is jacketed only in the boshes, the jackets being shown at *J*. The bustle pipe *B* and the tuyeres *T* are similar to those of the copper furnace. The shaft *S* above the boshes is built of fire brick and common brick, as shown by *W* and *V*, the structure being tied together by cast-iron plates and tie-rods. The weight of the shaft walls is carried by the mantle ring *M* which rests on the columns *C*. The water-jackets are supported by a solid fire-brick mass in which is the *lead well* *C'*. The molten lead is discharged through the siphon *K*, overflowing into molds by means of the spout *P*. The slag and matte are discharged by a tap at *q* and are separated by gravity in a forehearth or in slag pots. It will be noted that lead is separated from slag and matte by an interior separation, as in the case of iron smelting. The red hot molten lead and slag and matte dripping through the solid incandescent coke above the tuyeres settle down into the *well*, the matte and slag resting in layers on the lead. The partial pressure of the charge and that of the blast on the liquid contents of the well cause the lead to rise into the siphon channel *K* and discharge at *P*, there being a considerable difference in height between the discharge and the level of the lead in the well. The lead must always be kept above the level *z z*, to prevent the entrance of matte into the siphon channel. The top works of the lead furnace are very similar to those of the copper furnace.

Dimensions and blast in lead and copper furnaces. Small copper and lead furnaces may be made with a round cross-section, but the use of small furnaces is rare. The common form of section is rectangular. The width of the furnace is determined by the penetration of the blast. The pressure of this is comparatively low, since the smelting column or height of furnace is low. The pressure varies in different furnaces from 20 to 60 oz. per square inch, which is very much less than that employed in the iron blast furnace. The ordinary width of the lead furnace at the tuyere level is 32 to 48 inches (Australian furnaces have widths up to 62 inches with a length of 212 inches); in copper furnaces it varies from 40 to 56 inches, depending on the size of the furnace. The length of lead furnaces is usually from 108 to 168 inches (9 to 14 ft.), while copper furnaces will range from 80 in. to 612 in. The size of a furnace is expressed by its area at the tuyere section, since this gives the *smelting area* and, other things being equal, marks the capacity of the furnace.[1] The capacity of a 48 × 168 in. lead furnace on an ordinary charge is 160 to 200 tons of charge per day. The capacity of a 56 × 180 in. copper furnace (Butte practice) is 400 tons of charge per day. Of course, capacities vary much, as the nature of the charge, type of slag produced, etc., all have a very decided influence. The effective height of the furnace is the distance from the tuyere level to the charge floor. This distance in the copper furnace varies from 8 to 18 ft. approximately, ordinarily being about 10 ft. The higher furnaces are rapidly coming into use, especially for pyritic smelting. The height of the lead furnace does not vary very much and is usually from 16 to 20 ft. This height is essential as the lead furnace is a reducing furnace. The copper matting furnace, on the other hand, is an oxidizing furnace. Reduction cannot be accomplished in too shallow a shaft. A certain height is also necessary to effectually abstract the heat from the ascending gases.

The number of tuyeres is dependent upon the length of the furnace; they are usually spaced 10 to 12 in. apart, center to center. The diameter of the tuyeres varies from 3 to 5 in. at

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[1] For dimensions and capacities of many different types of furnace, consult, Leistungen Metallurgischer Öfen, Metallurgie II, 393 (1905); also, volumes of Mineral Industry, articles on lead and copper smelting by H. O. Hofman and L. S. Austin, respectively.

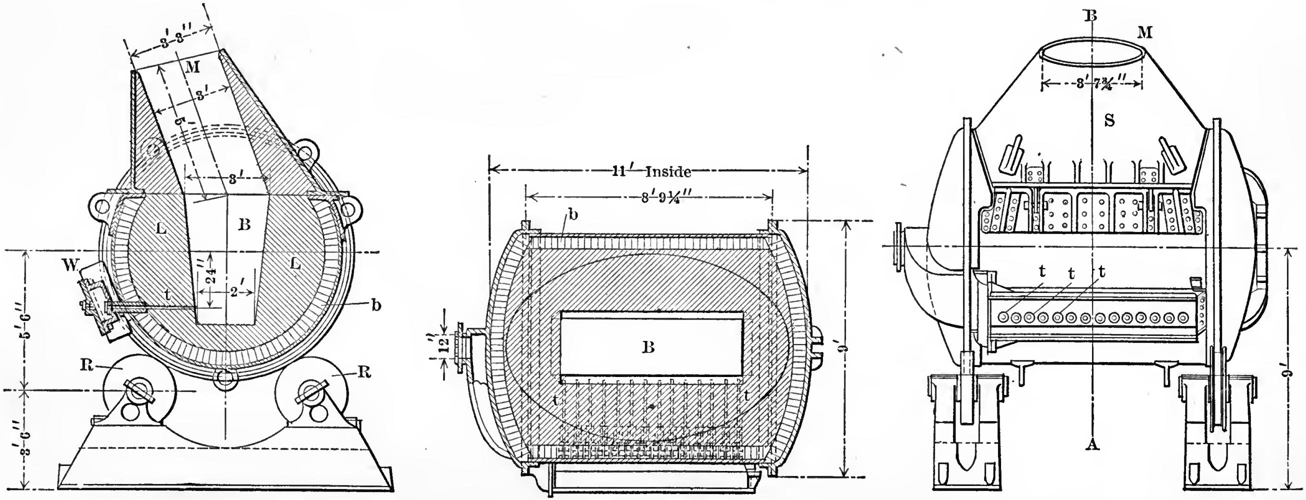

FIG. 144. — Copper Bessemer converter, after Shelby.

the nozzle, dependent upon the size of the furnace. The amount of air blown into the furnace depends upon the kind of smelting. In lead smelting an average is 100 to 150 cu. ft. per minute per square foot of hearth area; for ordinary copper matte smelting, 200 to 250 cu. ft., and for pyritic smelting 300 to 350 cu. ft. This air is determined by the displacement of the blower and its number of revolutions per minute, allowance being made for leakage in the blower and in the conveying pipes. As already stated, the amount of air is the important consideration, the pressure measuring the frictional resistance of the furnace to the passage of the furnace gases. The coke consumption in lead smelting is about 17 to 20 per cent. of the weight of the burden; in copper smelting it will vary from 14 to 16 per cent. in smelting oxidized ores, down to 2 to 3 per cent. when smelting pyritically.

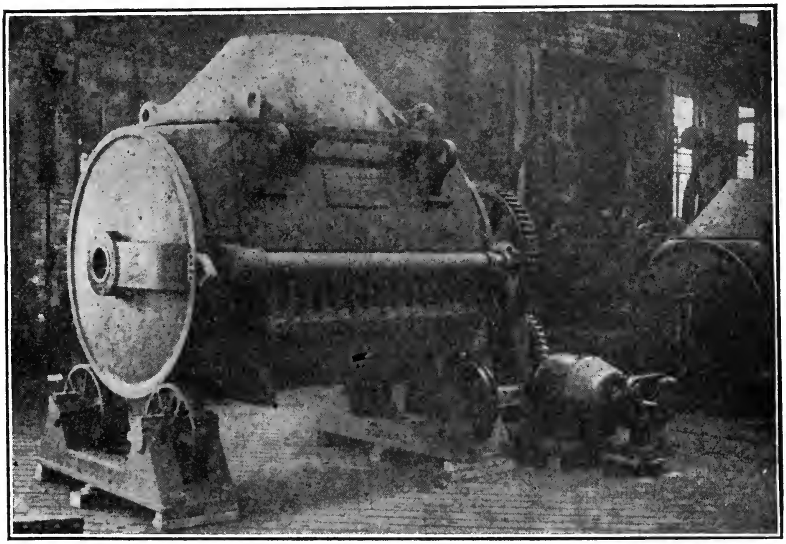

Fig. 145. — Electrically operated copper converter.

Converters. Fig. 144 shows a front elevation and two sections of the barrel type of converter for copper matte. It consists of a steel shell S thickly lined with gannister L inside of a course of fire brick b. On one side the converter is provided with the wind box W, into which open the tuyeres t, and which extend through the lining into the interior space B. The converter may be revolved by means of tires which rest on the rollers R,

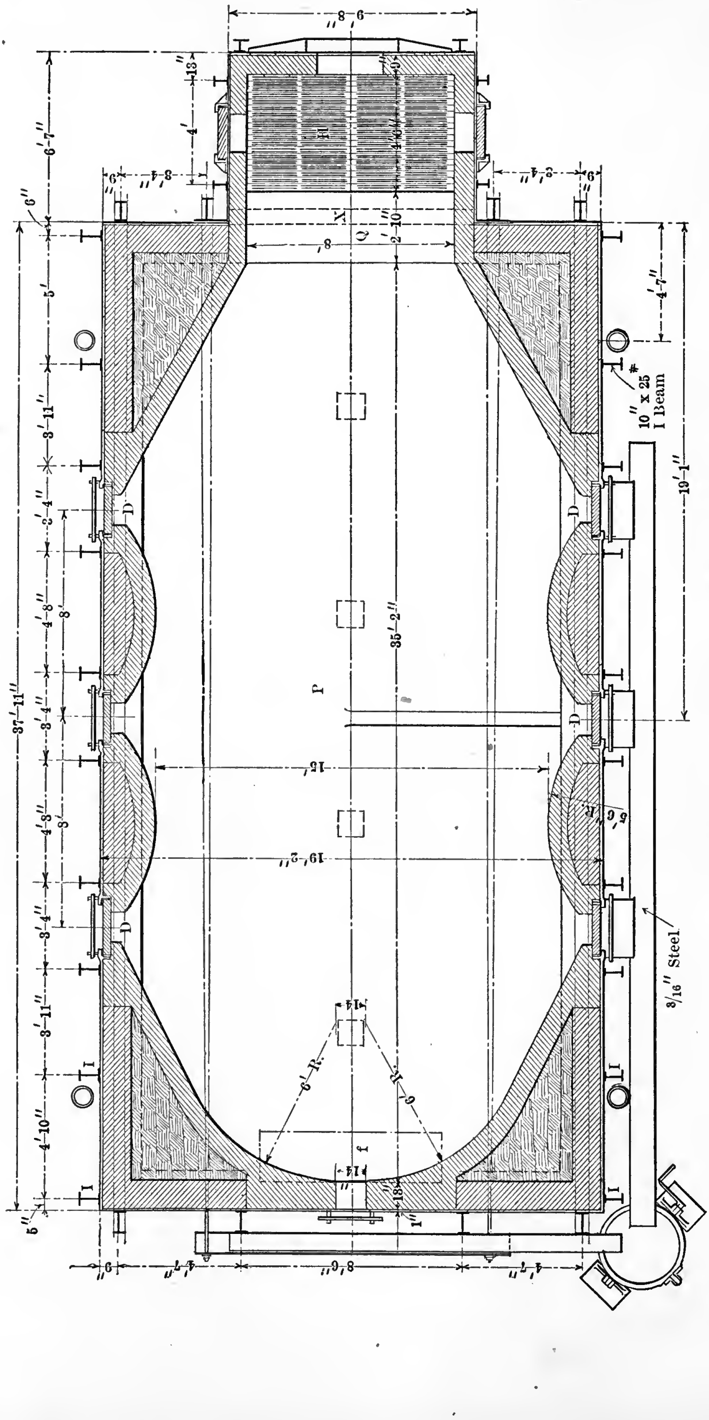

FIG. 146. — Reverberatory copper smelting furnace, plan.

by an electric motor, as shown in Fig. 145, or by a hydraulic cylinder. The mouth *M* of the converter discharges the gases produced by the reactions into a hood which leads to a flue and dust chamber. The converter, hot from a previous operation, is revolved to such a position, that in filling with molten matte, this will not run into the tuyeres. When filled with the proper amount of matte, the blast furnished by a blowing engine at 6 to 8 lbs. pressure is turned on, the converter revolved to its normal position, and the charge blown to copper, as briefly described on page 234.

When the converters are lined with an acid refractory material, this is corroded and must be renewed after three or five charges have been blown. The tuyeres are never allowed to blow air through the copper which has formed, but the converter is always held in such position that the blast enters such molten matte as still remains. Once or twice during the operation, slag is poured from the mouth, and at the end, when all the matte is converted into copper and slag, the copper is poured out into molds, and the converter is ready for the succeeding charge. Converter pots for roasting galena ores and copper ores by means of an air blast are very simple in construction and have been described on page 224.

II. Furnaces in which the fuel is not in direct contact with the furnace charge, but in which the latter is heated by conduction and radiation directly from the flame and products of combustion.

a. **Direct-Fired Reverberatory Furnaces.** — The reverberatory furnace consists essentially of an enclosed fire place upon which the fuel is burnt, the products of combustion and flame being conducted by means of draft created by a chimney into the hearth or smelting space, which is covered over by an arched roof so as to *reverberate* and reflect the heat back on the hearth upon which the operations of the furnace are conducted. The reverberatory furnace takes many different forms, dependent upon the purpose to which it is put, viz., smelting, liquating, roasting, etc. To fix the ideas as to the parts and construction of a reverberatory furnace, one for the smelting of copper ores is considered. Figs. 146, 147, 148, 149 represent the plan section, longitudinal section, and two cross-sections respectively. *H* is the fire place upon which the fuel is burnt, usually a long

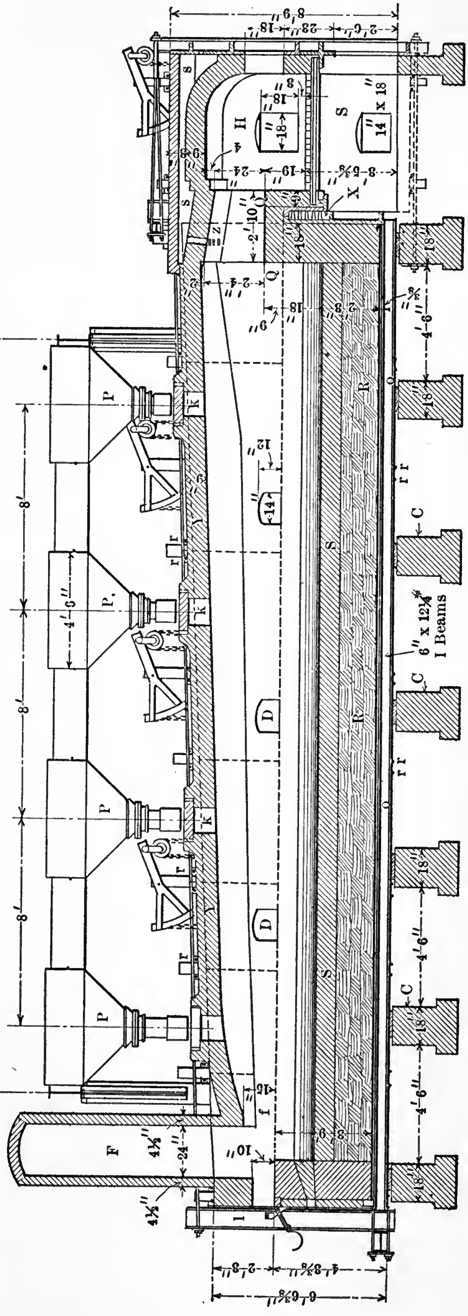

FIG. 147. — Reverberatory copper smelting furnace, longitudinal section.

flame bituminous coal. The fire place is divided from the hearth by the fire bridge or *bridge wall Q*, the flame and products of combustion passing over this wall into the hearth. The temperature at this point is very high, and to cool the bridge wall there is placed in it, extending from side to side, the hollow iron *conker plate X*. The air passes into this plate on one side of the furnace, then by a channel into the space *s* above the roof of the fire box, and thence through the openings *z* in the arch above the bridge wall, where it burns with the gases from the fuel. This device serves the double purpose of cooling the bridge wall and supplying preheated air for combustion. The proper supply of this secondary air is very important if complete combustion of the fuel is to be obtained. In some more modern furnaces, the conker plate serves merely as a cooling device, and the secondary air is admitted by a series of holes which can be kept open or closed as desired, placed in the roof above the bridge wall. The body of the furnace consists of the roof *Y*, which is an arch on the vertical cross-section, and which slopes

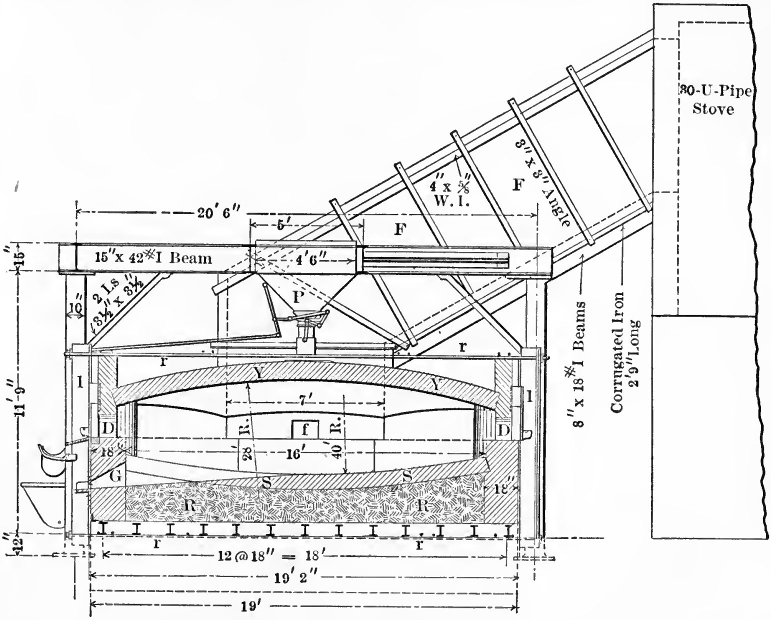

FIG. 148. — Reverberatory copper smelting furnace, cross-section through hearth.

back gradually to the flue *f;* the hearth proper or smelting bed, consisting of the *hearth arch S* resting on the filling mass *R* (either brick, cinder, rubble masonry), which in turn rests on the I-beams *o* which are supported on the piers *C*. In the best construction the hearth rests on a solid bed of slag or other suitable material and has no air space underneath, so as not to have an undue loss of heat by radiation at this point. The whole structure is tied together by means of the *buckstays I I*, which are held in position by the top and bottom rods *r r*. It is more desirable, however, to embed the lower ends of the buckstays in slag beds or masonry to avoid expansion. It is to be noted that the furnace is subjected to severe racking and strain due to expansion and contraction with changes of temperature, and that this firm binding is necessary to hold it together. During expansion the upper or roof arch rises and the hearth arch sinks in the crown, and during cooling tends to return to its normal position. When the hearth rests on a solid slag or masonry foundation the hearth *arch* may be absent. If the roof arch is originally too flat, this action may cause its collapse. The smelting hearth proper is built of furnace sand or magnesia

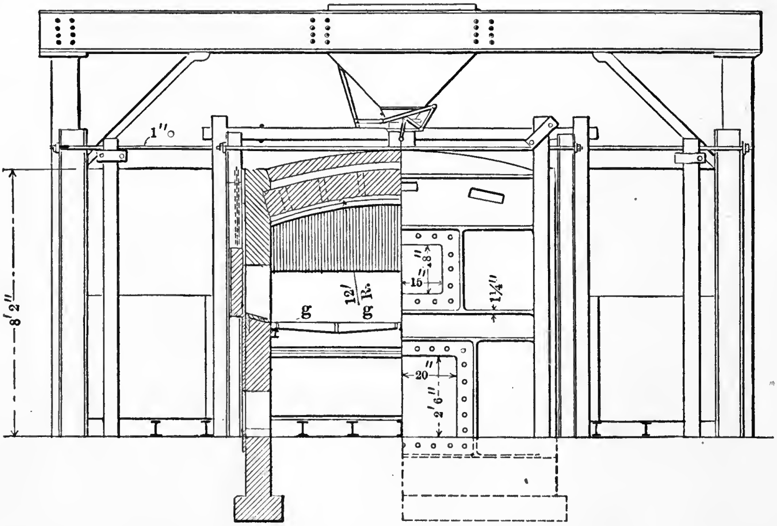

FIG. 149. — Reverberatory copper smelting furnace, cross-section through fire box.

on the arch, as described on page 335. The charge is introduced into the furnace from the hoppers P, through the openings in the roof K, most reverberatory furnaces being intermittent in their action, viz., finishing and discharging one charge before receiving the next one. The charge is leveled off, rabbled and stirred, by means of long furnace tools, through the doors D, which also serve to admit air for the combustion of unconsumed gases, though this method of furnishing secondary air is not desirable. The products of combustion pass out through the flue f to the main flue F, thence through dust chambers to the chimney. The roof and flues of the furnace are usually built of silica brick, while other parts are built of such refractory material as is best suited to the purpose.

Principles of construction of smelting reverberatories. (*a*) For any given smelting operation a certain temperature is necessary in the hearth of the furnace. This temperature will be termed the *working temperature,* and is that temperature at which the slag formed is thoroughly liquid and permits of the ready settling of matte or metal from it. For the smelting of ordinary copper ore mixtures it may be put at 1500° C. If the furnace be so designed in regard to grate area, draft, hearth area, etc., that this temperature attained represents the maximum effort[1] of the furnace, it is evident that considerable time will be consumed in reaching this working temperature, so that the smelting will be slow and the capacity of the furnace small, and usually the fuel consumption per unit weight of charge smelted will be large. In order to get a large capacity for any given furnace per day it is necessary that the various parts of the furnace be so designed that the *critical temperature,*[2] *i.e.* that at which the slag forms, plus 200 to 300° C. in addition as a margin be readily reached in a comparatively short time. This is done by employing a large fire place and a sharp draft so as to rapidly burn a comparatively large amount of coal per unit of time. The draft is obtained by the proper design of chimney and of the grate and flue areas.

(*b*) In order to make the whole hearth area of the furnace effective for smelting, the temperature at the flue end must be nearly

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[1] E. D. Peters, Metallurgie, II, 9 (1905).

[2] J. E. Johnson, T. A. I. M. E., XXXVI, 472 (1906). H. M. Howe, T. A. I. M. E., XXXVII, 217 (1907).

equal to the working temperature, and not much less than that at the fire-bridge end. This again implies the rapid combustion of large amounts of fuel. This high temperature at the flue end also necessitates the discharge of the products of combustion at a high temperature, which implies a great waste of heat unless the heat thus ordinarily lost can be utilized. In practice the waste gases are led through water-tube boilers, and the heat in part used for raising steam, or the *regenerative system* is employed (as in the metallurgy of steel) in which the waste heat of the products of combustion is used to preheat the air for combustion of the fuel, thus decreasing the amount of fuel used. Regenerative furnaces are described elsewhere in this chapter. In reverberatory furnaces for roasting ores, it is desirable that the temperature at the flue end of the furnace, where the ore is fed, be comparatively low, and that it gradually rise to its highest at the fire-box end of the furnace where the roasted ore is discharged. In this instance the products of combustion are at a temperature not much higher than is necessary to create the proper draft in the chimney.

(*c*) The main source of loss of heat in reverberatory furnaces is that by radiation and conduction through the walls, roof, and hearth of furnaces. The walls and roof should be built as thick as possible and still have enough radiation to prevent their burning out. High grade of refractory material should be used. Formerly the hearth of the furnace was built over cooling vaults to induce radiation and thus prevent the deepening of the hearth by corrosion, but modern furnaces are built with the hearth directly on solid slag blocks, or blocks of other suitable material, to prevent radiation and loss of heat, while the deepening of the hearth is avoided by keeping a bed of matte or metal on it, thus preventing the access of air. The deepening of the hearth is usually caused by a too complete draining of the furnace contents which permit the formation of metallic oxides on the hearth by the access of air, thus causing a rapid corrosion of the siliceous lining of the hearth.

(*d*) In the operation of reverberatory furnaces, loss of heat through open doors, unnecessary admission of air, and frequent stirring of the furnace charge should be avoided, as all these factors lower the furnace capacity. Older reverberatory smelting furnaces for copper ores were essentially non-continuous in their

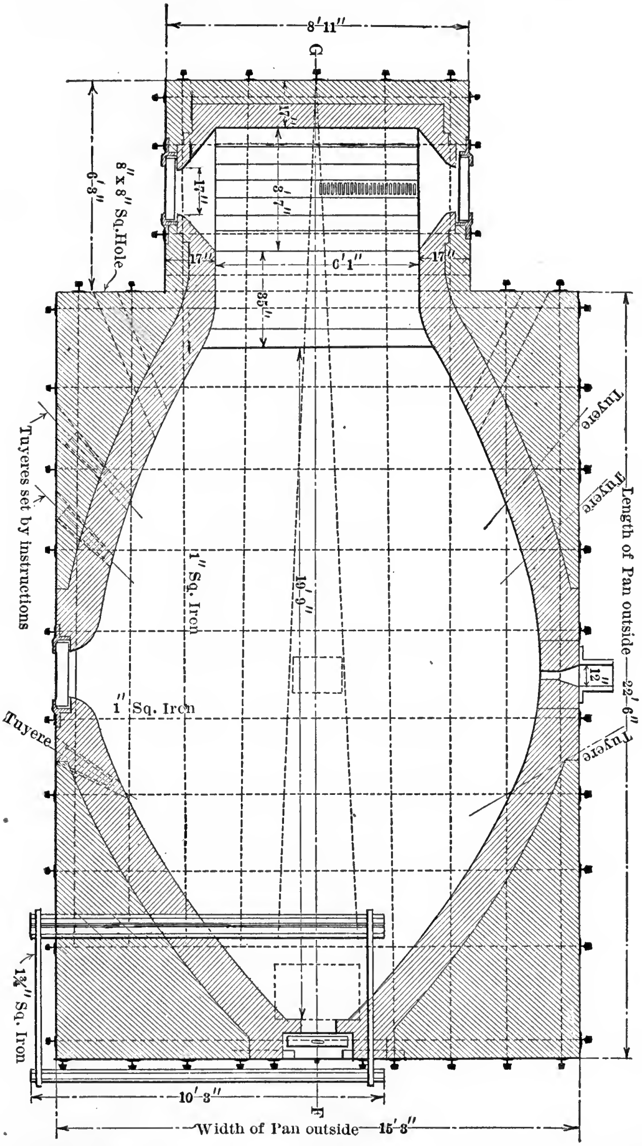

Fig. 150. — Reverberatory furnace for refining copper-lead matte, plan.
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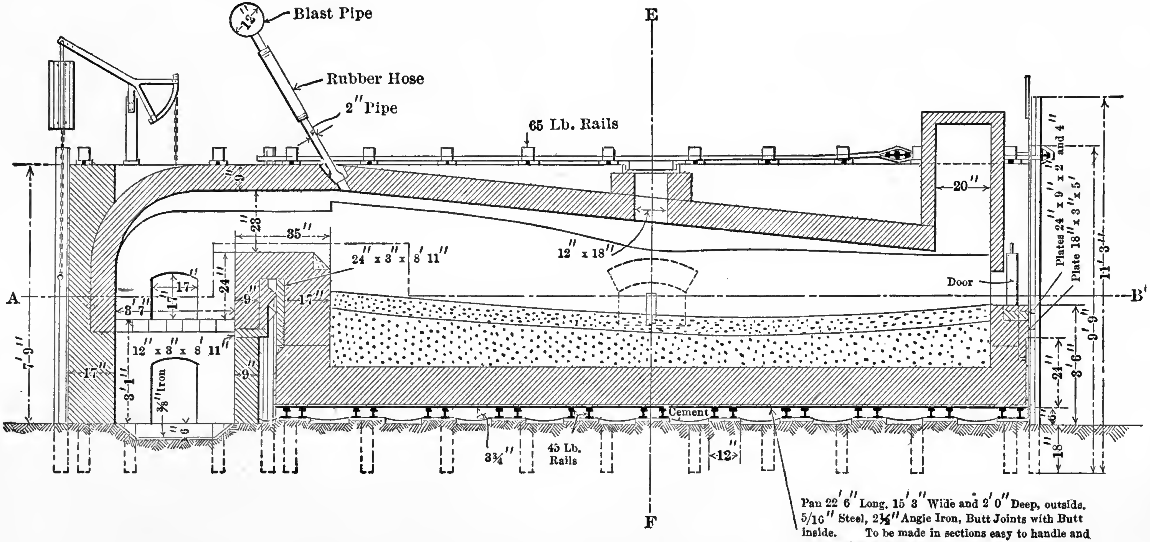

Pan 22′ 6″ Long, 15′ 3″ Wide and 2′ 0″ Deep, outside. 5/16″ Steel, 2½″ Angle Iron, Butt Joints with Butt inside. To be made in sections easy to handle and put together at smelter.

FIG. 151. — Reverberatory furnace for refining copper-lead mattes, section.

action. The ore charge was introduced into the furnace, then the fire urged until the charge began to smelt, the charge meanwhile being uniformly distributed over the hearth by long tools or *rabbles* worked through the furnace doors, and as the charge became molten, those parts which adhered to the hearth had to be loosened. When the charge was finally completely molten and the matte had settled, the slag was drawn off through the *slag* door and the last of it *skimmed* from the matte. As the last step, the matte was tapped from the furnace, which was practically emptied. A new charge was then introduced and the operation repeated. The complete discharge of the furnace and the frequent opening of the doors caused excessive cooling from which the furnace recovered but slowly. The smelting was therefore slow and the capacities were small. In the large modern furnaces a heavy bed of matte and some slag is always kept in the furnace and ore charged at regular intervals, in comparatively small amounts, while slag and matte are also with-

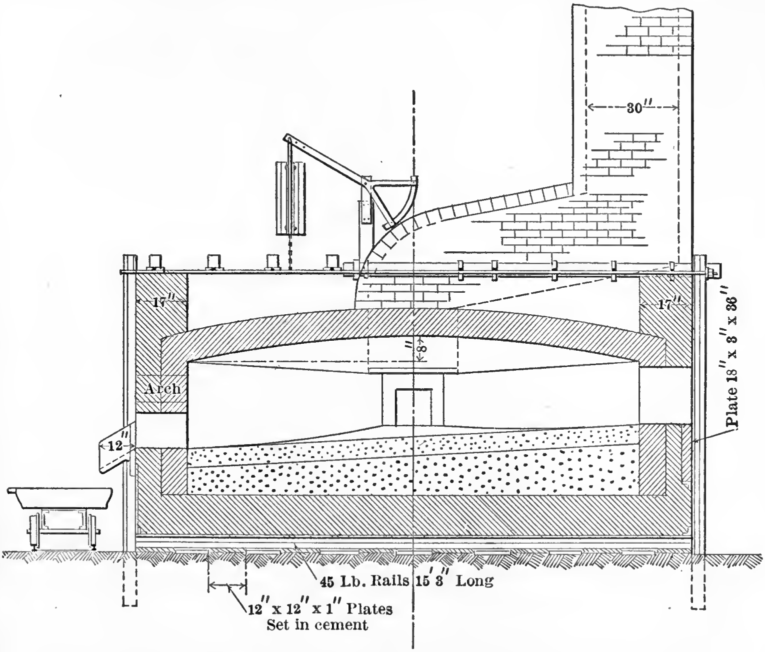

FIG. 152. — Reverberatory furnace for refining copper-lead matte, cross-section.

drawn at regular intervals, but no attempt is made to drain the furnace. This method avoids the difficulty due to unsmelted portions of the charge sticking to the hearth, and the frequent opening of doors with the accompanying loss of heat, and makes the operation of the furnace practically a continuous one.

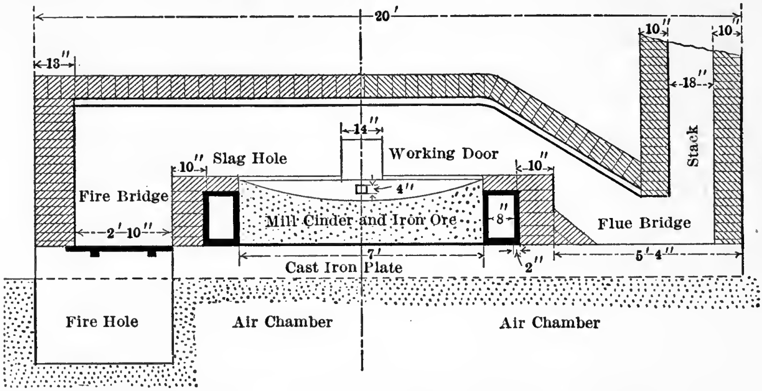

Fig. 153. — Longitudinal section of a puddling furnace.

(*e*) In the furnace, at the level of the liquid charge and at the junction of the hearth lining with the walls of the furnace, considerable corrosion of the lining sometimes takes place. From time to time, in some furnaces almost after every charge, repairs must be made at these points. This is done by tamping a mixture of three parts furnace sand and one part fire clay into

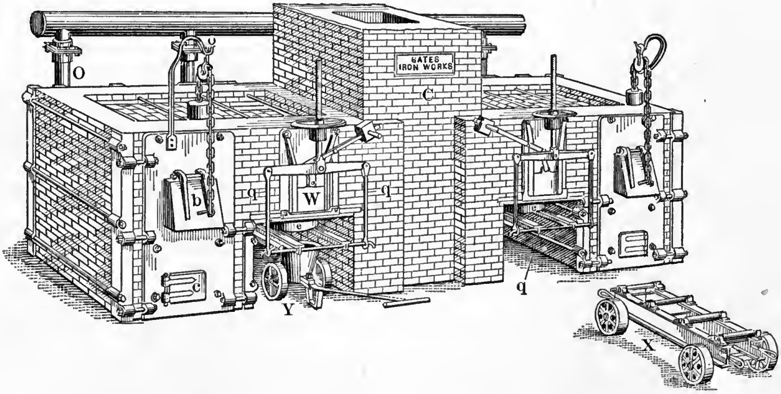

Fig. 154. — General view of an English cupeling furnace.

place and patching worn spots. This operation is known as *fettling*.[1] It involves very hard and arduous labor and is to be avoided as much as possible. In the large modern reverberatories which are operated as described, the amount of this repair work is much decreased. In the larger furnaces ample provision is made for expansion in roof and walls by building these in distinct sections, leaving spaces 2 to 3 inches wide between them. When the furnace heats up the sections join and the spaces disappear.[2]

Table LXXXVII gives data on various reverberatory furnaces.

TABLE LXXXVII. DATA ON REVERBERATORY FURNACES

Furnace	Dimensions of fire place, in feet	Dimensions of hearth, in feet	Dimensions of chimney, in feet	Lbs. coal per hour per square foot grate area	Lbs. coal per ton charge smelted or roasted	Tons charge smelted in 24 hrs.	Ratio grate area to hearth area	Ratio grate area to chimney area
Ore smelting, Swansea, 1848	$4\frac{2}{3} \times 4\frac{1}{4}$	13×9	$2 \times 2\frac{1}{3}$	—	1554	16.20	1:6	4.3 :1
Ore smelting, Argo, Colo., 1891	$6 \times 4\frac{3}{4}$	$24\frac{1}{3} \times 14\frac{1}{6}$	3×3	29.22	713	28.00	—	3.17:1
Ore smelting, Argo, Colo., 1894	$6\frac{1}{2} \times 5$	35×16	4×4	34.62	540	50.00	—	2.03:1
Ore smelting,[3] Butte, 1902	$10 \times 5\frac{1}{2}$	50×20	$5\frac{1}{2}$ dia.	55.00	655	112.50	1:15.6	2.31:1
Ore smelting, Anaconda, Mont., 1904	16×7	102×19	—	42.50	415	275.00	1:17.3	—
Ore roasting, sulphide, O'Harra straight line furnace	13×6.6	78×8	—	2.50	200	25.00	1:20	—
Hand reverberatory roasting furnace, sulphide ores	—	69.5×16	—	—	307	13.00	—	—
Edwards furnace, siliceous gold ores	—	111×13	—	—	300	110.00	—	—

Figs. 150, 151, and 152 show a plan section, longitudinal section, and cross-section of a reverberatory furnace for refining copper-lead mattes to blister copper. The door at the flue end is for skimming out the lead-iron slag. The door at the side of the furnace is for tapping out the copper, and its lower part or "breast" is made of crushed limestone, which is cut down as

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[1] H. M. Howe, Copper Smelting, Bul. 26, 46, U. S. G. S. (1885).

[2] C. Offerhaus, E. and M. Jour., LXXXV, 1189, 1234 (1908).

[3] H. O. Hofman, T. A. I. M. E., XXXIV, 292 (1904).

the level of the copper in the furnace decreases from successive tappings. The bottom of the furnace is made of a layer of fire brick on which is a layer of magnesite brick. The furnace is distinctively an oxidizing furnace as the air pipes will indicate. In modern practice the production of copper from lead-copper mattes is accomplished in basic lined converters to a large extent.

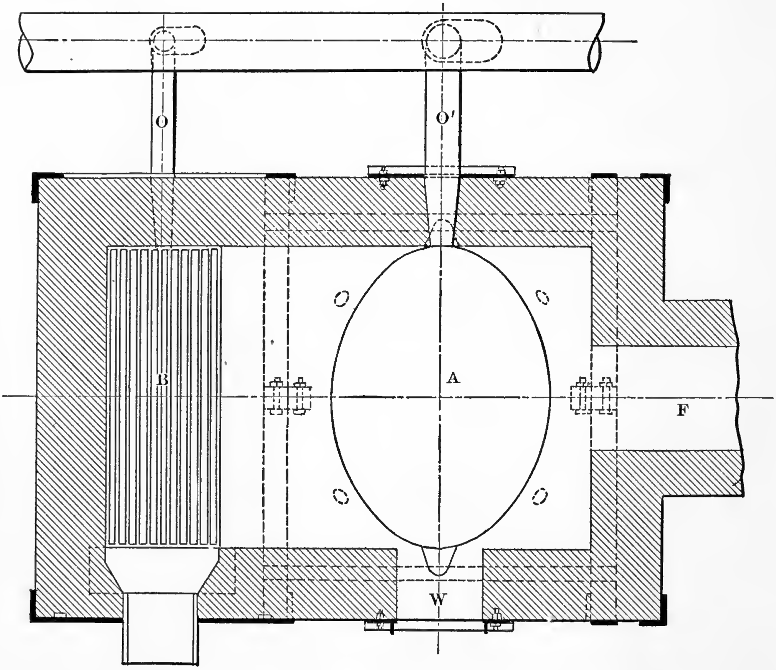

FIG. 155. — Elevation section of a cupeling furnace.

Fig. 153 shows the longitudinal section of a *puddling* furnace for the making of wrought iron from pig iron. The pig iron and scrap iron is melted down in the furnace, and the impurities — C, Si, Mn, etc. — are oxidized and in part slagged with some of the iron. As the impurities are driven off the mass becomes pasty and is worked with furnace tools into *blooms* or balls, which operation is known as puddling. The balls are removed from the furnace and hammered to expel the slag and then rolled into shapes.

Fig. 154 shows a general view of an English cupeling furnace, and Figs. 155 and 155*a*, a plan section and an elevation of the same, respectively. The furnace is used for the cupellation of gold or silver lead bullion, obtained from the desilverization of lead bullion by the Parkes or the Pattinson process or in any other manner. The furnace consists of a fire place *B*, the cupel or *test* *A*, and the flue and chimney *F* and *C*. The cupel or test is made of boneash, magnesia, limestone and cement, or other mixtures, is oval in shape, about 5 × 4 ft., and rests on a plate which is supported by the hangers *q* and may be readily removed by means of the car *X*. The test proper, or the

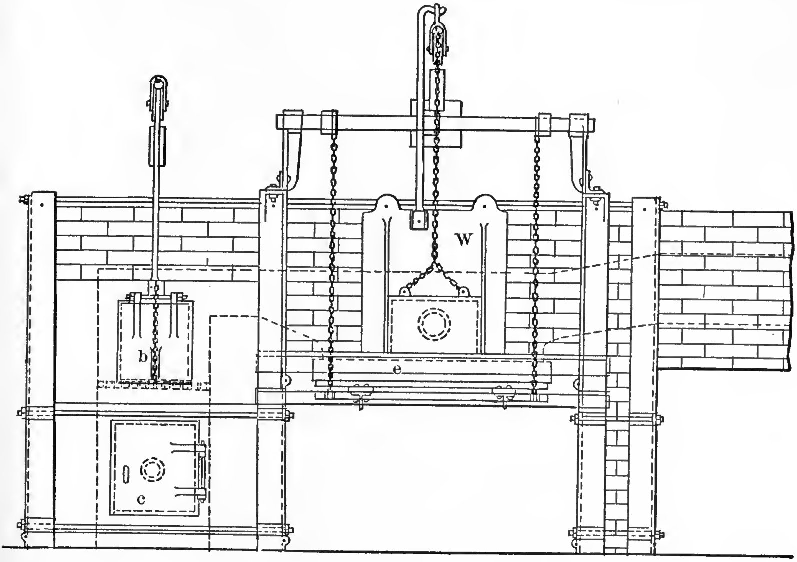

Fig. 155*a*. — Plan section of a cupeling furnace.

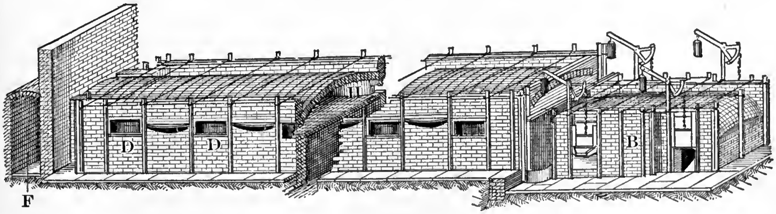

Fig. 156. — Hand roasting reverberatory furnace.

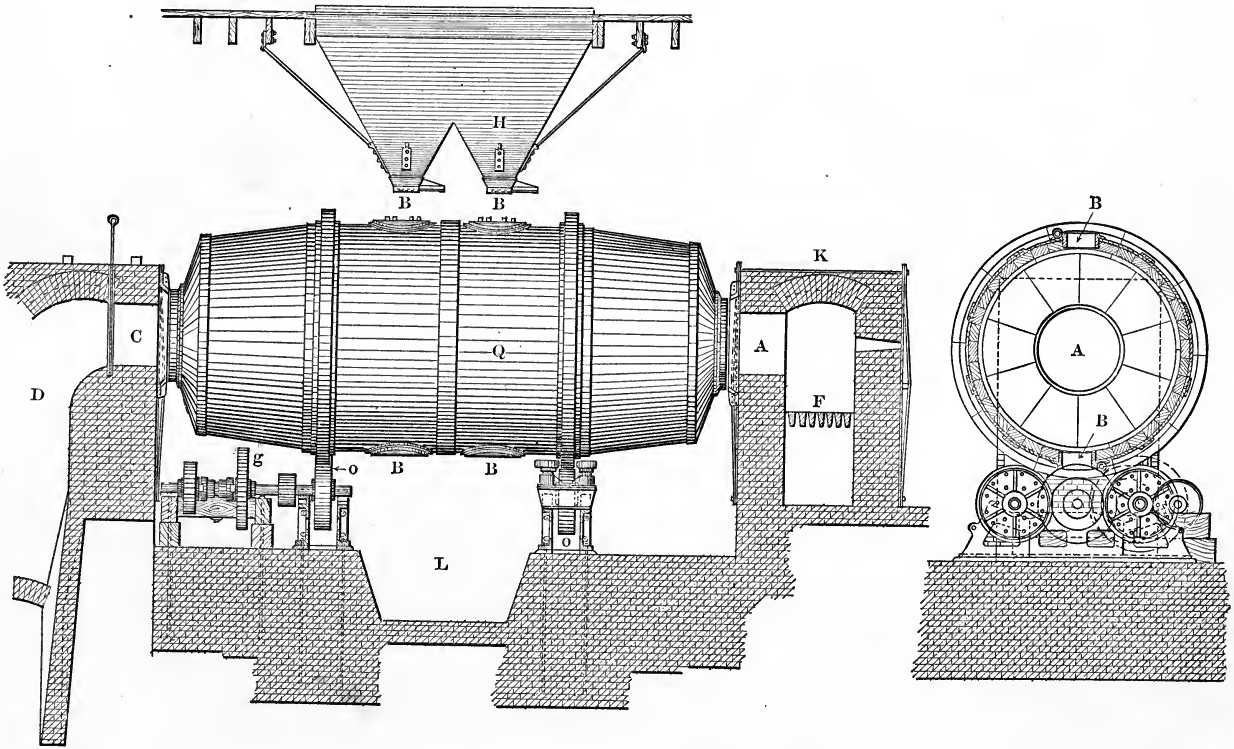

FIG. 157. — Brückner roasting furnace, 7 × 18 ft. size.

material of which it is constructed, is surrounded except at the litharge tap by an annular or elliptical hollow iron ring or water jacket *e*. The space in the water jacket occurs at the door *W*, where the litharge is drawn off into the pot *Y* through a gate cut into the test material. Forced draft may be applied to the fire through the blast pipe *O*, and air blown on the molten lead by means of the pipe *O'* to hasten the formation of litharge. The lead bullion is charged into the test and melted down. The litharge is skimmed through the door *W*. The fire and ash pit doors are shown in *b* and *c* respectively.

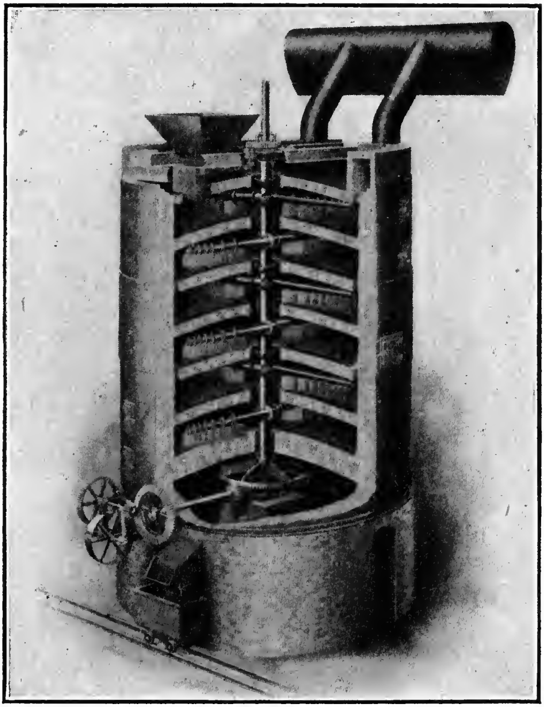

Fig. 158. — Multiple-hearth MacDougal roasting furnace.

Fig. 156 shows a reverberatory roasting furnace in which the ore is charged through a hopper in the roof of the furnace near the flue *F* and gradually worked forward by hand by means of rabbles operated through the doors *D*, toward a discharge slit in the hearth of the furnace near the fire bridge. The fire place of the furnace is shown at *B*. This type of furnace was formerly much used and is still used to some extent in the roasting of lead ores, and also for the roasting of copper and gold ores. It is the ancestor of practically all mechanically operated roasting furnaces, but has practically been displaced by these.

Fig. 157 shows the elevation and cross-section of the Brückner roasting furnace. It consists of the cylindrical iron shell *Q* lined with fire brick, which revolves slowly on tires bearing on the rollers *o*. The motive power is furnished by a shaft driven by the gearing *g*. The furnace revolves between the fire box *K*, in which the fuel is burnt on the grate *F*, and the dust chamber *D*. The flame and products of combustion pass through the opening *A* into the cylinder, and out at the flue *C*, through the dust chamber *D*, to the chimney. The ore charge to be roasted is fed into the furnace from the hopper *H*, through the doors *B B*. As the furnace revolves the ore is carried up on the walls of the cylinder and then falls through the flame, thus giving a very thorough exposure to the heat. When the furnace is ready to discharge, a car is run under it in the space *L*, the doors opened and the furnace revolved until empty. It is then recharged and the operation repeated. The furnace, like the hand roasting reverberatory, is non-continuous in its action, and for this reason has largely been replaced by the later type of automatic continuous furnaces. It is, however, still in use, and since the roast can be carried on for any desired time, insuring its completion before discharge from the furnace, it possesses certain advantages where it is essential that sulphur be completely removed from the ore.

Fig. 158 shows a multiple-hearth, automatic continuous roasting furnace of the McDougal type, employed very widely for roasting copper sulphide ores and concentrates sufficiently high in sulphur contents to be self-roasting (above 25 per cent.). The crushed ore (4 to 10 mesh) is fed into the hopper at the top of the furnace, from which it passes to the upper or first hearth by a roller feed, at a definite rate. A central water-cooled column, driven by gearing from below, has attached to it in each hearth a double water-cooled arm, to which are fastened the rabbles or plows. The ore is fed to the top hearth at its periphery, the plows on the rabble arm in this hearth being so inclined that it forwards the ore to the center of the hearth, at which point it drops through an annular opening to the hearth below. The rabbles on this hearth are set in an opposite direction to those above, so that the ore is forwarded from the center to the periphery, and then discharged through an annular slot to the hearth next below.

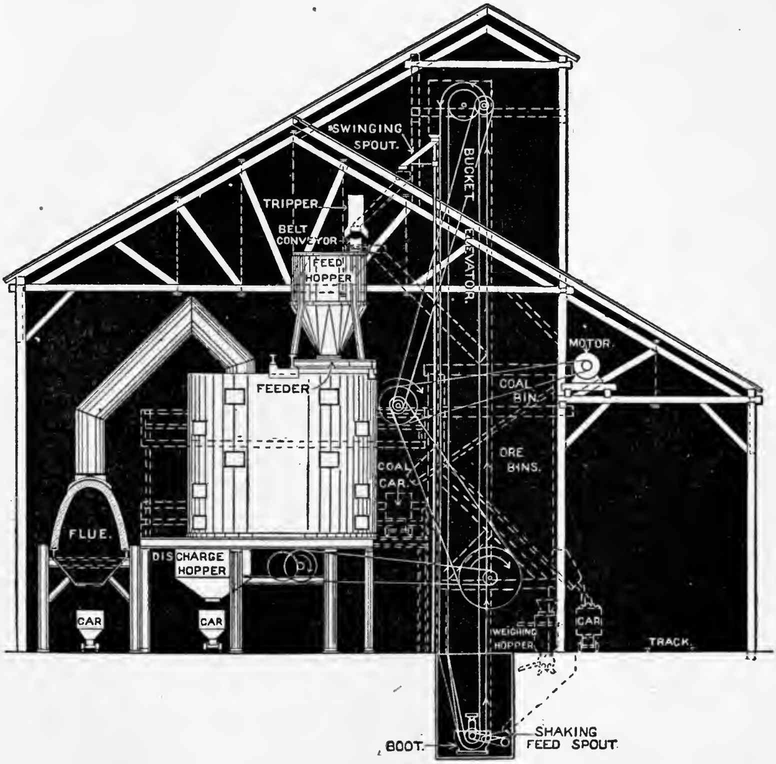

Fig. 159. — Cross-section of a roasting furnace house.

In this manner the ore is forwarded successively through all six hearths and discharged from the last one into cars, and conveyed while still hot to reverberatory furnaces for smelting. The furnace is provided with a fire place on one side which opens into the lower hearth and which is used to start the roasting when the furnace is put into commission, or may be used constantly when the sulphur in the ore is not high enough to make the ore

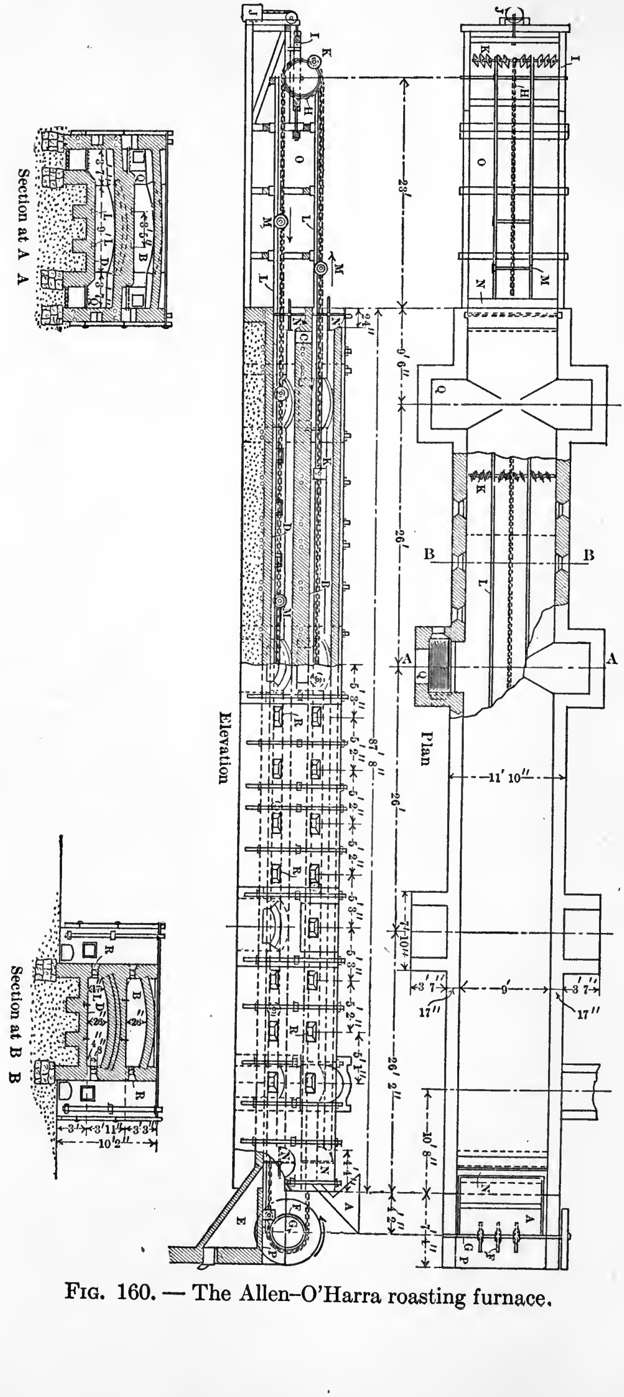

FIG. 160. — The Allen–O'Harra roasting furnace.

self-roasting. The roasted ore or calcines as discharged usually contain 7 to 8 per cent. sulphur.

Fig. 159 shows a cross-section of a roaster house which requires no further explanation.

Fig. 160 shows the Allen-O'Harra[1] roasting furnace. This is a double-hearth, straight line mechanical furnace, in which the ore is fed automatically from the hopper *A* on to the upper hearth *B* and is moved forward on the hearth by the plows until it drops through the slot *C* to the lower hearth *D*. It thence traverses the lower hearth until it reaches the discharge *E*. The chain is driven by the sprocket wheel *F*, on the shaft *G*, and is kept taut by the wheel *H* in the sliding frame *I*, which is provided with a weight *J*. Six sets of plows, *K*, are attached at equal intervals to the chain. They are carried on wheels running on the track *L*. The chain is also supported by simple trucks *M*, midway between the plow carriages. It will be noted that the vanes on the separate halves of the same plow turn furrows in opposite directions; also that the same plow on the upper floor turns furrows in a direction opposite to its furrows on the lower floor, and that each plow turns furrows in a direction contrary to those made by the plow preceding it. The hearths are closed at each end by horizontal turnstile doors *N*, actuated by the moving carriages. The cooling space *O* for chain and plows is 23 ft. in length. The grid *P* at the driving end of the furnace is intended for convenience in repairing chains and plows. There are five pairs of fire boxes, three for the lower hearth and two for the upper, though only one or two pairs are commonly used.

Fig. 161 shows a general view of the Edwards duplex roasting furnace, and Fig. 162 a cross-section of an Edwards tilting furnace. The latter illustrates the operation of the rabble, which is the same for all Edwards furnaces.

The furnace is a rectangular reverberatory, the hearth dimensions being 111 by 13 ft., giving an area of 1443 square feet. The slope of the hearth is one-half inch for one foot of length. The whole structure is well braced with buckstays and tie-rods. The steel structure supporting the rabbling mechanism is built on top of the furnace. It consists of angle-iron brackets and longitudinal angle irons extending the length of the furnace and

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[1] E. D. Peters, Modern Copper Smelting, 202 (1895).

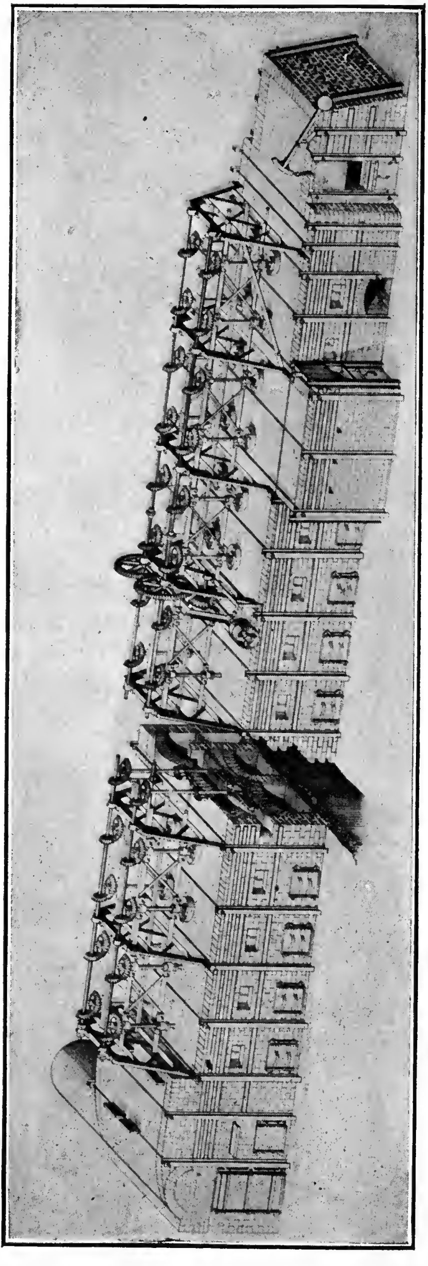

Fig. 161. — General view, Edwards duplex roasting furnace.

fastened to anchor bolts built into the side walls. Two line shafts run the length of the furnace and are supported in bearings on top of the brackets. These shafts are provided with spur wheels near the middle of the furnace and are driven with a center drive. From the line shafts are driven 44 rabbles by means of bevel crown and pinion wheels; the rabbles enter the roaster through cast-iron boxes built in the roof of the furnace. Each rabble is independent of the other and they revolve in opposite directions, the rabbles describing a circle. During a revolution each rabble bisects the circle of the adjacent rabble. They make three revolutions per minute.

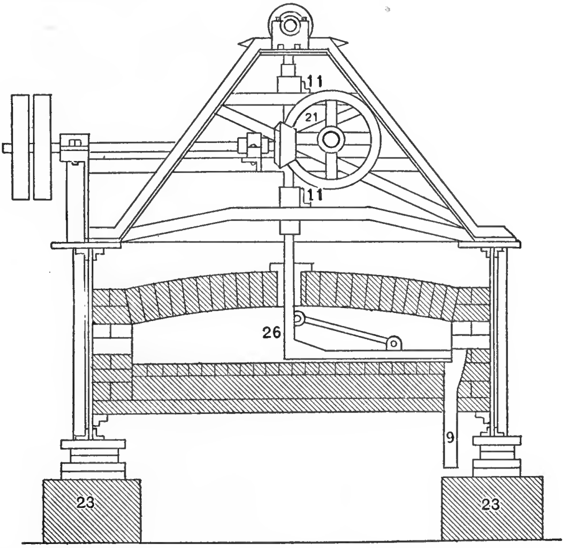

FIG. 162. — Cross-section Edwards tilting furnace.

The 44 rabbles are placed in two rows of 22 each along the length of the furnace, the bottom of the rabbles nearly touching the hearth. Each rabble has a circular path, the circumference of which almost touches the brick work on either side, and as the distance between the rabbles is only little greater than the radius of the circle described, each rabble works ore almost up to the heel of its neighbor, consequently the amount of hearth area unworked by the rabbles is very small; and as each rabble rotates in the opposite direction to the one next it — they are alternately right- and left-hand rabbles — the ore is not passed along too rapidly from one end of the furnace to the other, but gets a thorough stirring and exposure to the air as it proceeds on its course. To protect the rabbles in the hotter part of the furnace from the destructive action of the high temperature, in some furnaces water is circulated through the last three to keep them cool. There are two different kinds of rabbles used: One is solid and flat-footed, the front edge of which is beveled; the other is hollow and on the arm of it cast-iron shoes are fitted. The latter type rabble is the one used at the fire end of the furnace. The cast-iron shoes can be slid on or off the rabble arm without lowering the heat of the furnace or removing the rabble from it. When roasting concentrates, or ores high in sulphur, the first 15 rabbles, counting from the feed end, are generally of the solid, flat-footed type; these pass through the ore close to the hearth and effectively stir and expose the particles of ore so long as they carry a fair percentage of sulphur. The last seven rabbles are provided with cast-iron shoes, as by the time the ore reaches this part of the furnace it has lost most of its sulphur and is less lively. These shoes pass through and under the ore. They make a more effective stirrer when the ore lies dead, and leave a corrugated surface behind, thus exposing a greater area for oxidation than if the surface were level. When roasting ores that do not contain much sulphur, shoes are used on all the rabbles, though, of course, water need only be circulated through those subjected to the greatest heat. The wear and tear of the whole furnace is small and is confined almost exclusively to those rabbles nearest the fire. When they have to be removed, the cost is small and they can readily be renewed by unskilled labor in a few minutes. The power required to work the furnace is 8 horse-power. The ordinary flat-footed rabble arm is fastened to the spindle by placing the end in a socket and passing a pin through both. The water-cooled rabbles have a 3⅛ in. cast-iron hollow spindle with a flange at the bottom, which is bolted on to a corresponding flange on the upper part of the arm.

The ore is conveyed by an automatic feeder from the hopper to the hearth at the upper end of the furnace; after traveling to the lower end, near the fire, the ore is discharged down a pipe, situated near one of the sides; the bottom of this pipe passes through and works in a case leading to a conveyor, which effectively prevents any escape of dust. This conveyor pushes the ore into a pit. During the roasting air is admitted through end holes, situated above the fire bars.

In the furnaces for roasting telluride gold ores at Colorado City, Colorado, three fire boxes are attached to the furnace, one at the fire end and one on each side of the furnace, to insure the necessary temperatures for roasting. A series of portholes runs the whole length of the furnace on both sides These ports are provided with doors to admit air to any part of the furnace when necessary. The rabbles are all water-cooled, to protect them against the high temperature The furnace is equipped with automatic ore feeders and automatic discharge.

This furnace roasts about 100 tons of sulpho-telluride ore in 24 hours. The ore is crushed to 6 mesh, which produces a product of the following screen analysis:

Remaining on	30 mesh	66 per cent.
" "	40 "	6 " "
" "	60 "	8 " "
" "	80 "	4 " "
" "	100 "	3 " "
" "	150 "	4 " "
" "	200 "	1 " "
Through	200 "	8 " "
		100 " "

The ore is fed by an automatic feeder, delivered through a hopper with a pipe, and allowed to fall on top of the arch of the furnace in the center, close to the first four rabble spindles. To each of these rabble spindles is attached an involute curve made of 3 × $\frac{3}{8}$ in. flat iron and bolted firmly to the rabble. As these curves revolve they each take their portion of the coned ore and deliver it into the hearth of the furnace around each spindle, thus feeding the ore at four different points and giving an even distribution of the ore on the hearth from the start.

The ore to be roasted contains 2 per cent. sulphur. To handle the 100 tons in 24 hours, the furnace had a capacity of 138.60 pounds of ore per square foot of hearth area per 24 hours. The coal used is Colorado lignite, which is burnt in gas-producing fire boxes. The combustion is perfect if the boxes get proper attention, and cheap lignite under these conditions is preferable to more expensive bituminous coal burnt in open grates, though 25 to 30 per cent. more coal is used Test runs made on lignite coal, roasting 110.88 tons of ore in 24 hours, showed a consumption of 15.6 tons of fuel, or 300 pounds of coal per ton of ore.

Particular attention is paid to the nature of the discharged roasted ore. It should be of a good red color, the iron existing in the form of ferric oxide (Fe_2O_3) and little magnetic oxide should be found. The roasted ore, when the capacity of the furnace is 100 tons per 24 hours, contains on an average about 0.03 per cent. sulphur.

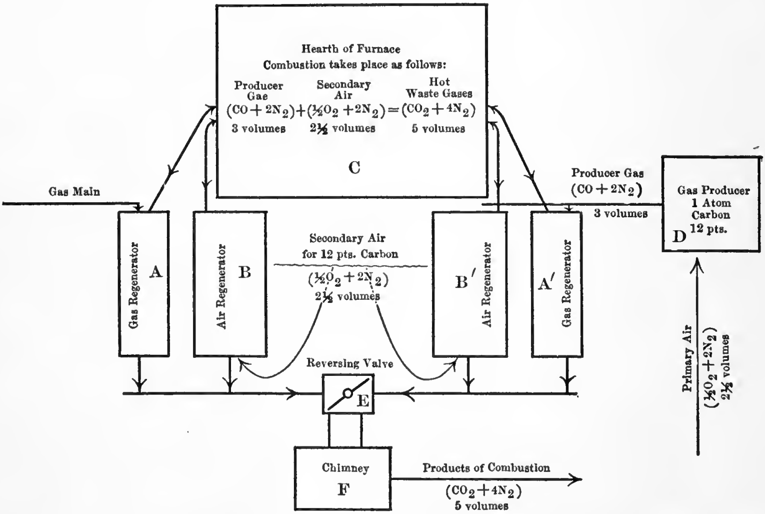

FIG. 163. — Diagrammatic sketch of a regenerative reverberatory furnace system.

The furnace requires one man per 8-hour shift, his duty being to feed coal to the fire boxes, and pay attention to the temperature and mechanism of the roaster.

b. **Regenerative Reverberatory Furnaces.** — Furnaces of this type are usually gas fired and designed with regenerative chambers to recover the heat in the waste products of combustion and transfer the same to the air and gas to be burnt in the furnace, thus preheating them. The effect of preheating air and gas has been dealt with in Chapter XII, p. 413. As the ultimate requirement of the combustion of fuel is the attainment of a certain working temperature in the furnace, dependent upon the specific work to be performed, it is evident that the less fuel is required to furnish the heat units necessary to attain this temperature, the more economical will be the operation. In the regenerative furnace the object is to transfer the calories of heat (all except those required to obtain chimney draft) in the products of combustion to the air and gas to be burnt, in this manner directly cutting down the amount of fuel used, in proportion to the heat furnished by the products of combustion. The practical application of this principle is due to Sir William Siemens, who applied it first to steel furnaces. Furnaces of the regenerative type are usually complex and costly to construct, and are employed only when the products of combustion have a high temperature, viz., above about 1200° C., since otherwise the heat recovered does not warrant costly installation. The regenerative principle may be applied to almost any reverberatory furnace either direct fired or gas fired, but is best adapted to gas-fired furnaces. Very high temperatures can be attained by the use of the regenerative principle, far in excess of those obtained by direct firing.

Fig. 163 is a diagrammatic sketch of a regenerative reverberatory furnace system. Gas is made in the producer *D*, $2\frac{1}{2}$ volumes of *primary air* uniting with 1 part carbon to produce 3 volumes of producer gas. This passes through the gas regenerator *A*, which is a brick structure enclosed in iron plates to make it tight and filled with special shaped fire brick, set checker fashion, so that the gas passing between the interstices of the many hot brick (about 1100 to 1200° C. at the beginning of the reversal) absorbs the stored heat and becomes highly preheated. The *secondary air*, $2\frac{1}{2}$ volumes, in the same manner passes through the air regenerative chamber *B*, becoming preheated. The gas and the air are conducted by canals to the hearth of the furnace, which they enter through separate ports, the gas port being situated below the air port. At the ports they burn and the flame sweeps across the hearth, the products of combustion, 5 volumes (one of CO_2 and four of N_2), passing out through ports similar to the first ones, through the second set of regenerative chambers, *A′*, *B′*, to which they give up their heat, and thence through flues and the reversing valve *E* to the chimney *F*. When the regenerative chambers *A* and *B* have become cooled by the passage of cold air and gas, and A′ and B′ become highly heated by the passage of the products of combustion, the valve *E* is reversed, and the gas and air now pass through the chambers *B′* and *A′*, becoming preheated, while the products of combustion pass through the cooled chambers *B* and A, giving up their heat to them. In steel practice the reversal of the regenerators takes place about every 15 to 20 minutes. It can be shown that the more frequent the reversal, the higher will be the temperature attained in the hearth.

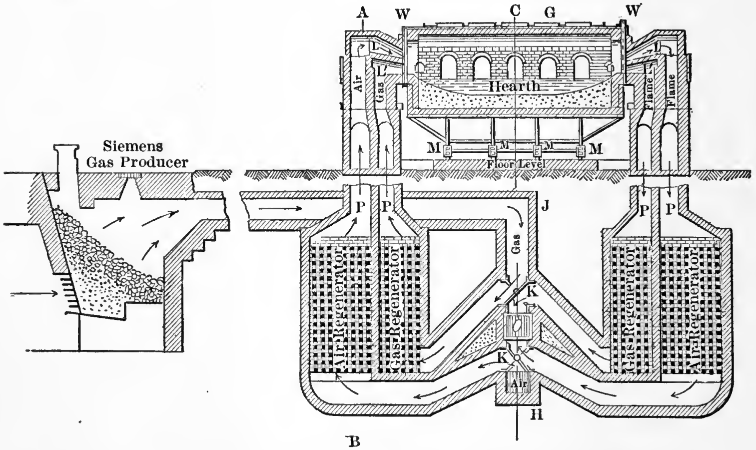

Fig. 164. — Plan view of regenerators, flues, and reversing valves.

Fig. 164 [1] shows a plan view of the regenerators, flues, and reversing valves and sectional elevation of the hearth, air, and gas ports of an open-hearth steel furnace. Figs. 165 and 166 show the front elevation and section and the end elevation and section respectively of a tilting open-hearth furnace,[2] with a capacity of 20 tons of steel per *heat*. This particular furnace is fired by natural gas and has air regenerators only, the gas not being preheated. The regenerative chamber is shown in *B*, the hearth at *H*, the air port at *C*, and the gas port at *D*. The furnace is charged mechanically by the hydraulically operated ram *K* which pushes the iron and steel scrap, which makes up

[1] By permission of H. M. Howe, from "Iron, Steel and other Alloys."

[2] Made by the Wellman, Seaver, Morgan Eng. Co., Cleveland, Ohio.

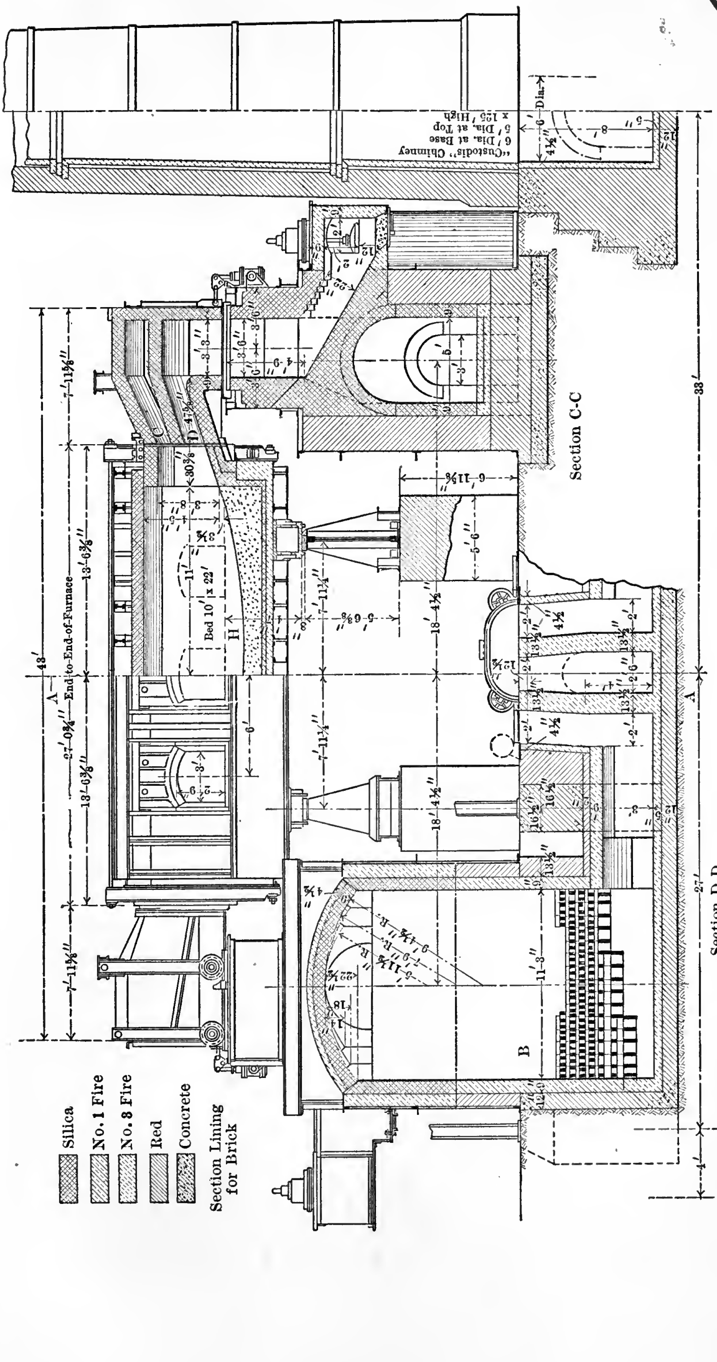

Fig. 165. — Front elevation tilting open-hearth furnace.

part of the charge, into the furnace from the car *O*. For pouring the finished charge into the great ladle in the pit in front of the furnace, the hearth is tilted by the hydraulic cylinder and piston *E*.

Furnaces in which the heat in the products of combustion is utilized for preheating the fuel or air necessary for combustion are known by the general term of regenerative furnaces. These are, however, divided into two types: (1) Regenerative furnaces proper, in which the products of combustion are passed intermittently through one set of two double chambers filled with brick work which absorbs the heat, while the other chamber previously preheated in this manner has the air and gas passed through it, thus preheating the same preliminary to burning them on the hearth. The function of the chambers is frequently reversed. (2) Recuperative furnaces, in which the products of combustion are passed through a chamber filled with iron pipes

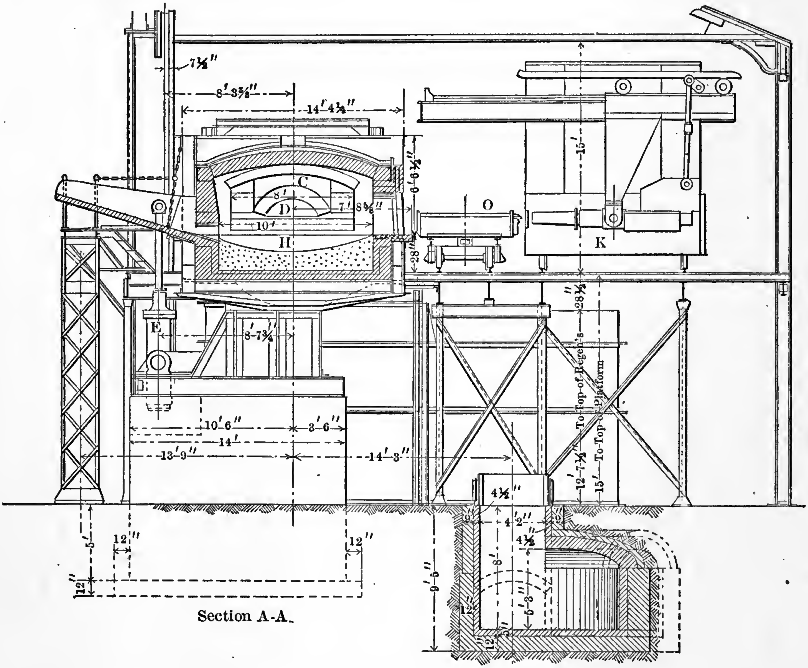

FIG. 166. — End elevation and section of tilting open-hearth furnace.

or tubes made of refractory material, through which the air for combustion is constantly passing. In this manner the heat of the products of combustion is conveyed directly to the

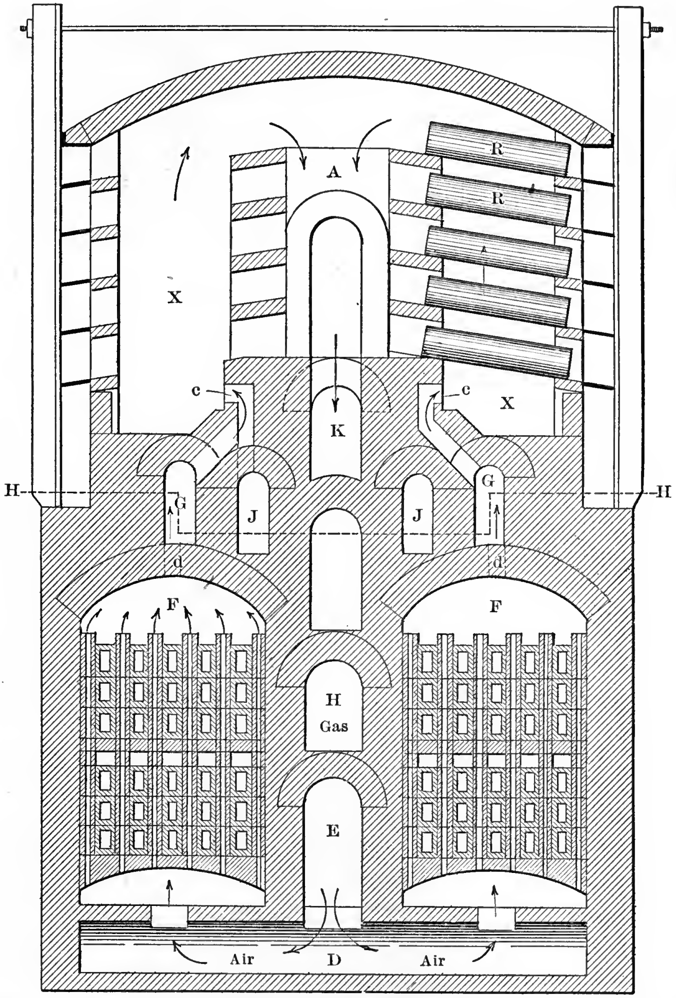

Fig. 167. — Recuperative furnace for the distillation of zinc, end section.

air through the tubes employed. Iron, of course, is used only for low temperatures. The recuperative system is continuous in its action and can readily be applied when low temperatures only are involved, but presents difficulties for high-temperature furnaces. A recuperative furnace is shown in Figs. 167 and 168. The hot blast stove, Fig. 184, for preheating the air blast for the iron furnace, is a regenerative apparatus, and the U-pipe stove, Fig. 185, sometimes used for preheating air for the copper blast furnace, is a recuperative apparatus.

III. Furnaces in which the charge to be heated is in a space insulated from contact with the fuel or the products of combustion.

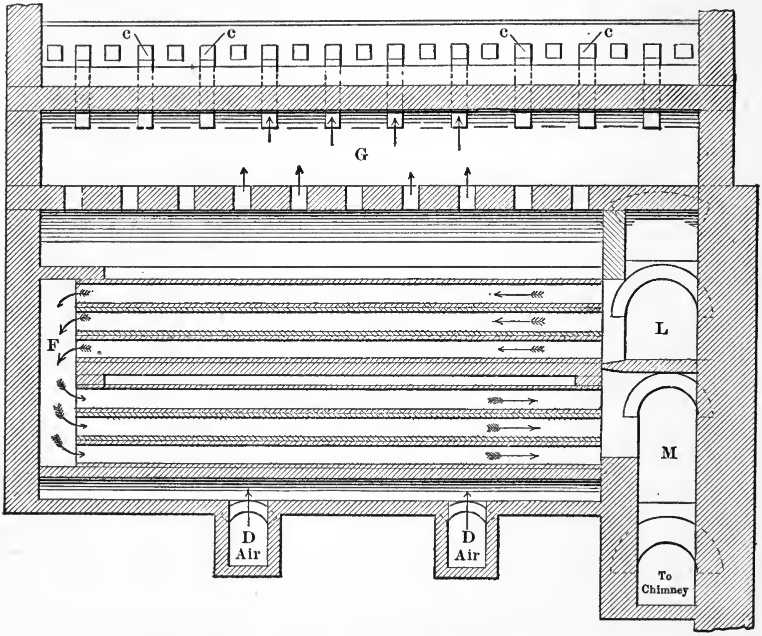

FIG. 168. — Recuperative furnace for the distillation of zinc, longitudinal section.

a. **Retort Furnaces.** — Furnaces of this type are widely used in the metallurgy of zinc, for the distillation of mercury from gold and silver amalgam, and in the metallurgy of arsenic, etc. Figs. 167 and 168 show the Convers and DeSaulles[1] distillation furnace of the recuperative type for zinc ore. The gas from the producers enters the canal *H*, passes to the uptake *I* into the canals *J J*, from which it is discharged into the combustion

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[1] W. R. Ingalls, The Metallurgy of Zinc and Cadmium (1903).

chamber through the ports *d*. The air enters through the canal *E*, passing into the flues *D D*, and thence rising through the spaces between the flues in the *recuperative chamber FF* into the canals *G G*, whence it is distributed into the combustion chamber *X* by means of the ports *c*, which alternate with the gas ports *d*. The products of combustion pass downward through the opening *A* into the canal *K*, whence, by means of the downtake *L*, they are divided to the right and left, entering the horizontal flues of the recuperative chambers *F F*. These flues are divided into two series so that the products of combustion are caused to make a return pass as shown in Fig. 168, finally entering the flue *M* from which they are led to the chimney The distillation retorts *R*, which are placed as shown and project from each side of the furnace, are shown in detail in Fig. 169. The crushed roasted

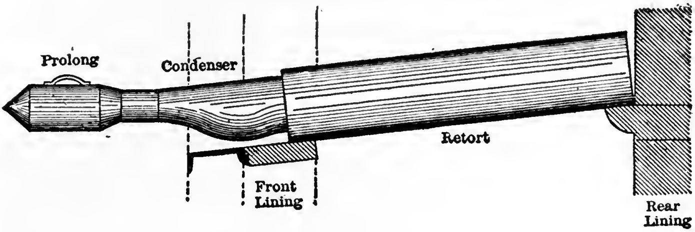

FIG. 169. — Zinc distillation retort with condenser and prolong.

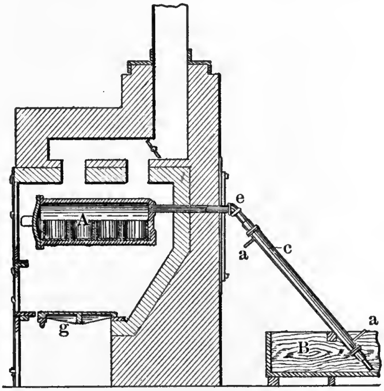

FIG. 170. — Retort furnace for the distillation of mercury from amalgam.

zinc ore is mixed with the proper proportion of crushed coal and shoveled into the retort, and the *condenser* and *prolong* attached. The zinc oxide is reduced to zinc which distils as vapor and is condensed in the condenser, while some zinc sublimes as *blue powder* or *zinc dust* in the prolong. Zinc furnaces, while all of the retort type, may be of many different designs as regards the methods of heating the retorts and the shape of these.[1]

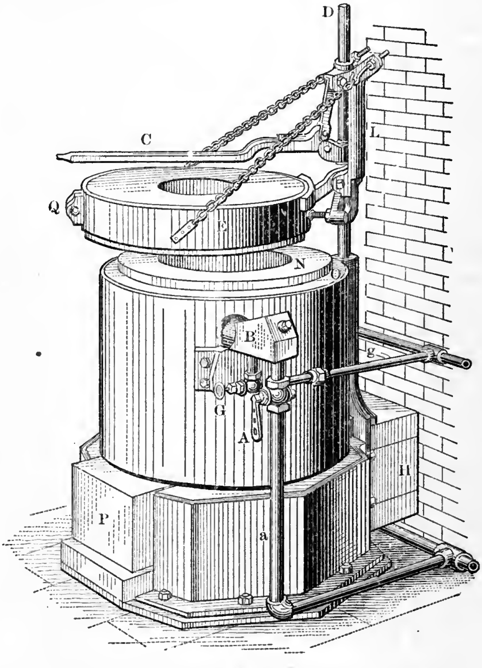

Fig. 171. — Crucible furnace heated by gas.

Fig. 170 shows the sectional elevation of a retort furnace for the distillation of mercury from gold and silver amalgam. The retort *A* is supported in the furnace on cast-iron lugs. It has a cover in front which is machined to fit tightly, and is secured with a clamp and by luting with clay. The amalgam in the form of balls is placed in a cast-iron tray, which is painted with whitewash or iron oxide, to prevent the gold from sticking to it. This tray fits into the retort. The furnace is fired by coal from the grate *g*. The mercury is vaporized and distils from the

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[1] W. R. Ingalls, "The Metallurgy of Zinc and Cadmium" (1903).

retort through the pipe *e*, which is jacketed by a condenser *c*, through which cold water is constantly flowing by means of the pipes *a a*. The condensed mercury is collected under water in the receiver *B*. For distillation the furnace is heated gradually to the boiling point of mercury, 357° *C*., until most of the mercury has passed off, then the fire is urged until the retort and its contents are a cherry red heat, to distil off the rest of the mercury. The operation takes 3 to 4 hours. The cover of the retort is then removed and the tray taken out. The gold and silver is in the form of *sponge*, a more or less porous mass of a silvery or gold color, in the form of the original amalgam balls. This is then melted in crucibles and cast into molds. The temperature should not be carried to such a point as to melt silver or gold, 962 to 1063° C.

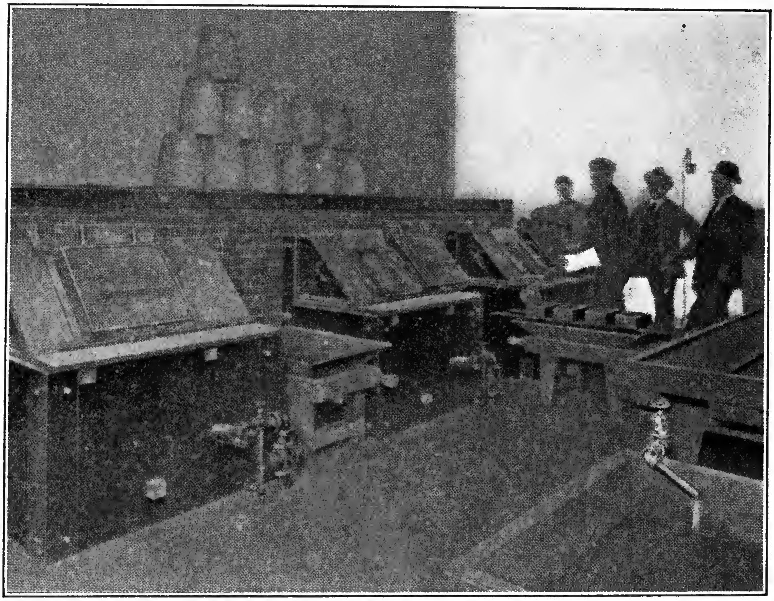

Fig. 172. — Crucible furnace for melting gold and silver bullion; gas fired.

b. **Muffle Furnaces.** — These are furnaces constructed in such a manner that the products of combustion from the fire pass round and about a receptacle of refractory material, or *muffle*, in which is placed the material to be heated. In this manner contact between the products of combustion and the furnace charge is avoided. Muffle roasting furnaces are used in roasting zinc blende ores and pyrite ores when it is desired to recover the sulphurous acid gases for the purpose of manufacturing sulphuric acid.

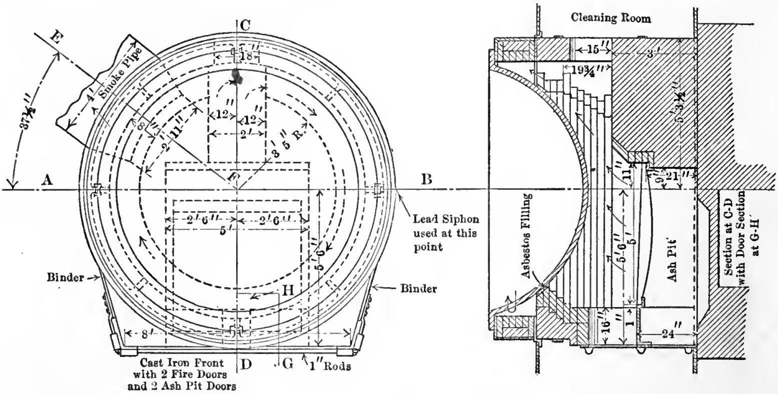

FIG. 173. — 35-ton lead drossing kettle.

c. **Crucible Furnaces.** — Fig. 171 shows a crucible melting furnace heated by gas for the melting of metals. The metal is put in graphite crucibles which are placed in the furnace, resting on the tile *P*. The furnace is lined with the cylindrical tiling *N*, on which fits the cover *E*, which may be readily raised and lowered by the lever device *C* and *L*. Gas enters the burner *B*, of which

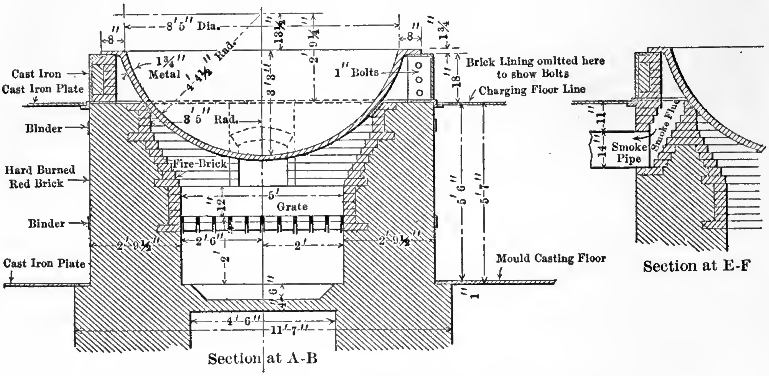

FIG. 174. — Lead drossing kettle, vertical section.

there are two, one on each side of the furnace, through the pipe *g*, while air enters through the pipe *a*. Gas and air are regulated by the valves *G* and *A*. The ports in the interior of the furnace are placed tangentially so as to give the flame a circular motion around the crucible. The products of combustion pass down around the crucible, through a flue in the base of the furnace, and out through *H* to the chimney. Fig. 172 shows crucible furnaces employed for melting bullion. Figs. 173 and 174 show drawings of a 35-ton lead drossing kettle. The lead is melted in the kettle and kept at a low heat. Certain impurities, as copper sulphide, iron, etc., rise to the surface in the form of a scum or dross, mixed with the litharge which forms. This dross is skimmed from the surface of the lead and pressed in Howard hydraulic presses, suspended over the kettles, to remove surplus lead. The lead is then siphoned into molds. This form of kettle is used also to desilverize lead by the addition of zinc (liquation, p. 241), and for the purpose of sampling lead bullion.

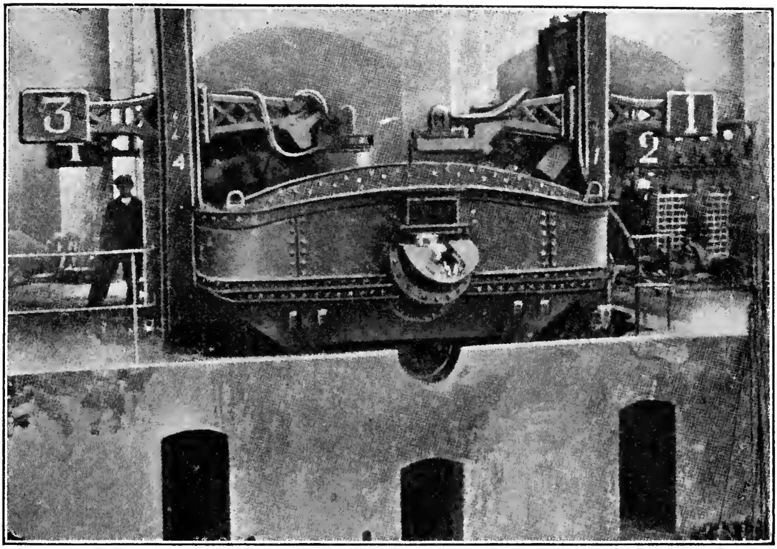

Fig. 175. — Girod Electric Steel Furnace. General view.

IV. Electric Furnaces. — Electric furnaces are now being widely used in the production of aluminium, iron alloys such as nickel, chromium, manganese, and tungsten steels, deoxidizing alloys for steel making, as ferro-manganese, ferro-silicon, etc., and for other special purposes. Electric furnaces may be broadly classified into (1) those in which the electric current is used for the generation of heat only, and which are subdivided into (*a*) arc furnaces, (*b*) resistance furnaces, and (*c*) induction furnaces, or a combination of these; and (2) those in which the electric current is used for the purpose of electrolysis, the heat produced being of secondary consideration.

As an example of class (1), Figs. 175, 176, 177, and 178 show a 12.5 ton Girod[1] electric furnace for the manufacture of steel from molten cast iron, or iron and steel scrap, and also for the manufacture of iron alloys. The Girod furnace is a combination of resistance and arc-heating furnace. Fig. 175 shows a general view of the furnace. In Figs. 176, 177, 178, representing sectional elevations and a sectional plan, *E* are 4 carbon electrodes 12 in. in diameter; *C′*, the furnace hearth lined with dolomite; *C*, the furnace cover also lined with dolomite; *S*, the pouring spout through which the molten steel is discharged by partially revolving the furnace on the rollers *r r*. *W* represents the bath of molten steel; *V*, the refining slag. The current passes through

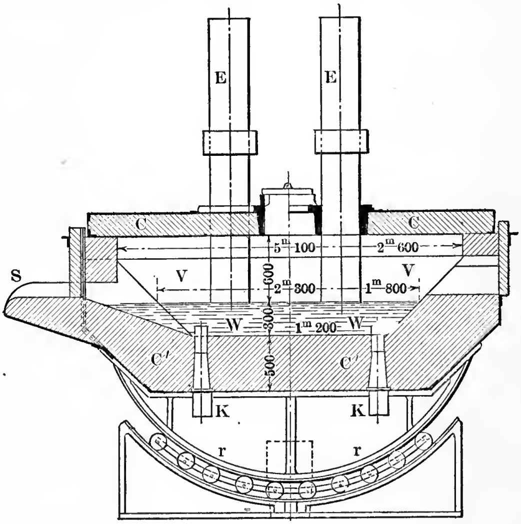

FIG. 176. — Cross-section view of electric furnace, Girod.

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[1] W. Borchers, T. A. I. M. E., Bul. 37, 1, Jan., 1910.

the cables *a a* to the electrodes *E*, which are held in position by the arms *P*, by means of which they may also be fed downward; thence through the molten slag and through the steel bath to the sixteen pure iron electrodes *K K*, of sufficient cross-section to prevent undue heating by resistance, and thence out by the conductor cables *a′ a′* to the generator. The electrodes *E* dip well into the slag but not into the steel bath. The alternating electric current passing from the carbon electrodes to the molten iron through the slag produces an arc, which has a great heating effect. The current passing through the slag bed also produces a heating effect by resistance. Heat is also produced by the passage of the current through the molten steel. The current is uniformly distributed from the centrally situated carbon electrodes through the whole of the steel bath to the various radially distributed electrodes in the bottom of the hearth. The heat thus produced raises the temperature of the furnace to a very high point and keeps the steel and slag bath thoroughly molten. The conversion of electric energy into heat is accompanied by a violent mechanical agitation of the bath which serves to bring the impurities of the steel bath into intimate contact with the refining slag, in this way removing them by oxidation.

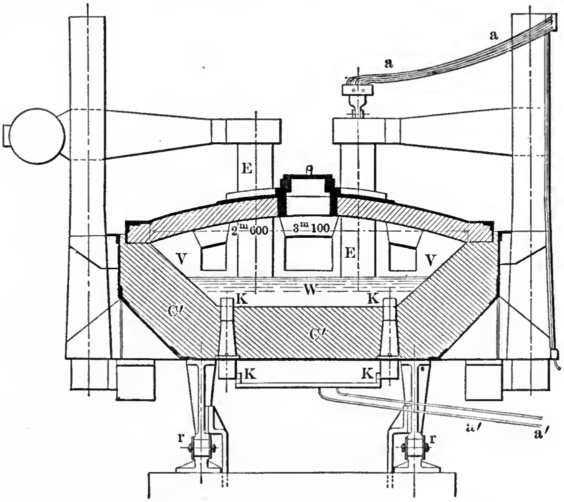

FIG. 177. — Cross-section view of electric furnace, Girod.

The current required for the furnace is from 1000 to 1200 kw. at 70 to 75 volts, the amount of electric energy required to make one ton of steel being 800 to 900 kw. hours. Carbon electrodes are consumed at the rate of 26 to 33 lbs. per ton of steel. The lining of the hearth and cover is dolomite, the hearth lining withstanding 80 to 150 heats without extensive repair, and the cover lining 20 to 25 heats.

The charge of the furnace consists of either molten pig iron or iron scrap, or both. When it is molten, 3300 to 3500 lbs. of oxide iron ore, and 600 to 700 lbs. of lime, are added to form the refining slag, the iron ore oxidizing the impurities in the charge, such as carbon, silicon, and phosphorus, the latter passing to the slag as lime phosphate, while the iron in the ore is reduced and enters the bath of steel. After four or five hours this slag is skimmed, and if necessary more iron ore and lime added. After the removal of the last slag some lime is scattered on the charge, and then skimmed off, and the steel poured into molds. The total time required for the operation is eight hours.

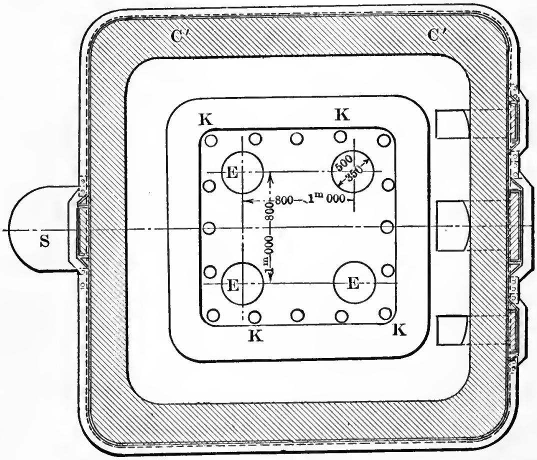

Fig. 178. — Sectional plan of electric furnace, Girod.

An electric furnace of the second type, such as is used for the production of aluminium, is briefly described on page 236.

The Production and Heating of Blast. — Air under pressure is extensively used in metallurgical operations, particularly in blast furnaces as already discussed. The machinery employed for the production of blast in large quantities is an important adjunct of a smelting plant.

In supplying air to furnaces the quantity of oxygen contained therein is the important factor. The composition of air is:

	Parts by weight	Per cent by weight	Parts by volume	Per cent. by volume
Oxygen	3	23.1	21	20.8
Nitrogen	10	76.9	80	79.2

One cubic meter of dry air at 0° C. and 760 mm. pressure weighs 1.293 kg. One cubic foot of dry air under the same conditions weighs 0.0808 lbs. av.

The volume of air increases or decreases $\frac{1}{273}$ for every degree C. rise or fall in temperature from 0°. In the same manner the volume of air increases or decreases $\frac{1}{490}$ for every degree Fahrenheit rise or fall in temperature from 32° F. The volume of air varies inversely as the pressure upon it, viz., doubling the pressure halves the volume, and halving the pressure doubles the volume. From this data can be calculated the weight of air at any given pressure and volume. Thus, what is the weight of a cubic foot of air at a pressure of 680 mm. (which represents an elevation of 3200 ft.) and at a temperature of 80° F.?

$$\underset{\text{Correction for Temperature}}{\frac{0.0808}{\left(1+\frac{80}{490}\right)}} \times \underset{\text{Correction for Pressure}}{\frac{680}{760}} = 0.0643 \text{ lbs.}$$

The quantity of air is usually estimated in cubic feet and as *free air,* viz., air at the atmospheric pressure prevailing, since the capacity of blast-producing machinery is based on volume. It is essential to note, however, that in order to carry on the reactions in the furnace, a definite weight of oxygen is required, so that the volume must be proportioned according to the temperature and pressure prevailing. Thus at high altitudes larger blowing machinery will be required than at low altitudes, or the smaller units will have to run at higher speed. In hot weather the speed must be increased to make up for less oxygen in a given volume.

Atmospheric air normally contains water vapor in varying amounts. For any given temperature and pressure a given volume of air can contain a certain maximum quantity of water vapor. This amount saturates it. Ordinarily air is not saturated with water vapor. The term humidity is used to express the condition of the atmosphere as regards its contents in water vapor. If air is saturated with water vapor for any given temperature, the humidity is 100 per cent.; *e.g.*, if the humidity is said to be 60 per cent. it means that the air contains 60 per cent. as much water as is possible for it to hold at the temperature in question. Table LXXXVIII gives the water contents of air for different months of the year.[1]

TABLE LXXXVIII. WATER IN AIR

Month	Weight of water per cubic foot of air	Month	Weight of water per cubic foot of air
January	2.8 grains	July	7 grains
February	2.7 "	August	7.1 "
March	3.1 "	September	5.4 "
April	3.3 "	October	3.2 "
May	4.7 "	November	3.3 "
June	7.3 "	December	3 "

One grain of water per cubic foot of air will carry into the furnace one gallon of water for every 60,000 cu. ft. of air. An iron blast furnace using 40,000 cu. ft. of air per minute, containing 5.6 grains of water per cubic foot, will have passed into it 224 gallons water per hour. The dissociation of this water vapor by the carbon is an endothermic reaction which takes heat from the furnace at a point where there is really none to spare, *i.e.* at the tuyeres. As will be pointed out in the next chapter, the reaching of a certain *critical temperature* in the smelting zone of the furnace is essential. Any factors which tend to lower the margin between this critical temperature and that which is obtained in the furnace by the combustion of the fuel, or which

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[1] At Pittsburg, Pa.

cause serious fluctuations of this margin are detrimental to the working of the furnace. The fluctuations in the margin of temperature are perhaps more serious than any small lowering of the temperature itself. For this reason it is desirable to have the air entering the furnace as dry as possible and of as uniform a water content as can be obtained. James Gayley[1] in dealing with the problem of water in air for blast-furnace use has applied a system of refrigeration to the air for the blowing engines, which takes out most of the water and reduces what is left to practically a constant figure for all seasons of the year. The device consists of cork-lined refrigerating chambers filled with pipes through which cold brine solution is forced, the brine being cooled by the expansion of ammonia in a separate apparatus. The moisture in the air passing into the refrigerating chamber condenses on the outside of the pipes as ice, while the dry cold air passes out of the chamber by means of large mains directly to the blowing engines. In this manner the moisture in the air is reduced to an average of 1.5 grains per cubic foot. This system is being applied rather widely in iron blast-furnace practice and affords a very appreciable economy in coke consumption in the blast furnace and power consumption in the

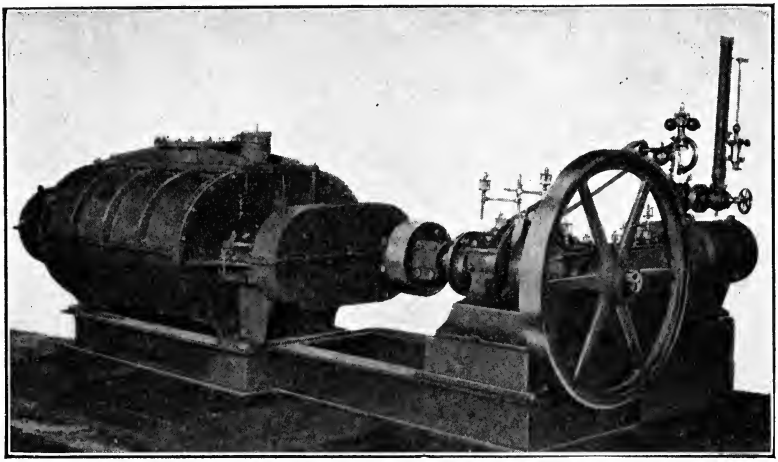

FIG. 179. — General view of Connersville rotary blower.

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[1] T. A. I. M. E., XXXV, 746 (1905).

blowing engines by furnishing the latter with denser air. The output of the furnace is also materially increased. At the Isabella furnaces near Pittsburg the output was increased by the use of dry blast from 358 tons per 24 hours with a coke consumption of 2147 pounds per ton of iron, to 447 tons with a coke consumption of 1726 pounds.

Blast-producing Machinery. — Blast-producing machinery for metallurgical furnaces is of three types: (1) Centrifugal fans or fan blowers operated either as pressure or exhaust devices for low pressure not exceeding a few ounces per square inch; (2) rotary blowers of the impeller type for the production of blast of pressure up to 64 oz. per square inch; and (3) blowing engines of the cylinder type for the production of blast of higher pressures.

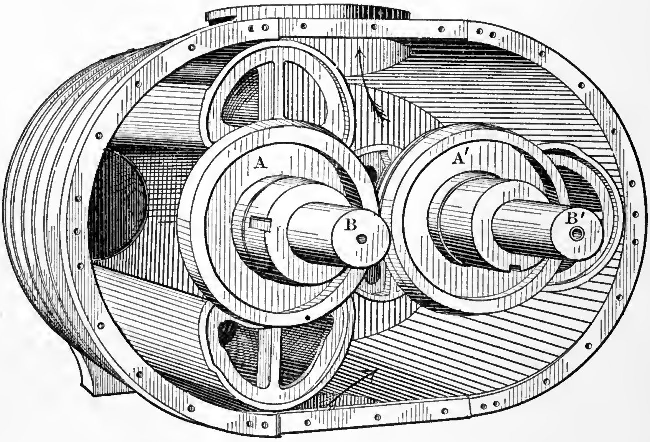

FIG. 180. — Rotary blower with end of casing removed.

Fans have but a limited application for metallurgical purposes and are therefore not discussed further. Rotary blowers of the impeller type are widely employed for the production of blast for lead and copper blast furnaces. Fig. 179 shows the general view of a Connersville rotary blower with direct attached engine. The engine is provided with a delicate governor so that it is possible to attain any desired number of revolutions per minute within certain limits, each revolution of the impellers displacing a certain number of cubic feet of free air, which varies with the size of the blower. Fig. 180 shows a rotary blower with one end of the casing removed. A and A' are the impellers, the impeller A being coupled directly to the engine by means of the shaft B. The shaft B' is driven by gearing from the shaft B. The impeller A is revolved clockwise and A' counter-clockwise; the air enters through the casing by the inlet as shown by the lower arrow, is then imprisoned between the vanes of the impellers and the casing as the first revolve, compressed to the extent of the pressure that prevails in that part of the chamber not at the moment connected with the air inlet, and constantly discharged at the outlet into the blast pipe. The pressure in the above part of the chamber is always that which prevails in the blast mains leading to the furnace. The principle[1] of operation of the rotary blower is the rotation of two moving parts in definite relation to each other, these two parts being composed of curves of such form that uniform clearance is constantly maintained between the outlines of the respective impellers, the point of contact being either on or contingent to a line joining the centers of the two rotating shafts. The clearance contact at this point prevents the return of the air which has been drawn in by the rotation of the lobe of the impeller in the case, thus enclosing the air lying between the outline of the two lobes and the case. This volume of air, therefore, is drawn in and discharged twice a revolution for each impeller, making the displacement of the blower equal to four times this amount. The air is drawn in under the conditions prevailing at the suction and is maintained at this same pressure until the upper edge of the case is reached. The impeller tip then passes the edge of the case, and the air between the case and the impellers is immediately raised to the discharge pressure. This sudden rise makes a certain fluctuation in the discharge of the blower by reducing the pressure at the entrance to the discharge pipe, so that the discharge pressure at that point represents a wave line.

Rotary blowers are usually driven by moderate speed engines, one impeller shaft being directly connected to the crank of the engine, while the second impeller shaft is driven from the first by a single set of gearing on the engine side of the blower. For large blowers compound engines are used, the cylinders usually

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[1] G. C. Hicks, Jr., E. and M. Jour., LXXXVII, 352 (1909).

connected tandem to one impeller shaft. When cross-compound engines are used, both cylinders should also be cranked to one shaft only, as it is not possible otherwise to apply equal power to both shafts. When blowers are driven by electric motors it is customary to double gear the impeller shafts, one set on each side of the blower, and drive each shaft by a separate motor. In plants where it is desirable to vary the speed of the blowers in order to regulate the air supply for the furnaces, it is best to drive by engine, as the motor drive does not furnish facility for variable speed.

The horse-power of a rotary blower may be calculated from the following formula:

H.P. = 0.00436 × displacement per min. in cu. ft. × pressure of air discharge in lbs.

To this amount about 10 per cent. should be added for internal friction in the blower.

Table LXXXIX gives the volumetric efficiency and horse-power required for a 39 × 84 inch Connersville blower driven by a 12 × 24 × 36 inch tandem compound Corliss engine.

Table LXXXIX. Data for a Rotary Blower

Pressure, lbs.	Total horse-power	Theoretical displacement cubic feet	Actual displacement cubic feet
0.0	19.30	19,250	—
0.05	23.76	"	19,212
0.5	52.83	"	18,727
1.0	100.91	"	18,508
1.0	100.93	"	18,508
1.5	132.67	"	18,344
2.0	176.11	"	18,200
2.5	223.20	"	18,028
3.0	256.87	"	17,965
3.5	287.56	"	17,863

Table XC gives important data concerning the Root Rotary Blower.[1]

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[1] L. S. Austin, Min. and Sci. Press, XCIX, 432 (1909).

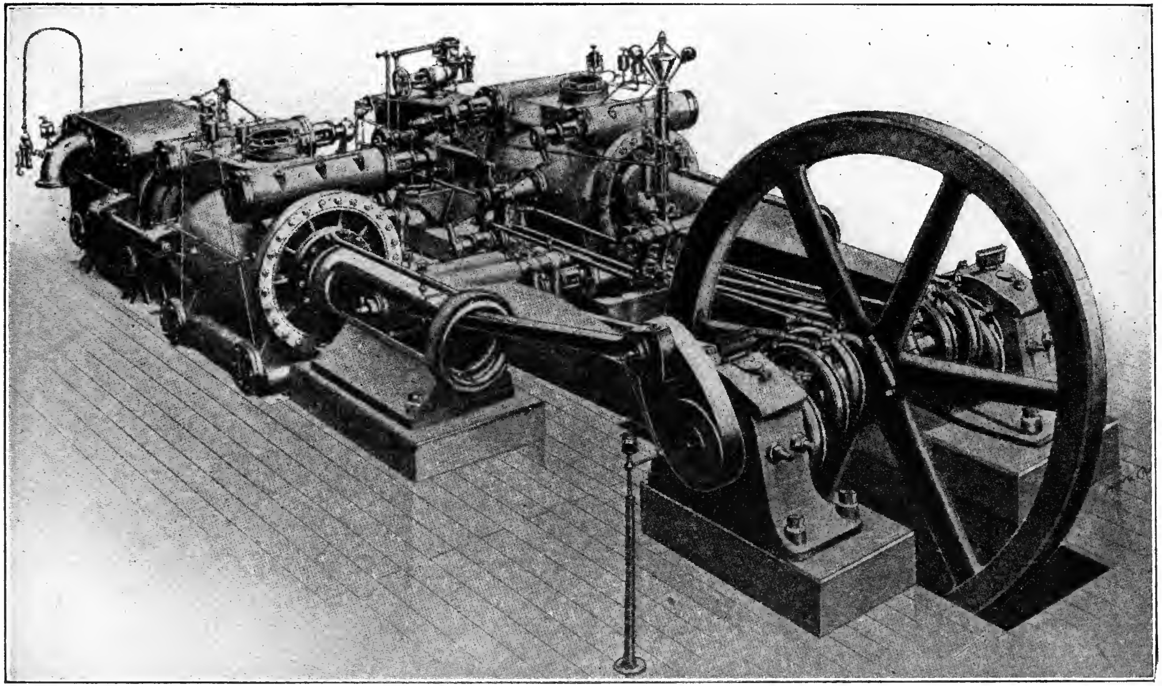

FIG. 181. — Blowing engine for copper converter.

Table XC. Data for Rotary Blowers

	Number of blower					
	3	4	5	6	7	8
Displacement per revolution	8	12½	24½	42	67	100
Ordinary speed for constant duty	250	200	175	150	125	100
Nominal capacity per min. at the above speed in cu. ft.	2000	2500	4287	6300	8375	10,000
Diameter of discharge opening, inches	12	14	16	20	24	30
Weight of blower, lbs.	3000	5500	8400	12,500	20,000	27,000
Corresponding furnace dimensions at tuyeres, in.	33×33	36×48	36×84	42×120	48×144	48×192
Horse-power at 2 lbs. per sq. in.	20	25	43	63	84	100
Horse-power at 1 lb. per sq. in.	10	12½	21½	31½	42	50
Capacity of furnace, tons (silver-lead)	42	52	89	131	137	208
Capacity of furnace, tons (copper-matting)	63	78	136	196	260	317

Fig. 181 shows a blowing engine for the production of blast for use in Bessemer copper converters; Figs. 182 and 183, views of blowing engines for the production of blast for the iron blast furnace. These blowing engines are all of the cylinder type and are essentially typical air compressors. While, however, the ordinary air compressor is designed to furnish a comparatively small amount of air at a high pressure, *i.e.* 60 to 500 pounds per square inch, blowing engines are designed to furnish very large volumes of air at comparatively low pressure, viz., 5 to 20 pounds per square inch. When rotary impeller blowers are used for pressures above 64 oz., the back leakage of air passed the impellers or the *slip* is considerable, so that the volume of air delivered ordinarily at the discharge orifice of the blower is not more than 70 to 75 per cent. of the rated capacity. Certain well-constructed blowers have a volumetric efficiency of 95 per cent. at 2 to 3 lbs. pressure, and about 78 per cent. at 10 lbs. pressure, which represents the maximum pressure at which

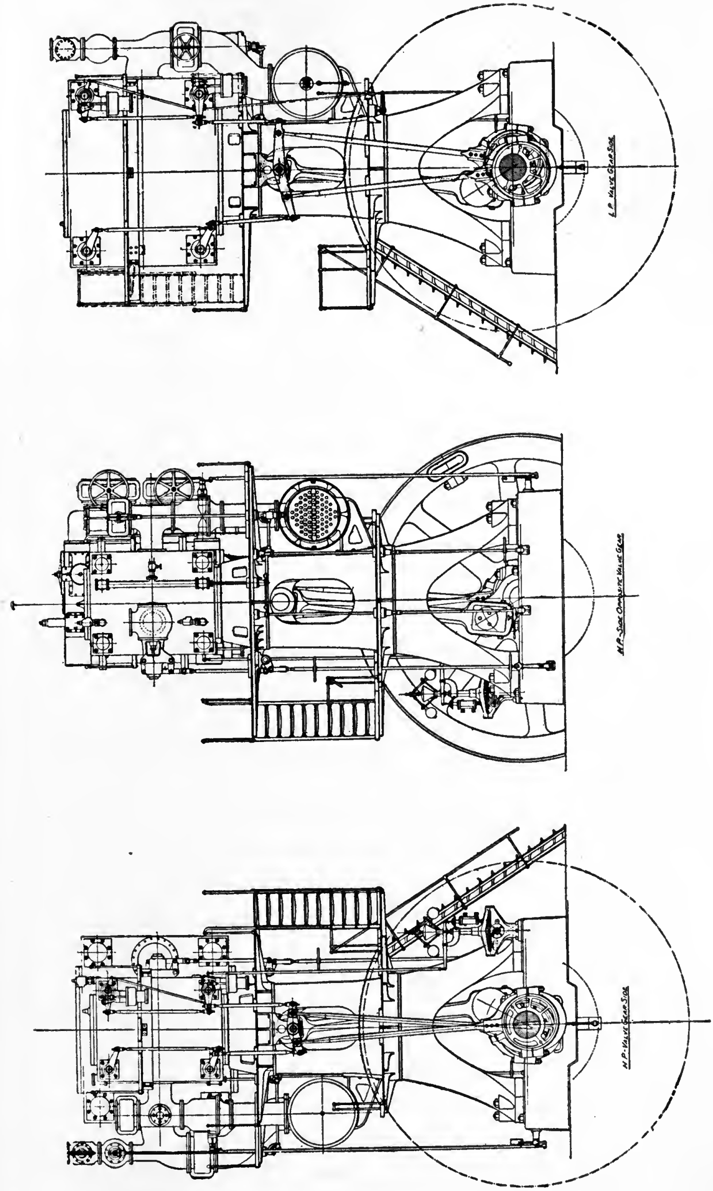

Fig. 183. — Elevations of blowing engine for iron blast furnace.

they can be used. The slip is due to the fact that in the construction of the blowers there must be a clearance between the vanes of the impellers and between the impellers and the casing, since to have these in contact would cause excessive friction and too great consumption of power. While this clearance is made as small as possible and the clearance spaces are practically filled with grease, still slip at the higher pressures is unavoidable.

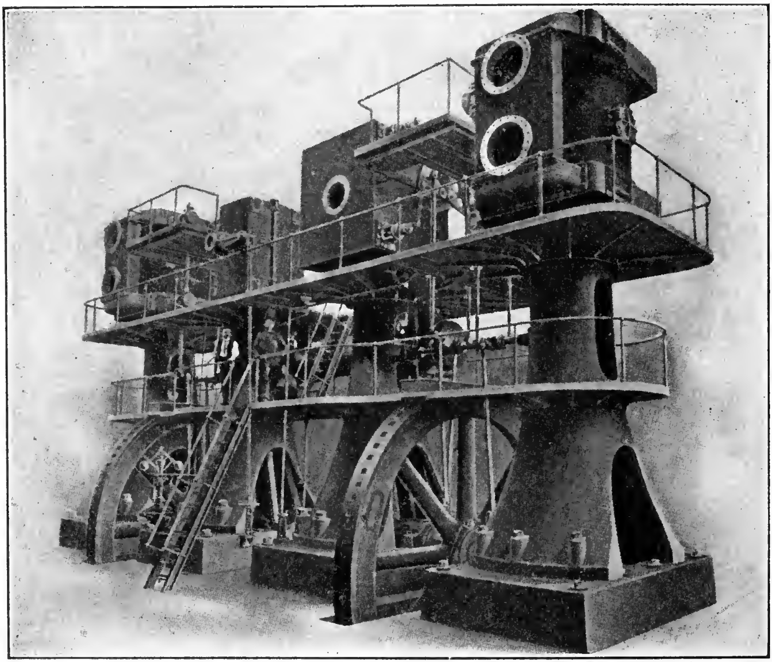

Fig. 182. — Blowing engine for iron blast furnace.

In fact, even at low pressures the volumetric efficiency, *i.e.* the ratio between the rated capacity and the air delivered, rarely exceeds 90 per cent. in old blowers. In the blowing engine, on the other hand, slip even at high pressures is very small, since in the air cylinders the piston and cylinder have tight metal contact. For this reason, when pressures above four pounds are used, the blowing engine is preferred to the rotary blower as a more satisfactory and economical mechanism. For pressures under four pounds, rotary blowers probably furnish the most

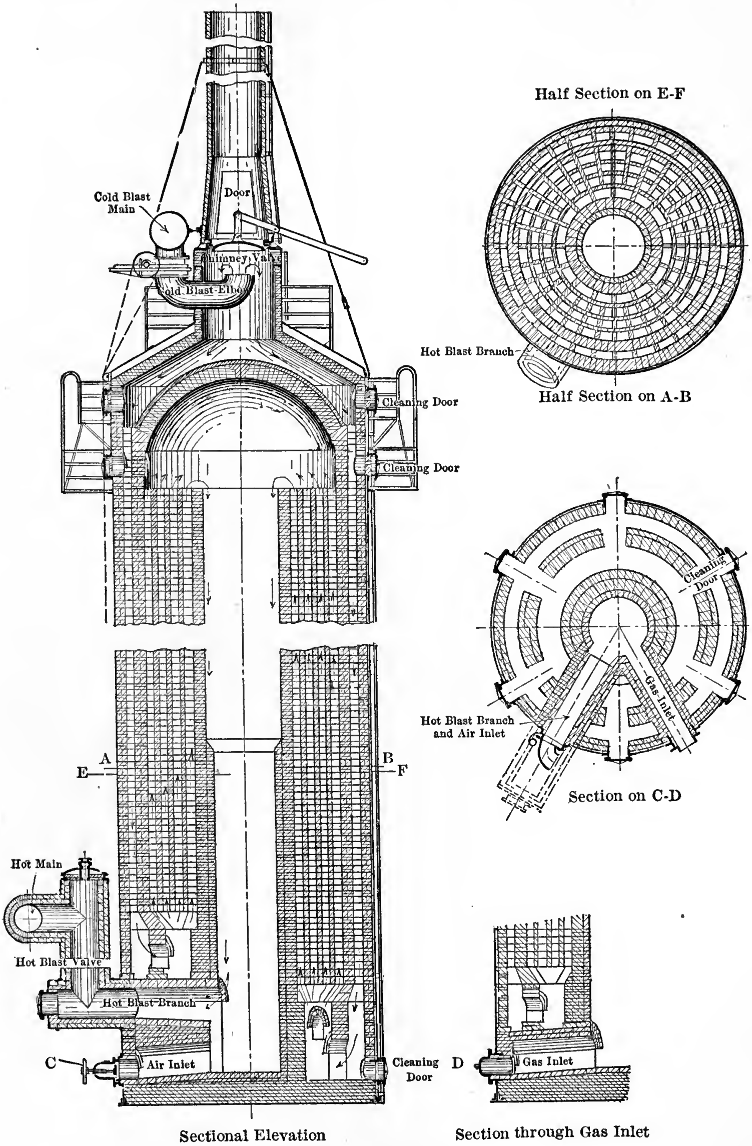

Fig. 184. — McClure 3-pass fire-brick hot blast stove.

economical apparatus as regards horse-power consumed and cost of installation.

Within recent years, the large blowing engines for iron blast furnace work have been driven by gas engines operated by blast-furnace gas. This affords a very considerable saving, since at most blast-furnace plants the supply of gas is ample for the hot blast stoves and for power purposes.

Apparatus for Heating Blast. — In blast-furnace smelting hot blast is used in the iron furnace and has been used to some extent in copper smelting. From what has gone before it is evident that heat introduced into the furnace in the form of heated air for combustion serves to replace fuel to the extent of the heat contained in the air. In the iron blast furnace enormous quantities of gas are produced which can be burned. This gas, which otherwise might go to waste, is employed in preheating the air for the furnace, in this manner making a direct saving in coke. When fuel has to be burned directly to preheat blast the economy of hot blast is questionable, since the fuel so consumed might be used with better advantage directly in the furnace. The exception to this is when the extra addition of carbonaceous fuel would disturb the chemical equilibrium of the furnace, as for instance in certain forms of copper matte smelting where economic conditions demand the making of a highly siliceous, difficultly fusible slag, with a small amount of high-grade matte. Then the large percentage of coke required to

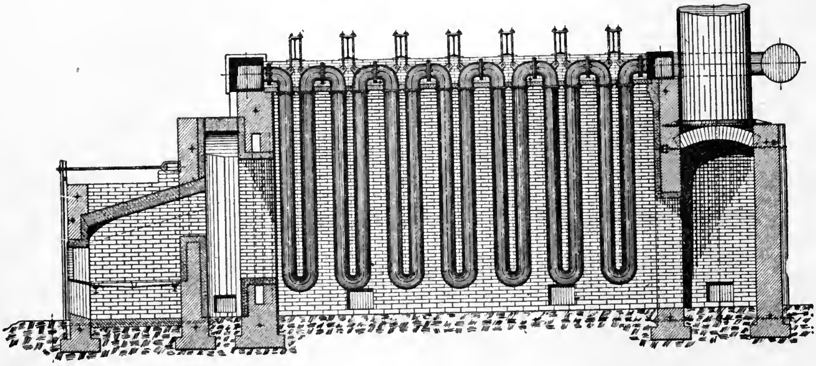

FIG. 185. — Longitudinal section of U-pipe hot blast stoves.

obtain the high temperature necessary will induce a reducing atmosphere in the furnace, which is detrimental to obtaining a small matte fall or high concentration. In this instance, if the extra heat required to obtain the working temperature can be introduced by means of hot blast, the process will be benefited. Thus, the extra fuel, instead of being added directly to the furnace, is employed in a separate furnace for preheating the blast. In a general way the question of hot blast therefore resolves itself into this: If waste heat is available, heated blast is usually desirable; if waste heat is not available and extra fuel must be burned for the preheating of the air, hot blast, except in special cases, is not economical.

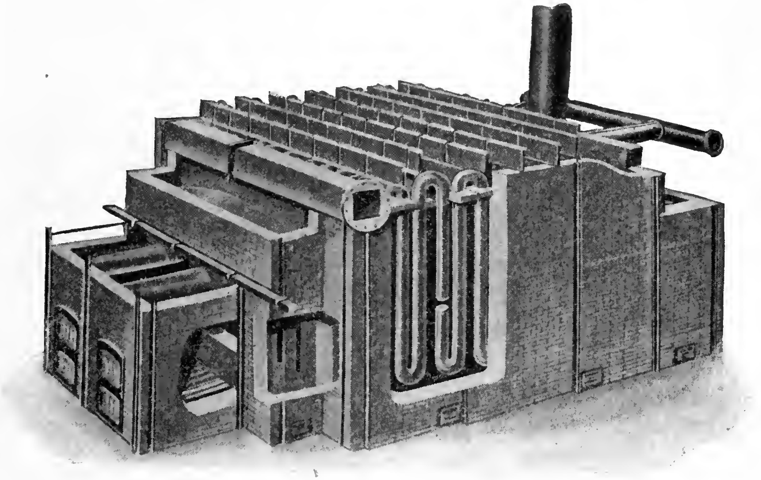

FIG. 186. — U-pipe hot blast stoves.

Fig. 184 shows a McClure three-pass fire-brick hot blast stove. This consists of a cylindrical steel shell tight against pressures of 20 to 25 lbs. per square inch, and filled with special fire brick set in the manner shown in the illustration. Four of these stoves are usually used with one blast furnace, one of them being on *air*, *i.e.* has the air blast from the blowing engines passing through it and absorbing the heat from the fire brick, while two are *on gas*, *i.e.* are having blast-furnace gas burned in them to heat the brick work. One is held in reserve. When the first one has been cooled down by the passage of the cold blast it is reversed, the air now passing through a newly heated stove, while the gas is turned on the cool stove. The manner of operation of the stove is as follows: To heat the stove, the hot blast valve and the cold blast valve are closed. Gas is admitted through the gas inlet, shown in section *CD*, and air admitted at the air inlet at *C*. The gas burns in the central open space, the products of combustion passing down through the spaces between the brick work and then up the peripheral space near the outer circumference of the stove, and out through the chimney valve which is open. When the stove has been heated sufficiently it is reversed, *i.e.* the chimney valve, air inlet, and gas inlet are closed, the cold blast valve opened and also the hot blast valve. The air then takes the direction as indicated by the arrows in the illustration, and issues from the stove to the hot blast main which leads to the furnace. By these means the blast is preheated to between 600 and 900° C. Stoves for preheating the blast to a moderate degree are shown in Figs. 185 and 186. Fig. 185 is a general view of a hot blast U-pipe stove, while Fig. 186 represents a longitudinal vertical section of the same stove. Stoves of this type have been used to preheat air for copper smelting. The U-pipe construction is employed since this allows for free expansion and contraction without strain, as otherwise it would be impossible to keep the pipes tight against leakage. The pipes are suspended freely from I-beams at the top of the structure. Coal is burnt on a grate, the products of combustion passing through and among the pipes to a flue. The blast enters at the front end of the stove and leaves at the rear end. Stoves of this type have also been heated by the waste hot gases from blast and reverberatory furnaces, and for this purpose the U-pipes are placed in special chambers connected with the flues. U-pipe stoves are not very efficient, due to leakage after being in use for some time.

CHAPTER XIV

AN EXAMPLE ILLUSTRATING THE PHYSICS AND CHEMISTRY OF A SMELTING OPERATION

THE BLAST FURNACE FOR COPPER

General Statement. — Copper matte smelting in the blast furnace may be divided into two main types: (1) pyritic smelting in which the iron sulphide serves as the fuel, and (2) oxidized or roasted ore smelting, with only enough sulphur present to form the required amount of copper iron matte. In the first type only a small amount (2 to 4 per cent.) of carbonaceous fuel is used, while in the second the amount of coke necessary is 14 to 16 per cent.

Dependent upon the nature of the furnace charge in regard to the amount of iron sulphide present, and the amount of coke used, copper matte smelting will range between the two types.

Since the sulphides of iron are fuel, the general aim is to add only enough of the expensive carbonaceous fuel, coke, as is necessary to generate the required number of heat units needed to attain the necessary *margin* above the *critical temperature* to carry on the smelting operation. The conditions existing in the interior of the furnace for the two types of smelting are shown in Fig. 187. This furnace is 15 ft. in height from the tuyere level to the charge floor level, and 54 by 240 in. in cross-section at the tuyere level. *A* illustrates the conditions existing in smelting roasted or oxidized ores with coke as fuel. The figure represents a vertical section of the furnace on the short diameter. The zone of the furnace in which oxidation or combustion takes place, and in which the heat is developed, is called, for pyritic smelting, the *focus*, after Robert Sticht. The term is here applied to both types of smelting. The focus is of comparatively limited volume, the cross-section of which is shown in the figure. *B* represents a cross-section of a furnace in which pyritic smelting is carried on. In both cases, *A* and *B*, the furnace is filled with solid charge from the stock level near the feed floor to a short distance below the tuyeres, the weight of the charge being sustained by arching on the boshes, by the lifting effect of the rising gas current, and by resting on the liquid contents of the hearth. The charge is made up to form the proper slag and is fed as described on page 435.

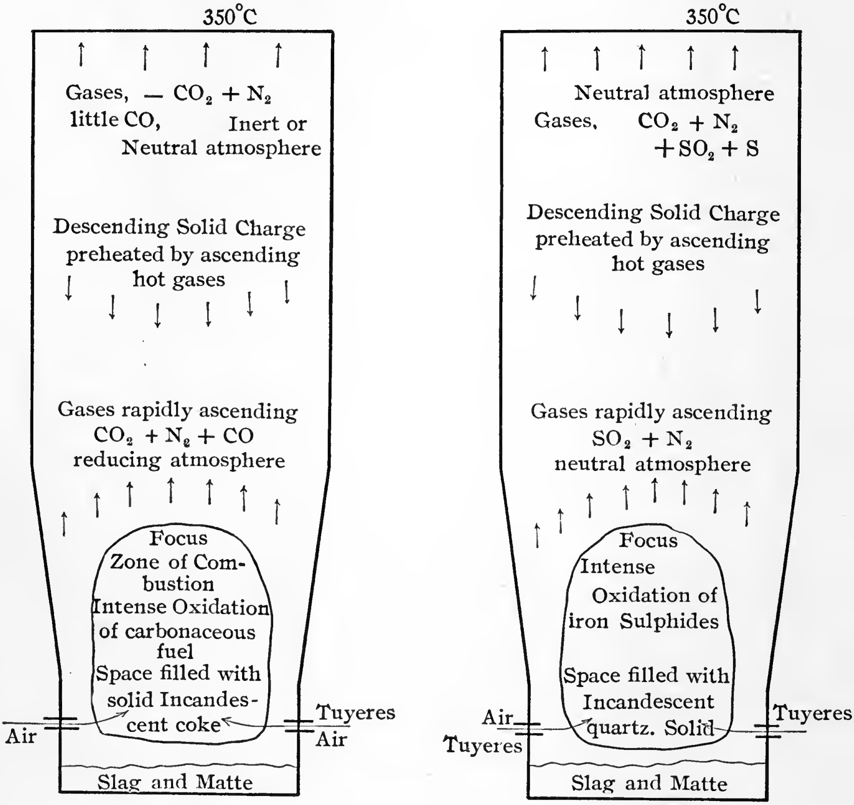

FIG. 187. — Diagram representing conditions in the interior of a copper matting blast furnace.

A. Smelting roasted ore with coke. B. Pyritic smelting.

In case of the coke furnace, the solid material in the focus of the furnace is chiefly incandescent coke, which burns away rapidly at the tuyere level, while in the upper part of the focus, and just above the focus, all the other parts of the charge become liquid and form slag and matte which trickle down through the interstices between the pieces of coke and collect in the hearth below the tuyeres. In the case of the pyritic furnace the solid material in the focus of the furnace is chiefly the quartz and the earthy base constituents of the charge, while the sulphides, deprived of part of their sulphur by distillation, become molten somewhere a short distance above the focus and trickle down through the silica, etc. In the focus they are struck by the hot oxygen of the air and in the presence of the silica rapidly converted to ferrous silicate, ($2FeO \cdot SiO_2$), which absorbs the earthy bases present, and thus forms the slag. The matte is that part of the sulphides which escape oxidation, the relative amount of slag and matte being a function of the completeness of oxidation of the sulphides, which is dependent on the air supply.

In both types of smelting the amount of blast is such that the oxygen is practically entirely used up in the focus, and only little free oxygen exists above the focus.[1] It follows, therefore, that in coke smelting the furnace atmosphere above the focus is reducing and then nearly neutral near the top, while in the pyritic furnace it is neutral. The zone of oxidation, or the actual smelting zone, is a limited area, and the main body of the furnace fulfils the function of preparing the charge, in its descent in the furnace, for the reactions in the focus.

In order to have the blast furnace continuous in its action it is necessary to have the products leaving the hearth thoroughly liquid. In the copper furnace these products are slag and matte, and it follows that there must be attained in the focus a certain *working temperature*, viz., a temperature sufficiently high that this slag and matte will be liquid enough to freely run out of the furnace and permit of separation by gravity in the forehearths. The freezing temperature of matte (875 to 1050° C.) is usually

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[1] J. Herman, West. Chem. & Met., 1, 145 (1905). This condition is not always realized in practice, though it should be. The following gas analyses from copper furnaces show the difference prevailing in practice: Morenci, Ariz., smelting with 10.6 per cent. fixed carbon: CO_2, 10.9 per cent.; SO_2, 2.5 per cent.; CO, 2.15 per cent.; O_2, 8.00 per cent.; N_2, 76.45 per cent. by volume. Globe, Ariz., smelting with 10 per cent. fixed carbon: CO_2, 17.2 per cent.; SO_2, 3.5 per cent.; CO, 3.2 per cent.; O_2, none; N_2, 76.1 per cent. by volume. Mt. Lyell, Tasmania, smelting with 1 per cent. fixed carbon: CO_2, 5.45 per cent.; SO_2, 8.93 per cent.; CO, none; O_2, 0.70 per cent.; N_2, 84.92 per cent. by volume.

well below that of the slag, so that the working temperature may be defined as that at which the slag is thoroughly molten. The critical temperature is that required to form the slag, and in order to provide for contingencies it is necessary to have a certain margin above this. The critical temperature plus the necessary margin is the *working temperature* of the furnace. It follows from this that the composition of the charge must be such that it will generate enough heat units to attain this working temperature in the focus of the furnace. What the working temperature is for any given case depends upon the nature of the slag made. The formation temperatures and melting-points of slags have been discussed in Chapter VIII.

The composition of the slag, which may vary rather widely within certain limits, is fixed within these limits by commercial considerations, viz., nature of ores and fluxes available. The slag made is usually the most economical under the conditions prevailing. Thus if siliceous ores are plentiful and iron bearing ores and limestone scarce, a slag high in silica will usually be made. Its precise composition is, however, also influenced by other factors. Thus, a highly siliceous slag (45 to 50 per cent. SiO_2) has, in most cases, a high formation temperature and is normally very viscous even with considerable superheating, so that its movement through the focus is sluggish. This very much retards the rate of smelting and thus gives a low furnace capacity, which very materially increases the cost per ton of charge smelted, since the daily labor charges and the fixed charges remain the same. The heat units that must be developed per unit of charge are also greater, requiring a large percentage of fuel and thus increasing the cost of smelting. It may therefore be more economical to make a slag lower in silica than could be made, even though it will entail the use of more ore containing iron and more limestone.

Factors Influencing Capacity. — In considering the capacity of the furnace it is evident that the primal factor is the rapidity with which slag is formed in the focus and removed therefrom into the hearth, for if this takes place rapidly the furnace charge will sink faster per unit of time, a direct measure of the capacity. A fast forming and fluid slag will therefore give a high capacity. The rate at which the slag forms is dependent upon the speed of the particular reaction involved, which in turn is largely a function of the temperature.[1] It follows, therefore, that the higher the temperature in the focus within limits, the greater will be the furnace capacity. In the case of pyritic smelting the particular reaction involved is that of the oxidation of iron sulphide with the formation of the monosilicate of iron slag, and SO_2 gas. It is evident that if the air be blown into the furnace in such quantity per unit of time as to cause a maximum velocity of reaction in the focus, nearly the theoretical temperature of combustion will be reached (the highest possible) and the speed of the furnace be the greatest attainable. The reason that the theoretical temperature of combustion will be nearly reached under these conditions is as follows.

If we conceive carbon and oxygen in contact in proper proportion in a space insulated against all radiation, and reaction takes place between them, a definite amount of heat is liberated when the reaction is complete, which will raise the products of combustion to a certain temperature. Under the conditions of insulation against radiation, the time it takes to complete the reaction has no influence. The final temperature is the same whether the reaction takes a second or a year. If, however, the reaction takes place under ordinary conditions, radiation plays an important part, and the above temperature can only be approximately reached if the velocity of reaction is so great that the amount of radiation, which has as a factor, time, will be comparatively small in the interval that the reaction completes itself. The slower the reaction, therefore, the lower will be the temperature of the products of combustion. If now a unit mass of fuel, whatever it may be, is considered in the act of combustion, and the oxygen is not supplied fast enough to attain the maximum speed of reaction, for the existing temperature, it is evident that the heat units will not be developed as fast as they might be, thus raising the products of combustion to the highest attainable temperature, but that radiation will have time to dissipate heat units, which would serve to increase the temperature of the products of combustion. On the other hand, an excess of air will lower the temperature by increasing the amounts of the products of combustion to be heated. The air, therefore, must be supplied in such quantity and at such a rate as is called for by the maximum velocity of the reaction in question. When

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[1] Nernst, Theoretische Chemie, 668 (1909).

this is the case the maximum velocity will be attained and at the same time the maximum temperature possible. This represents the limit beyond which no furnace can be *driven*, and this limit can be established only, for any given case, by experiment. The capacity of any given furnace is dependent upon its smelting area, *i.e.* the cross-sectional area at the tuyeres, for it is over this area that combustion takes place and which, other things being equal, determines the total quantity of slag that can form in a unit of time.

The size of the furnace also has a decided influence on the temperature attainable, since a large furnace will have relatively less surface per unit of volume than a small furnace, and hence the radiation losses per unit of volume will be somewhat smaller in a large furnace than in a small one, as the amount of radiation is a direct function of the surface exposed. Thus, considering two furnaces, one 2 × 6 ft. in cross-section at the tuyeres and the other 4 × 16 ft., for 1 ft. of height in the tuyeres jackets, the volume of the first is 12 cu. ft. and of the second 64 cu. ft. The surface area for the first, for 1 ft. height, is 16 sq. ft., and for the second, 72 sq. ft. The first has $1\frac{1}{3}$ sq. ft. of surface per cubic foot of volume, while the second has $1\frac{1}{8}$ sq. ft. and thus a smaller loss by radiation.

Volume of Air and Blast Pressure. — The quantity of air required has been mentioned on page 457 and is calculated for a given case in the following pages. In this connection it must be pointed out that the quantity of air is usually stated in terms of blower displacement. The blower, however, never furnishes its theoretic quantity of air, but always appreciably less, and when the various sources of leakage are considered, such as those in the blast pipes, at the tuyeres, etc., it is probable that the air entering the furnace does not exceed 50 to 75 per cent. of that of the rated capacity of the blower. It is necessary to briefly discuss the blast pressure.

The blast pressure is indicated by the manometer gage on the blowers and is expressed in either ounces or pounds avoirdupois per square inch of area. The energy represented by the blast pressure is expended in (1) forcing the air through the air mains to the furnace, (2) forcing the air through the tuyeres at the required velocity, (3) forcing the air through the charge column of the furnace. The pressure required to force the blast through the tuyeres can be readily calculated by Zeuner's formula adapted to this purpose, and which is:

$$(P_1 - P_2) = 2.4 \left(\frac{T_1 V^2}{P_1 d^4}\right)$$ [1]

P_1, P_2 = absolute pressure in bustle pipe and in furnace outside of tuyeres respectively.

$(P_1 - P_2)$ = difference in pressure between air in bustle pipe and in the furnace in pounds.

T_1 = absolute temperature of blast, Fahrenheit degrees.

V = volume of free air passing through tuyeres per minute, measured in thousands of cubic feet.

d = diameter of tuyere in inches.

Taking, for example, a copper furnace, 48 × 192 in. in section, with fifteen 3-in. tuyeres on the side or 30 in all, blown with 300 cu. ft. of air per minute per square foot of hearth area, there will pass into the furnace 19,200 cu. ft. free air per minute, and each tuyere will take 640 cu. ft. per minute. Applying the above formula and assuming a blast pressure of 2 lbs. or 32 oz. in the bustle pipe and a temperature of 70° F., we have:

$$P_1 - P_2 = 2.4 \times \frac{(460 + 70) \times \left(\frac{640}{1000}\right)^2}{(14.7 + 2) \times (3)^4} = 0.38 \text{ lbs.}$$

or a difference in pressure of 6 oz. between the bustle pipe and the interior of the furnace at the tuyeres. The energy of the blast jet from the tuyeres varies as the square of the velocity and hence directly as this difference in pressure, and as it is this energy which gives it its penetrative power or its ability to reach the center of the furnace, the diameter of the tuyere is of importance. It will be readily seen that tuyeres of too large a diameter will cause too small a difference in pressure and the

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[1] J. E. Johnson, Jr., T. A. I. M. E., XXXVI, 460 (1906). In this formula air is taken at a pressure of 760 mm. and 70° F., and 1000 cu. ft. assumed to weigh 75 lbs. If other conditions prevail, the following formula should be used in which W = weight of air in pounds passing each tuyere per minute, A = area of tuyere orifice in square inches, and other data as above.

$$W = 63.6\, A \frac{\sqrt{P_2(P_1 - P_2)}}{T_1}$$

blast will be deficient in penetrative power and not reach the middle of the furnace, with the result that there will be *dead* material there and the smelting area be decreased. If the tuyeres are too small the penetrative power will be too great, with the result of throwing most of the blast to the center, thus forming dead areas on the walls of the furnace. The proper proportioning of tuyeres and their distribution must be determined by experience.

By far the larger part of the blast pressure is required to force the furnace gases through the charge column. The height of the column is the most important factor, though the nature of the charge has a decided influence. If the charge be open and porous, viz., made up of rather large pieces, the resistance will be comparatively low. If a large proportion of fine material is present, the resistance will be much increased and it will take increased pressure to force the same volume of air into the furnace. It is evident that the amount of air needed for any given smelting operation is a fixed quantity, but that the blast pressure may be variable, dependent upon the conditions of the charge. With the higher pressures incidental to fine material in the charge, considerable flue dust is made, as the high velocity of the escaping gases entrains fine particles of charge and carries them to the dust chambers. Since the heat from a charge is developed locally in the focus of the furnace and there absorbed by the products of combustion, viz., the slag, matte, and the furnace gases, and these latter contain a great many heat units as they leave the focus, a certain height of furnace is necessary so as to allow time for this hot ascending gas current to transfer a large part of its heat to the descending solid charge, preheating it. If the height of the furnace is insufficient to accomplish this, the gases will carry off a large quantity of heat, which is wasted, and must be again supplied to the focus of the furnace by additional fuel on the charge.

The Thermal Balance of the Pyritic Furnace. — It has been stated that the heat units in the furnace are developed locally in the focus by reaction between constituents of the charge and the air blown in, and are there transferred to the products of combustion, viz., the slag and matte which escape downward into the hearth, and the gases which ascend through the charge. These gases give up a large part of their heat to the charge, preheating it to the temperature of the upper part of the focus, and then escape at the top of the furnace. In the calculations, therefore, which follow, the basis is the *unit of charge*, the weight of which is taken as one kilogram. The following is a general statement of the problem: One kilogram of charge is capable of developing a certain number of heat units. To burn this weight of charge requires a definite amount of air; the reaction gives rise to definite quantities of gases, slag, and matte, each of which contains a certain number of heat units. The reaction causes a certain maximum temperature in the focus of the furnaces. The melting-point of the slag will be called the *critical temperature,* and the difference between this and the temperature attained is called the margin of temperature above the critical temperature.

In pyritic smelting the iron sulphide furnishes the fuel. The iron sulphides are pyrite, FeS_2, and pyrrhotite, Fe_7S_8, the copper being present in these as intermixed sulphide, Cu_2S, or $CuFeS_2$ or other sulphides. In the descent of this material in the neutral atmosphere of the furnace distillation of sulphur takes place (which requires heat) and the sulphide reaches the upper part of the focus of the furnace as FeS[1] and is assumed to burn as such with oxygen in the presence of silica. The silica must be in the form of quartz, *i.e.* free silica, for such as is combined as a silicate with bases is not available to form silicate of iron. In certain ores silica exists in the form of silicate minerals, as the feldspars, chlorite, amphibole, pyroxene, etc., in which case the silica is not available. Some lime is needed for the slags (added in the form of limestone if it is not present in the ore), in order to decrease its specific gravity and afford a ready separa-

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[1] Robert Sticht, Metallurgie, III, 388 (1906). E. D. Peters, Principles of Copper Smelting, 221. Sticht states that the sulphide reaches the focus of the furnace in the form of Fe_5S_3, approximately, a mixture of FeS and Fe, thus containing less sulphur than FeS. This of course very appreciably lowers the fuel value, below that of FeS, *per unit of charge*. Gas analyses which would furnish competent evidence on this point are still lacking. Gas analyses made at Mt. Lyell, Tasmania, are from the nature of the process so variable as to be inconclusive. From the author's experience with the process, he would say that it is at least probable that the sulphides reach the *upper part* of the focus as FeS and perhaps as Fe_7S_8 in part, and burn as such, while the matte, which is that portion of the sulphides escaping oxidation, loses additional sulphur by the higher temperature to which it is subjected in falling to the hearth.

tion from the matte, and also for the reason that if less than 4 to 5 per cent. CaO is present, the slags will contain more than the permissible amount in copper. The following equation expresses the chemical reactions involved in pyritic smelting, with a copper-bearing pyrrhotite as the main ore. The pyrrhotite is expressed as a mixture of FeS and FeS_2 in such proportion as to make Fe_7S_8, for convenience in calculation. There is probably no great error involved in this assumption.

$$\overbrace{\overbrace{\underset{8424}{13(6FeS + FeS_2)} + \underset{158}{Cu_2S}}^{\text{Pyrrhotite}} + \overbrace{\underset{3600}{60SiO_2}}^{\text{Quartz}} + \overbrace{\underset{2000}{20CaCO_3}}^{\text{Limestone}}}^{\text{Charge}} + \overbrace{\underset{3904}{122O_2} + \underset{13664}{488N_2}}^{\text{Air}} =$$

$$\overbrace{\underset{8160}{40(2FeO\cdot SiO_2)} + \underset{2320}{20(CaO\cdot SiO_2)}}^{\text{Slag}} + \overbrace{\underset{1062}{Fe_{11}S_9 + Cu_2S}}^{\text{Matte}} + \overbrace{\underset{5248}{82SO_2} + \underset{416}{13S} + \underset{880}{20CO_2} + \underset{13664}{488N_2}}^{\text{Gases}}$$

The heat balance of this equation is expressed in Table XCI.

TABLE XCI. HEAT BALANCE OF EQUATION REPRESENTING PYRITIC SMELTING.

Left Side of Equation				Right Side of Equation			
Substance	No. of Molecules	Heat of Formation	Total	Substance	No. of Molecules	Heat of Formation	Totals
Pyrrhotite .	—	—	—	$2FeO\cdot SiO_2$	40	318,200	12,728,000
FeS	78	24,000	1,872,000	$CaO\cdot SiO_2$.	20	329,350	6,587,000
FeS_2	13	66,900	869,700	$Fe_{11}S_9$.	1	264,000	264,000
Cu_2S	1	20,300	20,300	Cu_2S	1	20,300	20,300
SiO_2	60	180,000	10,800,000	SO_2	82	69,260	5,679,320
$CaCO_3$	20	273,850	5,477,000	S	13	—	—
O_2	122	—	—	CO_2	20	97,200	1,944,000
N_2	488	—	—	N_2	488	—	—
			19,039,000				27,222,620
Balance or heat evolved. .			8,183,620				

Taking the weight of the *charge* as unity = 1 kg., and calculating from the atomic weights, which are indicated by the figures underneath the substances in the equation, we obtain the following data:

One unit or kilogram of charge contains,

Pyrrhotite	$\frac{8{,}528}{14{,}182}$	= 0.604 kgs.
Quartz	$\frac{3{,}600}{14{,}182}$	= 0.254 "
Limestone	$\frac{2{,}000}{14{,}182}$	= 0.141 "
		1.000 kgs.

The per cent. of copper on the charge is 0.88 per cent.

One unit or kilogram of charge requires the following amount of air:

Oxygen to burn sulphides	$\frac{3{,}904}{14{,}182}$	= 0.275 kgs.
Nitrogen accompanying the same	$\frac{13{,}664}{14{,}182}$	= 0.917[1] "
Total air		= 1.192 kgs.

This weight of air is equal to 0.921 cubic meters under standard conditions. This expressed in tons and cubic feet is as follows. One ton of charge requires 29,506 cu. ft. of air.

The furnace products from the reaction are as follows:

Slag .... $\frac{10{,}480}{14{,}182} = 0.738$ kgs.

Matte .... $\frac{1{,}062}{14{,}182} = 0.0748$ kgs., equal to a matte fall of 7.48 per cent.

The slag and matte have the following composition:

SLAG	MATTE
FeO = 54.50 per cent.	Fe = 58 per cent.
SiO_2 = 34.50 per cent.	Cu = 12 per cent.
CaO = 11.00 per cent.	S = 30 per cent.

This matte in sinking to the hearth (it is the sulphide which escapes combustion) loses some additional sulphur, 4 per cent., with a corresponding increase in the iron and copper contents.

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[1] In the equation four volumes of nitrogen are supposed to accompany one volume of oxygen. This is slightly in excess of what it should be and the correction is here made so that ten parts N_2 by weight accompany three parts by weight of oxygen.

This sulphur burns in the focus, but is not taken into account in the heat balance as the amount is small.

The furnace gases produced are as follows:

Nitrogen from combustion of sulphides	$\frac{13,664}{14,182}$	= 0.917[1] kgs.
Sulphur from distillation of sulphides	—	0.030 "
SO_2 from combustion of sulphides	$\frac{5,248}{14,182}$	= 0.370 "
CO_2 from dissociation of limestone	—	0.062 "
Total gases		= 1.377 kgs.

The total heat evolved by the reaction is 8,183,620 kg. calories. The weight of the *charge*, *i.e.* molecular weight, is 14,182. Therefore the heat evolved by one kilogram of charge is

$$\frac{8,183,620}{14,182} = 577 \text{ calories, with products at } 20° \text{ C.}$$

This heat is expended as already described and will be found in the products of combustion. The critical temperature of the furnace is assumed at 1040° C., the melting-point of a slag similar in composition to that produced.[2] This temperature is therefore taken as that to which the descending charge must be preheated before it reaches the focus of the furnace. The actual temperature of combustion is then calculated.

Table XCII gives the calories absorbed in heating the 1 kg. of charge and the air for combustion to 1040° C.

The pyrrhotite is assumed to be changed to FeS at 1000° C. and loose sulphur; with the copper sulphide present the FeS will melt at about 1020°.[3] The FeS melts and absorbs its latent heat of fusion, 31.9 cal. per kg.[4] The limestone persists as such to 800° C., when it is dissociated into CaO and CO_2, the latter passing off with the ascending furnace gases. The CaO is heated to 1040° C., as is also the silica. The air for combustion of the

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[1] In the equation four volumes of nitrogen are supposed to accompany one volume of oxygen. This is slightly in excess of what it should be and the correction is here made so that ten parts N_2 by weight accompany three parts by weight of oxygen.

[2] J. H. L. Vogt. Die Silikatschmelzlösungen, II, 62 (1904).

[3] *Vide supra,* iron-sulphide, p. 290.

[4] Bornemann, Metallurgie, V, 61 (1908).

sulphides is preheated to 1040° in the furnace. The necessary heat for this of course reappears in the products of combustion (gases). The heat absorbed by the vaporization of the sulphur is included, since in the equation the final products are at 20° C. while the sulphur leaves the Fe_7S_8 at 1000° C. The heat of dissociation of the Fe_7S_8 into FeS and S, and that of the dissociation of limestone, are provided for in the equation by the use of the proper heats of formation. In this connection it must be noted that the heats of formation of Fe_7S_8 and FeS_2 are not known. The heat of combustion of pyrite and marcasite, in the presence of about one-half the necessary amount of SiO_2 to form $2FeO \cdot SiO_2$, and with the sulphur burning to SO_3, is given as 1550 calories.[1] While the data is somewhat indefinite, the heat of formation of pyrite is calculated from this as 66,900 gram

TABLE XCII. HEAT ABSORBED IN HEATING SOLID CHARGE TO 1040° C.

Substance	Weight in kg.	Temperature through which heated	*Sm.* Mean specific heat	No. of degrees through which heated	Calories absorbed
Fe_7S_8	0.604	20 to 1000° C.	0.2138	980° C.	126.55
FeS	0.574	1000 to 1020° C.	0.2324	20° C.	2.67
S (vaporization) ...	0.030	at 1000° C.	—	—	2.16
FeS (liquid)	0.574	1020 to 1040° C.	0.2334	20° C.	2.67
FeS (latent heat) ..	0.574	—	—	—	18.31
$CaCO_3$	0.141	20 to 800° C.	0.2630	780° C.	28.92
CaO	0.079	800 to 1040° C.	0.3030	240° C.	5.76
SiO_2	0.254	20 to 1040° C.	0.2649	1020° C.	68.63
Slag (latent heat) .	0.738	at 1040° C.	—	—	62.73
					318.40
N_2	0.917	20 to 1040° C.	0.2632	1020° C.	246.56
O_2	0.275	20 to 1040° C.	0.2302	1020° C.	64.57
					311.13
				Total	629.53

Note to Table. Of this total heat, 629.53 calories, 318.40 calories, or that required to preheat the charge to 1040° and form slag, is again regained by the next succeeding charge, from the gaseous products of combustion ascending in the furnace, so that the heat required is that necessary for preheating the air for combustion at 1040° C., or $629.53 - 318.40 = 311.13$ calories.

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[1] Alfred Cavazzi, Rend. R.Acad. Sci. Inst. Bologna, N.S. 2, 205–209 (1898).

calories. This is probably high. The calculation assumes also that the heat of formation of $2FeO \cdot SiO_2$[1] is 318,200, which is an approximation, but probably nearly correct. In the table the latent heat of fusion of the slag is included. This is assumed at 85 cal. per kg., which is the figure Vogt gives for a slag similar in composition.[2]

The mean specific heats used in the table are calculated as per example:—

$$\begin{aligned}&\text{Pyrrhotite, } Sm \text{ per kg. } (20^\circ - 100^\circ) = 0.1602\\ &Sm = a + 0.00039a\,(t_1 + t_2)\\ &0.1602 = a + 0.00039a\,(20 + 100)\\ &1.0468a = 0.1602\\ &a \text{ at } 0^\circ = 0.1530\end{aligned}$$

Then $Sm_1 = 0.153 + 0.00039 \times 0.153 \times (1100^\circ + 700^\circ)$ or $Sm_1 = 0.2600$.

From this data may now be calculated the theoretical temperature attainable in the focus under the conditions prevailing. The equation for this calculation is generally stated as follows:

$$T = \frac{C}{MSm}$$

as explained on page 406.

The data applied to this formula will give the following equation:

T° above 1040° C. =

$$\frac{577 - 311.13}{\underset{\text{Slag}}{(0.738 \times 0.27)} + \underset{\text{Matte}}{(0.075 \times 0.2334)} + \underset{\text{SO}_2\text{ Gas}}{(0.37\,[0.125 + 0.001\,\{1040 + T^\circ\}\,])} + \underset{\text{N}_2\text{ Gas}}{(0.917\,[0.2405 + 0.0000214\,\{1040 + T^\circ\}])}}$$

$$\begin{aligned}0.00006\,T^2 + 0.535\,T &= 265.87\\ T \text{ above } 1040^\circ \text{ C.} &= 472^\circ \text{ C.}\end{aligned}$$

The temperature attained in the focus is therefore 1040 + 472 or 1512° C.

In Table XCIII are given temperatures of slags leaving the blast furnace, for different types of smelting.[3]

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[1] J. W. Richards gives this as 320,300. Metallurgical Calculations, III, 459.

[2] *Vide supra*, p. 282.

[3] Private communication. Dr. M. N. Bolles.

TABLE XCIII. TEMPERATURE AND COMPOSITION OF CERTAIN BLAST-FURNACE SLAGS

Kind of Smelting	Composition						Temperature °C	Remarks
	SiO_2 %	FeO %	CaO %	Al_2O_3 %	Zn %	MnO %		
Partial Pyritic Copper smelting	31.0	52.0	—	—	—	—	1201 to 1207	Average.
" "	31.0	52.0	—	—	—	—	1197 to 1227	Smelting at normal rate.
" "	31.0	52.0	—	—	—	—	1255 to 1261	Smelting fast.
" "	31.0	52.0	—	—	—	—	1123 to 1137	Smelting slowly.
Pyritic smelting	—	—	—	—	—	—	1240	
Copper smelting	—	—	—	—	—	—	1346	On roasted ore.
Lead smelting .	31.0	38.6	12.0	8.0	10.0	—	1126	
" " . .	34.0	30.5	15.0	6.4	5.8	3.7	1167	
" " . .	32.0	31.0	14.5	6.6	5.8	3.8	1149	

Fig. 188 gives the heat distribution in diagram form, as the products leave the focus. In this instance the latent heats of slag and sulphide are calculated into the gases. The balance is as follows, with products of combustion all at 1512° C.

Heat in gases (including latent heat of fusion of slag and sulphides)	548.35 cal.
Heat in slag	297.30 cal.
Heat in matte	26.12 cal.
Gross total	871.77 cal.

Heat returned by solid charge to focus

$$318.40 - \left\{ \begin{matrix} 13.51 + 8.00 \\ CO_2 \quad\quad S \end{matrix} \right\} = 296.89 \text{ cal.} \qquad \text{Net total,} \quad 574.88 \text{ cal.}$$

318.40 cal. is the heat required to preheat the solid charge to 1040° C. (Table XCII), and 13.51 and 8 cal. is the heat in the CO_2 gas from the limestone and the S vapor respectively.

If this balance is recast, transferring the latent heats of fusion from the gases to the slag and matte, we have:

Slag,	297.12 + 62.73 + 18.31 cal.	= 378.16	= 66. per cent.
Matte,	26.12 "	= 26.12	= 4.5 per cent.
Gases,	548.35 − (296.89 + 81.04) "	= 170.42	= 29.5 per cent.
		574.88	

All the latent heat, both that of slag and the sulphide, have been figured to the slag, as the amount of matte is so small that this makes no appreciable error.

If 15 per cent. of the total heat developed is used for jacket water and radiation, and driving out the moisture from the ore and this be taken from the gases, there is still left in the gases at the throat of the furnace (167.99 – 85.80) = 84.62 cal.

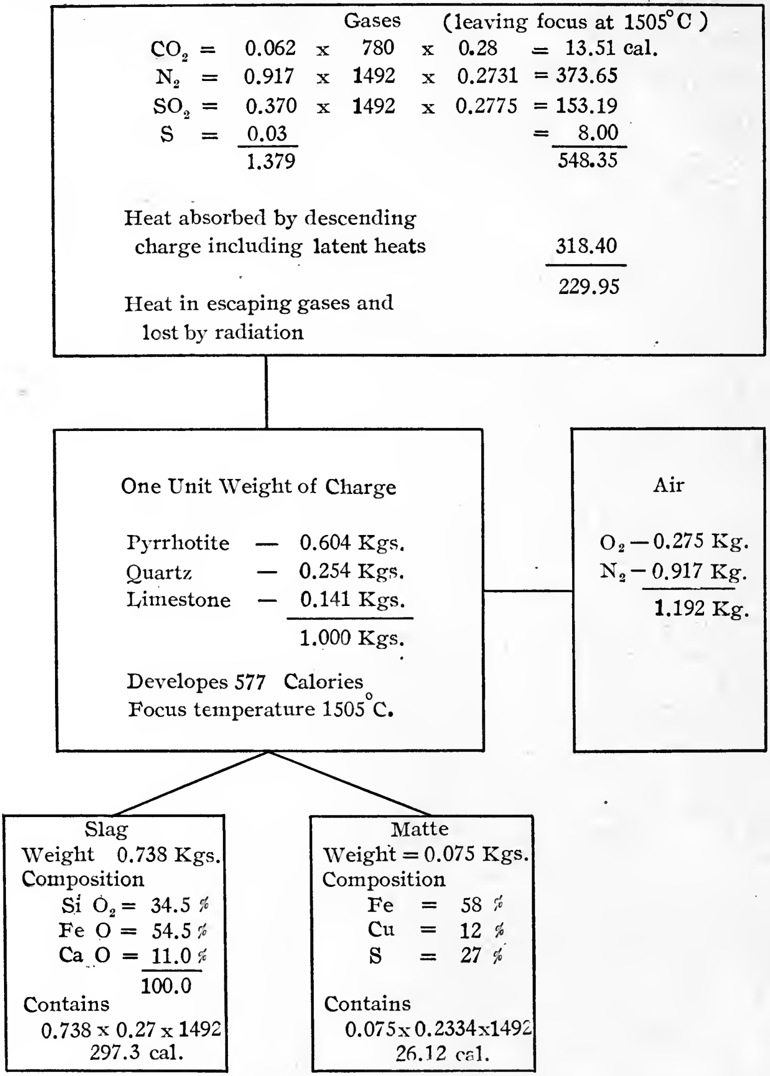

FIG. 188. — Diagram showing heat distribution in pyritic smelting.

This is sufficient to discharge the gases, assuming a mean specific heat of 0.24 for the same, at 225° C. This is lower than occurs in practice where the gases are discharged at from 350 to 400° C., but it must be borne in mind that in the calculation the slag and matte are assumed to be discharged at 1512° C., while actually it will be discharged at about 1250° C. This difference makes heat units available in the furnace, which in part are transferred to the gas; in fact, it is evident that there is some surplus of heat above that required. The calculation shows that from the thermal standpoint pyritic smelting with pyrrhotite can be carried out without the use of carbonaceous fuel.

From a similar calculation, but with pyrite as the base, it can be shown that per unit of charge only 329 calories, instead of 577, are liberated, on the assumption that 66,900 is the formation heat of pyrite, which, as already stated, may be high. In this case some coke would be required to get the required number of heat units to carry on the process.

Since the furnace gases in pyritic smelting contain only traces of CO, but some SO_3, it may be assumed that in the reactions throughout the furnace, eventually the whole of the calorific power of coke is liberated. It is true that coke descending in the furnace charge in an atmosphere rich in SO_2 is subject to the following reaction:

$$SO_2 + C = S + CO_2$$

which liberates only 2328 calories per kg. of coke, but this dissolving action seems to be weak, since in the author's experience when smelting with 3 per cent. coke, considerable coke sometimes appears at the tap hole of the furnace with the slag.

Composition of the Charge for Pyritic Smelting. — A unit weight of charge in order to carry on the process must be capable of developing a certain number of heat units, which from the calculation is not far from 577. This number represents a fair margin. The composition of this charge is shown by the equation on page 520. The question arises as to how much this composition may vary and still enough heat units be liberated to carry on the smelting. It is at once apparent that if the charge contains too large an amount of limestone, or any other minerals that do not enter into a heat-producing reaction, the heat units liberated per kilogram of charge will be much decreased and the furnace will require extra fuel in the form of coke. As to whether more heat is liberated by the formation of a monosilicate iron slag, or a bisilicate iron slag, can readily be shown by the accompanying equation, taking pyrite as a basis:

$$\begin{array}{lllllll} (1) & 2FeS_2 & + SiO_2 & + 3O_2 = & 2FeO\cdot SiO_2 & + 2SO_2 & + 2S. \\ & 133{,}800 & 180{,}000 & & 318{,}200 & 138{,}520 & \end{array}$$

or 1 kg. charge liberates 446 calories.

$$\begin{array}{lllllll} (2) & 2FeS_2 & + 2SiO_2 & + 3O_2 = & 2(FeO\cdot SiO_2) & + 2SO_2 & + 2S. \\ & 133{,}800 & 360{,}000 & & 509{,}200 & 138{,}520 & \end{array}$$

or 1 kg. charge liberates 427 calories.

The monosilicate slag liberates 19 calories more per kg. of charge. It is evident, therefore, from the main equation on page 520, that this represents the proper composition of furnace charge, the amount of limestone representing in general the non-heat-producing minerals which may be carried on the charge without greatly lowering the number of heat units produced. The composition of the charge for successful pyritic smelting may be deduced from the main equation. The charge contains 36 per cent. Fe (unoxidized) and 25.4 per cent SiO_2. The following data gives some charge compositions from practice:

Locality	Per cent. Fe on charge[1]	Per cent. SiO_2 on charge[1]	Per cent. Limestone on charge	Per cent. Slag on charge
Mt. Lyell, Tasmania........	31.2	23.25	6.1	10.6
Rapid City, S.D.	31.2	23.40	3.3	4.4
" " "	29.4	22.9	—	—
" " "	30.8	23.6	—	—

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[1] The charge in these instances is the ore and quartz and first matte going into the furnace, viz., the total weight of charge minus the limestone, coke, and ballast slag.

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