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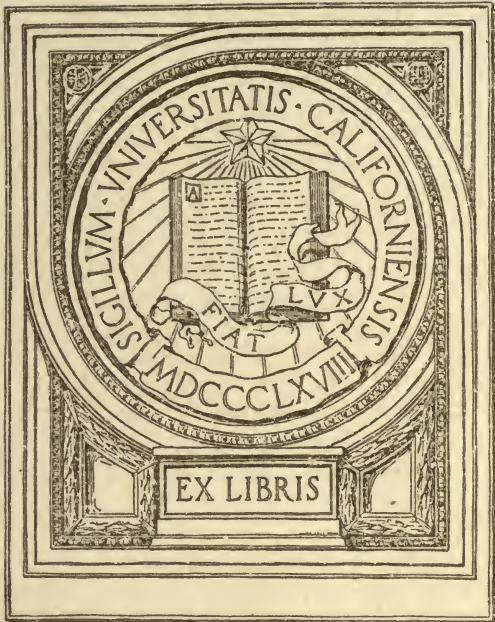
INTRODUCTION TO THE STUDY

OF

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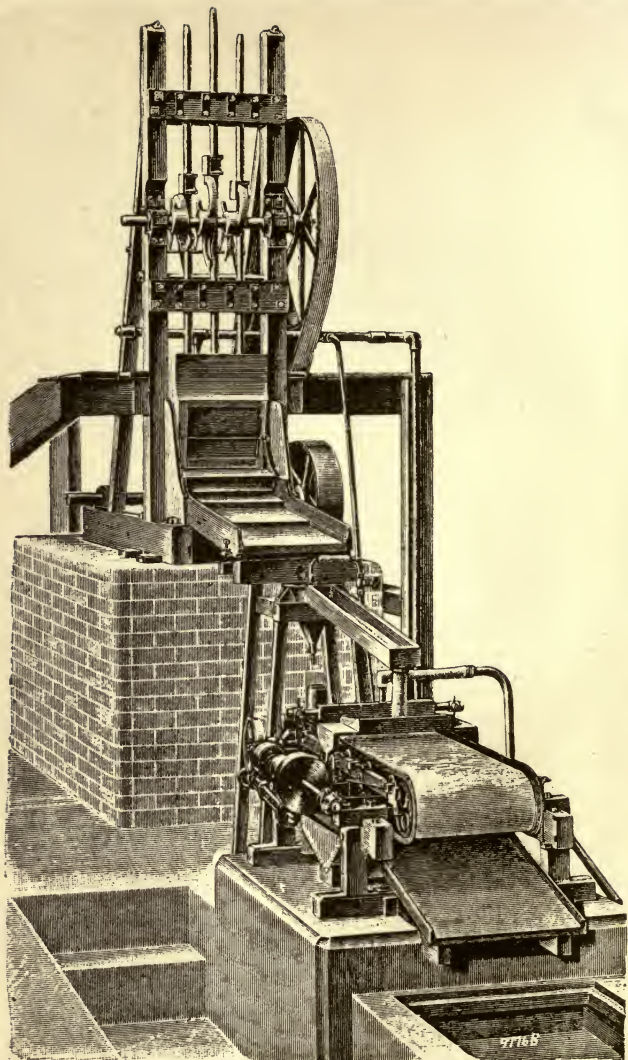
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AN INTRODUCTION TO THE STUDY

OF

METALLURGY.

BY

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PROFESSOR OF METALLURGY IN THE ROYAL COLLEGE OF SCIENCE, WITH WHICH
THE ROYAL SCHOOL OF MINES IS INCORPORATED.

WITH NUMEROUS DIAGRAMS.

LONDON:

CHARLES GRIFFIN AND COMPANY,
EXETER STREET, STRAND.
1891.

PREFACE.

THE literature of metallurgy is rich, but those who are beginning to study it need guidance to a knowledge of the principles on which the art is rightly practised. It depends, as is well known, on the application of chemistry, physics, and mechanics; but the methods of metallurgists vary greatly from those of chemists, who, however, frequently fail to appreciate the nature of the difference.

Ten years' experience has convinced me that it is more important at the outset for the student to know what was the scope of mind of the early practisers of metallurgy, and to see what kind of aid the art may be expected to receive in future from the sciences, than to acquire familiarity with complicated details of processes and appliances. In this little volume I have, therefore, devoted four chapters to these branches of the subject, embodying in them portions of lectures which I have delivered from time to time.

In all English works on metallurgy, the important metals are dealt with separately and in detail. In this, however, an attempt has been made to treat the subject as a whole, giving no minute descriptions of processes, but choosing typical appliances and indicating their use in connection with groups of metals. Such a method was adopted by the late M. Gruner, Professor of Metallurgy at the *École des Mines*, Paris, to whom I have reason to be grateful, for I have closely followed him in my class lectures.

The student will, I trust, be led to study the works in which

the extraction of metals from their ores and fitting them for use are fully discussed. Such are the classical treatises of Percy, the monographs of Sir Lowthian Bell, and the manual of Phillips and Bauerman, from which volume a few illustrations have been borrowed. The literature of the subject has been enriched by Howe, of Boston, who has collected a store of facts in his elaborate and recently-published volume on steel.

In the preparation of a portion of this little work, I have been aided by my colleague, Mr. Bennett Brough, whose help has been specially useful in passing the work through the press.

I hope that the book will be found useful to my own students, for whose progress I feel sincere solicitude.

CHILWORTH, SURREY,
       December 23, 1890.

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INTRODUCTION TO THE STUDY

OF

METALLURGY.

CHAPTER I.

THE RELATION OF METALLURGY TO CHEMISTRY.

THE distinguished metallurgist who may be said to have created the English literature of the subject concluded the introductory lecture he delivered * at the Royal School of Mines, by pointing out to the students who were then beginning their course, that "in proportion to the success with which the metallurgic art is practised in this country, will the interests of the whole population, directly or indirectly, in no inconsiderable degree, be promoted."

During the period of nearly forty years since Dr. Percy began to teach, the conditions under which metallurgy is practised have changed considerably; for the field of knowledge has so widely extended, the scale on which operations are conducted is now so great, and the mechanical appliances they involve are so varied and complicated, that while the interest of the subject is deepened, its difficulty is gravely increased. Metallurgy involves not only a knowledge of "the art of extracting metals from their ores," but also of the means of "adapting them for use," which is effected by complicated mechanical operations, and, strange as it may seem, by varying the degree of purity, often to a very slight extent. It will thus be evident that the student must possess adequate knowledge of Inorganic Chemistry, Mechanics, and Physics. Besides this, he must acquire aptitude for dealing with economic details.

* *Records of the School of Mines*, vol. i. pt. i. (1852), p. 127

Historical Sketch.—In turning to the history of metallurgy, it is easy to be led away by the charm of the antiquarian store of riches into devoting too much time to literary research. It should be remembered, however, that much of what is both interesting and full of suggestion, even at the present day, is to be found buried in the treatises by the old writers whose work we inherit and continue.

Primitive metallurgical processes are referred to in some of the oldest known historical records ; naturally, therefore, the scientific development of metallurgy must have been long preceded by its empirical practice as an art, an art for which a place has even been claimed among the religious systems of antiquity.* The earlier literature of the subject consists mainly of descriptions of processes ; but it is well known that chemistry was to a great extent built up on a metallurgical basis, and Black's singularly advanced definition of chemistry as the " effects produced by heat and mixture " † might well be applied to metallurgy. The library of Leyden contains a papyrus which has been described by M. Reuvens,‡ and which is considered by Kopp§ to be the oldest known chemical manuscript, its date being possibly as early as A.D. 200. It treats generally of metallurgical matters, and the purification of gold and silver is frequently mentioned. Of all chemical phenomena, probably none have more contributed to advance chemistry as a science than those bearing upon the relations between oxygen and lead ; and the interest attaching to the mutual behaviour of these two elements is so great that the student will do well to consider the influence of one very ancient metallurgical process on the scientific views of the present day.

When lead is melted with free access of air, a readily fusible substance forms on its surface. This substance may be allowed to flow away, or, if the metal is contained in a suitable porous receptacle, the fusible oxide sinks into this containing vessel ; in either case the oxidation of the lead affords a means of separating it from precious or inoxidisable metals, if any were originally present in the lead. The above fact has been known from remote antiquity, and the early Jewish writers allude to it as old and well-known. They clearly show, for instance, that lead can be removed from silver by being " consumed of the fire," while the silver is not affected. That the Greeks knew and practised this

* Rossignol, *Les Métaux de l'Antiquité* (1863).
† *Lectures.* By Joseph Black, M.D., vol. i. pp. 11, 12 (Edin. 1803).
‡ Reuvens, *Lettres à M. Letronne* (Leyden, 1830), quoted by Prof. Ferguson in an address to the Glasgow Phil. Soc. (1876), p. 19.
§ *Beiträge zur Geschichte der Chemie,* 1869.

method of *cupellation* is abundantly proved, if only by certain specimens of gold and silver which were discovered by Dr. Schliemann on the site of ancient Troy. The Arabians investigated the subject, as is shown by the writings of Geber,* the greatest of the early chemists (he died in 777), who gives a remarkable account of cupellation ; he also describes the conversion of lead into a fine powder by calcination with much clearness, and he noticed the fact that after calcination the mass has " acquired a new weight in the operation." His subsequent observations on the reduction of altered metals from their " calxes " show that he knew the weight to be increased ; in any case it is interesting to remember that his work was, in a sense, quantitative. He, moreover, was cognisant of the fact that two different substances may be produced by heating lead in air, and he assumed that " in the fire of calcination a fugitive and inflammable substance is abolished." The alchemists refer continually to the subject, and " deliver themselves," as Roger Bacon said, in his *Speculum Alchimie*, " in the enigmas and riddles with which they clouded and left shadowed to us the most noble science." Eck of Sulzbach showed (1489) that metals augment in weight by calcination, and that what we now call red oxide of mercury gives off " a spirit " when heated ; had he named and isolated the spirit, he would have discovered oxygen. The great metallurgist of the sixteenth century, Agricola,† points out that lead increases in weight when it is exposed to the action of moist air. In the middle of the sixteenth century, the equally accomplished metallurgist, Biringuccio,‡ contemporary of Paracelsus and Agricola, seems to have been specially attracted by the phenomenon in question, and he remarks :— " If we had not lead we should work in vain for the precious metals, for without its aid we could not extract gold or silver from the stones containing them. . . . . The alchemists also," he says, " make use of it in their operations, calcining it by itself or with other substances ; but," he goes on to observe, " the calcination, conducted in a reverberatory furnace is accompanied by a marvellous effect, the result of which should not be passed by in silence, for lead thus treated increases ten per cent. in weight, and considering that most things are consumed in the fire, it is remarkable that the weight of lead is increased and not diminished." Although he subsequently gives evidence of much accurate know-

* The works of Geber, translated by R. Russell (1686), pp. 74, 78, 220, 234.
† *De ortu et causis subterraneorum*, p. 519.
‡ *Pirotechnia* (Vinezia, 1540), translated into French by T. Vincent (Rouen, 1627), p. 41.

ledge of practical metallurgy, his views as to this particular phenomenon were hardly in advance of Geber's; but we may claim Biringuccio as an early metallurgist, who knew the facts and recognised that they were theoretically important. Cæsalpinus, in his work, *De Metallicis*, showed that the film which covers lead exposed to moist air and augments its weight, is due to an aëriform body. It was not till nearly a century later (1630) that a French chemist, Jean Rey,* stated that the increase in weight came from the air. The problem attracted much attention in England, and it is not a little interesting that among the very first experiments recorded by our own Royal Society, is a metallurgical series relating to the weight of lead increased in the fire on the "copels" at the assay office in the Tower, the account being brought in by Lord Brouncker in February, 1661.† Subsequently, in 1669, John Mayo showed that the increase in weight of calcined metals was due to a "spiritus," or distinct constituent of ordinary air.‡ Nevertheless, Boyle heated lead in a small retort,§ and attributed the increase in weight, as Lemery also did,‖ to his having "arrested and weighed igneous corpuscles." One of the most curious passages known is in the *Hippocrates Chemicus* of Otto Tachen, a German who lived at Venice, and published his book there in 1666. He describes how lead, when burnt to minium, increases in weight. This increase he ascribes to a substance of acid character in the wood used for burning, and then, by a very ingenious course of argument, based on the saponifying powers of litharge, makes out that lead is of the nature of, or contains an alkali which combines with, the "occult acid of the fat." This is a curious anticipation of a very modern classification, which brings lead into relationship with the alkalies and alkaline earths, as well as of Chevreul's investigations on saponification. Cæsalpinus had previously called lead "a soap" which in cupellation washes gold and silver.

It is hardly necessary to point out how important this calcination of lead was considered by those who defended the Phlogistic theory in regard to chemical change, the theory propounded by the metallurgist Becker, which, for more than a century, exerted so profound an influence on scientific thought. His views were first embodied in the *Physica Subterranea* (1669) and in the *Alphabethum Minerale* (1682).

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* *Essais de Jean Rey* (reprinted in Paris, 1777), p. 64.
† MS. register book of the Royal Society.
‡ *Tractatus quinque Medico-Physici*, p. 25 *et seq.* (Oxonii, 1674).
§ Collected works, vol. iii. (1744), p. 347.
‖ *Cours de Chymie* (1675), 2nd English edition (1686), p. 107.

According to his still more famous pupil Stahl, the litharge produced by the prolonged calcination of lead in air, is lead deprived of its phlogiston; but he and his followers were indifferent to the fact that when lead is burnt the weight of the resulting mass is greater than that of the original metal, and were content to insist that the burnt lead had lost its inflammable principle—that is, Phlogiston.

Tillet, assayer of the Paris Mint, made some quantitative experiments which led up in a singular way to the work of Lavoisier, who, as is well known, overthrew the old phlogistic theory by showing that a chemical combination takes place, resulting in an augmentation of weight which represents the exact weight of the gaseous body added. At the same time it should be remembered that the phlogistic chemists made a great step in advance, as was admitted by J. R. Mayer* in his memoir on the mechanical theory of heat; and Odling, discussing the experiments on the oxidation of lead, has pointed out † that an error has arisen in consequence of the same word being used in a different sense at different periods of time; chemists, in fact, now substitute the words potential energy for phlogiston, or, as Dr. Crum Brown well observed,‡ we recognise "that no compound contains the substances from which it was produced, but that it contains them *minus* something. We know now what this something is, and can give it the more appropriate name of potential energy; but there can be no doubt that this is what the chemists of the seventeenth century meant when they spoke of phlogiston."

It will thus be evident that the main aim of chemical investigation down to the end of the last century was the explanation of calcination, combustion, or oxidation, and that lead was especially useful in solving the problem. It might, perhaps, be added that the absorption of oxygen by molten litharge furnished Ste. Claire Deville,§ a physicist and metallurgist, with an important step in the argument as to dissociation, thus connecting the history of the metal, lead, with the great advance on the borderland of chemistry and physics which has been made in modern times.

The above remarks will be sufficient to show that conclusions of the utmost importance in the history of chemical theory were based on the very ancient metallurgical process of cupellation of lead, a process which affords an appropriate illustration, because,

* *Bemerkungen über die Kräfte der unbelebten Natur*, Liebig's Ann., vol. xlii. (1842). p. 233.
† *Proc. Roy. Inst.*, vol. vi. (1871), p. 323.
‡ *Edin. Roy. Soc. Proc.*, vol. v. (1866), p. 328.
§ *Ann. de Chim. et de Phys.* [3], vol. xlvi. p. 182.

in the gradual development of the knowledge derived in the first instance from the metallurgy of lead, there is much that is typical of the mutual relation of theory and practice that still prevails.

Now, as in the past, in the study of metallurgy, a prominent position must be given to the production of high temperatures, as it will be obvious that metallurgists have principally to consider the reactions of the elements when under the influence of heat. In the first half of the present century, temperatures higher than the melting point of zinc had not been determined with any degree of certainty; but, in 1856, Henri Ste. Claire-Deville pointed out that chemistry at high temperature, that is to say, up to the blue-white heat at which platinum volatilises and silica fuses, remained to be studied, as under such conditions ordinary chemical reactions may be modified or even reversed. Since then, in conjunction with Troost, he has given certain fixed points, such, for instance, as the boiling-points of cadmium and zinc; and his researches on dissociation have entirely modified the views generally entertained in regard to the theory of combustion. Indeed, so much is due to this illustrious teacher, that the best homage that can be offered him will be to work in the directions he has indicated.

The essential difference in the properties of metals produced by a small difference of composition introduces one very distinctive feature of metallurgy—the enormous influence exerted on a large mass of metal by a " trace " of another metal or metalloid, that is, by a quantity so small that it appears to be out of all proportion to the mass in which it is distributed; and it may safely be asserted, that in no other branch of applied science has the operator to deal with quantities that are at once so vast and so minute.

It may be that the trace is alone of value, as, for instance, the few grains of gold that can be profitably extracted from a ton of material, which, though containing only one part of gold in five millions by volume, is thereby entitled to be regarded as an auriferous deposit that can be profitably worked; or it may be that the presence of a minute percentage of a metalloid is prejudicial and must be extracted, in order that the physical properties of the remaining mass of metal may not be such as to render it useless. Due prominence is given to such facts in the following pages.

CHAPTER II.

PHYSICAL PROPERTIES OF METALS.

Molecular Structure.—The physical aspects of metals are so pronounced as to render it difficult to abandon the old view that metals are sharply defined from other elements, and form a class by themselves. The term metal is in fact somewhat arbitrary. Zinc and bismuth, when they were first discovered, were considered to be semi-metals, and it was not until mercury was frozen by Braune in 1759 that it was recognised as a metal. Like all other elements, metals are composed of atoms grouped in molecules, and any force that alters the relations of the atoms in the molecules modifies the physical properties of the metals. Indeed, it would be easy to show that the physical constants of each metal vary with its degree of purity. The molecular grouping of metals is doubtless very varied, and little definite is known regarding the structural stability of most of them ; but it may be assumed that it is not very great, as some metals split up into single atoms when they are volatilised, and most of them unite readily with chlorine and with oxygen.* It is probable that in many pure metals, such as gold, silver, copper and iron, the individual molecules are of simple atomic constitution, and that these fundamental molecules bear a uniform relationship to one another. Consequently, any mass, of which the fundamental molecules are the constituent particles, may practically be regarded as a single molecule. Two fundamental molecules must, however, be held to be capable of uniting to form complexes that have less power of cohering, and any circumstance tending to bring about the formation of such complexes would also tend to make the material less tough. This may account for the extraordinary alteration in the properties of many metals produced by very small quantities of incompatible foreign matters.† It will be shown in a future chapter that the effect produced by a small quantity of an im-

* Lothar Meyer, *Modern Theories of Chemistry*, English translation, 1888, p. 568.
† H. E. Armstrong, *Min. Proc. Inst. C.E.*, vol. xciii. (1888), p. 112.

purity added to a mass of metal bears a close relation to the
atomic volume of the added element.

Density.—The density of a metal is dependent on the intimacy
of the contact between the molecules. It is dependent, there-
fore, on the crystalline structure, and is influenced by the tem-
perature of casting, by the rate of cooling, by the mechanical
treatment, and by the purity of the metal. With the exception
of bismuth, all metals are lighter when molten than when in the
solid state. In the case of cast iron, which passes through a
pasty state on solidification, the density is less in that state than
in the fluid or solid. The density of a metal is augmented by
wire-drawing, hammering, and any other physical method of
treatment in which a compressing stress is employed. Mere
traction, however, may diminish the density by tending to de-
velop cavities in the metal. Pressure on all sides of a piece of
metal increases its density. The density of standard gold, for
example, by compression between dies is increased by 0.9, and
cast discs of platinum, having a density of 21.21, may have the
density increased to 21.46 by striking; whilst annealing such
struck discs will again diminish their density. This shows that
the compression is not permanent, and is solely due to the closing
of pores. W. Spring * has even shown by careful experiments
on lead, tin, bismuth, antimony, cadmium, aluminium, and zinc,
that a pressure of 20,000 atmospheres continued for many days
is insufficient to effect the obliteration of all the pores. A
metal can only be really compressed if the result of the applica-
tion of pressure is to cause it to pass to an allotropic state, that is
denser than that which it originally possessed. The specific
gravities of the various metals are given in the table on p. 9.
Lithium is the lightest metal, and iridium the heaviest, the specific
gravity of the former being 0.6, and that of the latter 22.38.

So early as 1845, Joule † recognised the importance of deter-
mining the specific gravity of melted metals, seeing that "this
condition would completely obviate the influence of cohesion, or
that of any particular molecular arrangement." His method,
which was essentially that afterwards adopted by Mallet ‡ and by
the author,§ may be described as follows :—It consists in filling
with molten metal a vessel, the capacity of which may be calcu-
lated for the particular temperature at which the molten metal is
introduced. The weight of the metal when cold, divided by the

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* *Bull. Soc. Chim. Paris*, vol. xl. (1883), p. 515.
† Collected Papers. Published by the Physical Society, vol. ii. p. 136.
‡ *Proc. Roy. Soc.*, vol. xxii. (1873), p. 366 ; and vol. xxiii. (1874), p. 209.
§ *Ibid.*, vol. xxiii. (1875), p. 481.

weight of water which the expanded vessel is capable of holding, gives the fluid density of the molten metal. Subsequently, working in conjunction with T. Wrightson, the author [*] determined, by the aid of an instrument called the oncosimeter, devised by the former, the fluid density of several metals. The results which have as yet been obtained may be briefly summarised in the following table :—

	Specific Gravity of Solid.	Fluid Density.		Percentage of Change in Volume from Cold Solid to Liquid.	
		By Mallet's Method.	By Oncosimeter.		
Bismuth . .	9.82	10.039	10.055	Decrease of vol.	2.30
Copper . .	8.80	—	8.217	Increase of vol.	7.10
Lead . . .	11.40	10.650	10.370	,, ,,	9.93
Tin . . .	7.50	6.974	7.025	,, ,,	6.76
Zinc . . .	7.20	6.550	6.480	,, ,,	11.10
Silver . . .	10.57	9.460	9.510	,, ,,	11.20
Iron (No. 4 foundry pig) . .	6.95	—	6.880	,, ,,	1.02
Iron, cast (mixed brands) . .	7.17	6.650			

The question of the fluid densities has also been investigated by Nies and Winkelmann,[†] who have adopted another method, determining the liquid density by observing the weights of blocks which just sink and just swim. With regard to bismuth, C. Lüdeking[‡] finds that this metal, like water, attains a maximum density just before becoming solid, the expansion at the moment of solidification being about 3 per cent. of the volume.

Fracture.—The appearance of the fractured surface of a metal depends partly on the nature of the metal and partly on the manner in which solidification occurred. Sudden cooling to a great extent prevents the formation of crystals, whilst slow cooling facilitates their development. Long-continued hammering, frequent vibrations, and intense cold will produce the latter result. Any condition that affects either the cohesion or the crystalline structure of a metal affects its fracture. Thus, lead broken when hot has a columnar structure; when broken cold, this structure is not exhibited.

* *Phil. Mag.*, vol. xi. (1881), p. 295; vol. xiii. (1882), p. 360.
† *Sitzungsber. der Acad. der Wissen. zu München*, 1881, p. 63.
‡ *Ann. Phys. Chem.*, vol. xxxiv. (1888), p. 21.

The ordinary mineralogical terms regarding colour and fracture are used in relation to metals. Practice, however, can alone enable the student to accurately describe these appearances.

Malleability.—This is the property of permanently extending in all directions, without rupture, by pressure produced by slow stress or by impact. As a rule, crystalline metals are not malleable, and any circumstance that tends to produce crystallisation must affect the malleability. Thus, in nearly all metals the malleability becomes impaired when they are subjected to rolling or long-continued hammering; but this property may be regained by annealing, which consists in raising the metal to a high temperature and allowing it to cool, either rapidly or slowly, usually the latter. At different temperatures metals behave in different ways; some are malleable when at a red heat, but not so when cold. These are defined as being *cold-short*. Others are malleable when cold, but not when at a red heat. These are described as being *red-short*. Some metals are malleable at all temperatures, others are not malleable at all. Zinc is brittle when cold and when hot, but at a temperature of 150° it is malleable. The malleability of a metal is dependent on its purity. Relative malleability may be determined by the degree of thinness of the sheets that can be produced by beating or rolling the metals, without annealing.

Ductility is the property that enables metals to be drawn into wire. It generally decreases with an increase in the temperature of the wire at the time of drawing, but there is no regular ratio between the two. Iron is less ductile at 100°, and more ductile at 200°, than it is at 0°. Malleable metals are also ductile, but they do not possess the two properties in the same order. Arranged according to their malleability, the more important metals follow this order:—1. Gold; 2. Silver; 3. Copper; 4. Tin; 5. Platinum; 6. Lead; 7. Zinc; 8. Iron; 9. Nickel. The order of ductility, on the other hand, is:—1. Gold; 2. Silver; 3. Platinum; 4. Iron; 5. Nickel; 6. Copper; 7. Zinc; 8. Tin; 9. Lead. The rate at which the traction is applied, exercises an important influence on the properties of malleability and ductility.

Tenacity is the property possessed by metals, in varying degrees, of resisting the separation of their molecules by the action of a tensile stress.

Toughness is the property of resisting the separation of the molecules after the limit of elasticity has been passed.

Hardness is the resistance offered by the molecules of a substance to their separation by the penetrating action of another sub-

stance. Great differences are observable between the hardness of the different metals. The results of the experiments of Bottone gave valuable information. In his scale the hardness of the diamond was found to be 3010, whilst the relative hardness of twenty metals was determined with the following results :—

Manganese	.	.	.	.	1456	Gold	.	.	.	979
Cobalt	.	.	.	.	1450	Aluminium	.	.	.	821
Nickel	.	.	.	.	1410	Cadmium	.	.	.	760
Iron	.	.	.	.	1375	Magnesium	.	.	.	726
Copper	.	.	.	.	1360	Tin	.	.	.	651
Palladium	.	.	.	.	1200	Lead	.	.	.	570
Platinum	.	.	.	.	1107	Thallium	.	.	.	565
Zinc	.	.	.	.	1077	Calcium	.	.	.	405
Silver	.	.	.	.	990	Sodium	.	.	.	400
Iridium	.	.	.	.	984	Potassium	.	.	.	230

In these determinations the time necessary to produce a cut of definite depth was taken as a measure of the hardness of the material, and Bottone concluded that the hardness so obtained was proportional to the specific gravity of the metal divided by its atomic weight. Metals that possess high limits of elasticity are usually very hard. The softness increases with an increase of temperature. Mr. T. Turner,[*] of the Mason College, Birmingham, a former pupil of the author, has also investigated the hardness of metals and devised a useful instrument for the purpose.

Brittleness is the sudden interruption of molecular cohesion when the substance is subjected to the action of some extraneous force, such as a blow or a change of temperature. It is largely influenced by the purity of the metal.

Elasticity, Extensibility, and Strength of Metals.—At first sight it might seem that testing the mechanical properties of metals is more within the province of the engineer than that of the metallurgist. The latter has, however, not only to extract metals from their ores, but also to fit them for use. He must therefore know what mechanical properties[†] are possessed by the more important metals and alloys, and be able to submit them to experimental tests instead of merely trusting to statements recorded by others.

Elasticity is the power a body possesses of resuming its original form after the removal of an external force which has produced a change in that form. The point at which the elasticity and

[*] *Proc. Birmingham Phil. Soc.*, vol. v. part 2.
[†] The more important recent works dealing with this subject are :—Kennedy, *Proc. Inst. C.E.*, vol. lxxxviii. (1887), p. 1 ; Unwin, *Testing of Materials of Construction*, 1888 ; Lebasteur, *Les Métaux à l'Exposition Universelle*, 1878.

the applied stress exactly counterbalance each other, is termed
the **limit of elasticity.** If the applied stress were then re-
moved, the material acted upon would resume its original form.
If, however, the stress were increased, the change in form would
become permanent, and **permanent set** would be effected.
Within the limit of elasticity, a uniform rod of metal lengthens
or shortens equally under equal additions of stress. If this
were the case beyond that limit, it is obvious that there
would be some stress that would stretch the bar to twice its
original length, or shorten it to zero. This stress, expressed in
lbs. or tons for a bar of 1 inch square cross section is termed
the **modulus of elasticity.** As an illustration, let it be supposed
that a bar of steel 1 inch square is stretched to its limit of
elasticity by a force of 139,000 lbs., and to have elongated under
the action of this stress 0.00418 inch, the modulus of elasticity of
this bar would be the force that would be required to elongate it
by 1 inch, and this would be—

$$0.00418 : 1.0 :: 139,000 : x$$

$x = 33,253,588$ lbs. per square inch. Hence the modulus of
elasticity is a stress that bears the same proportion to the original
length of a uniform bar as the stress that will produce any given
amount of strain bears to the length of this strain, the term
stress meaning an equilibrating application of force to a body,
and the term **strain** meaning any definite alteration of form or
dimensions sustained by that body. The modulus of elasticity
may thus be defined as being the number obtained by dividing
the number expressing the stress by that expressing the strain
that it produced. Unwin expresses this as follows :—

Let p be the stress reckoned on unit of area, and λ the exten-
sion or compression reckoned per unit of length.

Then, by Hooke's law—$\dfrac{p}{\lambda} = E$, a constant which is termed
the coefficient of direct elasticity, or Young's modulus. It has
the same value for tension and compression.

Thus, to take the case of a hardened sample of steel in which
the extension up to the limit of elasticity was small, the load,
however, being considerable :—

Load up to limit of elasticity, 139,000 lbs. per square inch.
Extension up to limit of elasticity, 0.00418 inch.

$$E = \frac{139,000}{0.00418} = 33,250,000 \text{ lbs. per square inch.}$$

Professor Kennedy finds the **specific extension** to be a quan-
tity most useful in works. This is the extension in thousandths
of an inch on a length of 10 inches under a stress of 1000 lbs.

per square inch. Its reciprocal, multiplied by 10 millions, is the modulus of elasticity in lbs. per square inch.

In measuring the strength of metals, it is necessary to determine—

1. The **limit of elasticity** ;

2. The greatest **stress** the metal can sustain within the limit of elasticity ;

3. The **strain** within the limit of elasticity ;

4. The total extent of the **strain**, or alteration of form before rupture takes place ;

5. The ultimate **tensile strength** or maximum stress the material can sustain without rupture.

The limit of elasticity and the breaking stress are the points which have usually to be determined, and these alone will be considered here. For information as to torsional and compression tests, the student is referred to the works of Unwin and Kennedy.

In testing a piece of metal, the first point to be determined is the limit of elasticity. When a metal, such as iron or steel, is submitted to stress by pulling its ends in opposite directions, it stretches uniformly throughout its length. There is, however, in such a solid a limit in the application of the stress up to which the metal, if released, will return to its normal length. This point is the limit of elasticity. It is, however, certain that a very small application of load produces permanent deformation, so that the determination of the exact limit of elasticity will depend upon the delicacy of the instruments used for its measurement. It is safe to consider the limit of elasticity to be the point at which the stresses and strains cease to be exactly proportional. If the strains are plotted as abscissæ and the stresses as ordinates, points will be obtained on a curve giving the relation of stress and strain for the whole test. Up to the limit of elasticity, this curve is almost a straight line ; but when that point has been reached, the molecular arrangement of the metal breaks down, and, as Professor Unwin expresses it, probably the breaking down point (which is not to be confounded with the limit of elasticity*), is a kind of physical record of the condition of constraint in the bar at the moment of rolling or hammering. It has been shown by Osmond that in the case of iron or steel, any stress which produces a permanent deformation is attended by a re-arrangement of the atoms within the molecules of the metal. This will be shown in a subsequent chapter to mark the passage of iron into an allotropic state. In support of this view, it may be mentioned

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* See also Gautier, "Discussion on Testing Machine," *Journ. Iron and Steel Inst.*, vol. ii. (1888), p. 31.

that Carus Wilson,* has examined this point of the stress-strain curve with much care ; and shows that the peculiar bending of the curve indicates the condition of strain in a steel bar, since by gradually increased stress the steel may be converted from an elastic solid to a viscous fluid. He compares such curves (I to IV) for steel of different hardness with the stress-strain curves of a gas at different temperatures, there being strong probability that in both cases the apparent discontinuity, at AF, BE, and CD, is really a double inflection due to a change taking place piecemeal through-

FIG. I.   FIG. 2.
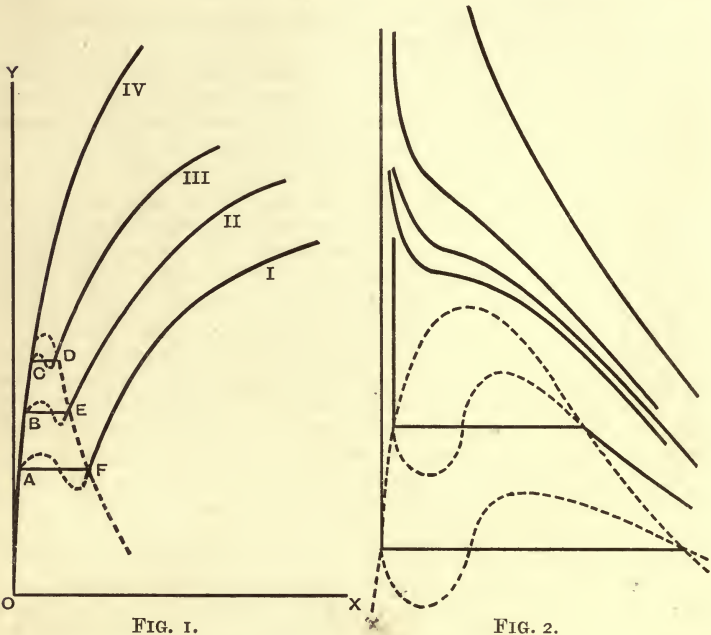
out the mass. Figs. I and 2 show Carus Wilson's curve for the yield-point of steel, and Andrew's curve exhibiting the passage of carbonic anhydride from the gaseous to the liquid state. Probably the increase in the breaking stress and diminution in the elonga-tion, which has been found to result from the application of long continued stress to steel, is the result of the molecular change in the metal. It is also known that the prolonged application of a

* *Phil. Mag.*, vol. xxix. (1890), p. 200.

load to steel raises the limit of elasticity. This appears to afford additional evidence of molecular change. If the load is slowly applied the stress-strain curve will be flatter than if it is applied rapidly. Colonel Maitland* has conclusively shown that in the case of unhardened steel used for the manufacture of guns, the ultimate elongation is increased from 27 to 62 per cent. by rapid application of the load.

It is important to ascertain in what way the mechanical properties of metals are modified when they are submitted to tests while hot. André le Chatelier† has published some experiments in this direction in connection with a research on the influence of temperature on the mechanical properties of iron and steel. His results as regards pure varieties of "cinder free" ingot iron containing 0.05 per cent. of carbon, and steel with 0.8 per cent. of carbon are given in the curves (Fig. 3). The amount of man-
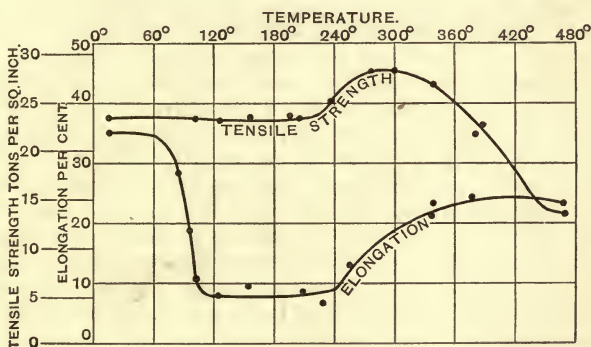
FIG. 3.

ganese varied from 0.35 per cent. to 0.4 per cent. The effect of heat is to produce two modifications in the mechanical properties of iron and steel; one of these becomes evident at 80°, the second at about 240°. These changes depend both on the temperature and on the speed with which the load is applied. The fragility of iron to shock is at its maximum at 300°, but it also possesses at this temperature a maximum resistance both to longitudinal stress and to extension if the load is slowly applied.

With reference to the strength of alloys at different temperatures,

* *Min. Proc. Inst. C.E.*, vol. lxxxix. p. 120.
† *Comptes Rendus*, vol. cix. (1889), p. 58.

Prof. Unwin* observes that, in the case of commonly used alloys, such as gun-metal and brass, the question is one of practical importance. Some experiments made by him in 1877 for the Admiralty proved that Muntz-metal and phosphor-bronze showed a fairly regular decrease in tenacity as the temperature was raised to 260°, but in the case of gun-metal the tenacity diminished regularly up to a temperature of 150° to 175°, while beyond that temperature there was a sudden decrease of tenacity, generally of more than 50 per cent., and in several cases at a temperature of 260° the tenacity had become *nil*. This is important, because at the high pressures and correspondingly high temperatures at which steam-engines are often worked, gun-metal may be exposed to temperatures of 175° to 230°, and in order to ascertain whether at such temperatures the strength of such alloys is seriously impaired, Prof. Unwin has made a further series of experiments. The results showed that with yellow-brass, Muntz-metal, and Delta-metal the decrease of tenacity follows a regular law without any sudden loss of strength. Even at temperatures of 315° to 345°, all the bars had a not inconsiderable tenacity. The ultimate elongation of the bars was measured, and a peculiarity in the influence of temperature was observed. In most cases the ultimate elongation diminishes with increase of temperature. With Muntz-metal the decrease is regular, and there is still a considerable elongation before fracture at temperatures above 340°. With yellow-brass the decrease is more rapid, and there is very little elongation before fracture at temperatures above 260°. The elongations of the gun-metal bars were very irregular, and at temperatures of over 260° the elongations were but small. On the other hand, in the case of Delta-metal bars, the elongation increased regularly with the increase of temperature. The composition of the above-named alloys will be found in Chap. III.

The elasticity and strength of metals are determined by the aid of testing machines, the more important of which are based on Kirkaldy's constructive principle of applying the load by water pressure and measuring it by dead weight. In small machines, the hydraulic ram may be replaced by a screw and gearing. Figs. 4 to 7, copied from Prof. Kennedy's admirable paper on engineering laboratories,† illustrate the principle of several types of testing machine, without indicating their proportions. The Werder machine (Fig. 4) is largely used on the Continent. The test piece, a, is held at one end in the frame of the machine, e, and at the other pulled from the short arm, c_1, of a knee-lever, to the long arm of

* *Report Brit. Assoc.* 1889, p. 746.
† *Min. Proc. Inst. C.E.*, vol. lxxxviii. (1887).

which hangs a scale-pan, d. The ratio of c_2 to c_1 is 500 : 10. The central fulcrum of the lever rests on the end of the ram, b, so that the whole measuring apparatus moves along as the piece extends
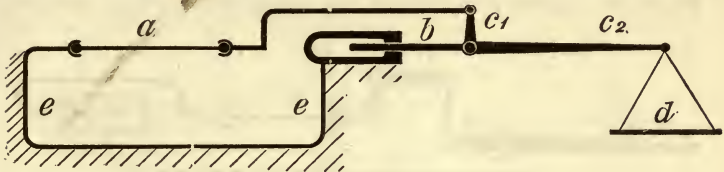
FIG. 4.

and the ram moves out, the arm, c_2, being always kept horizontal by the aid of a spirit level.
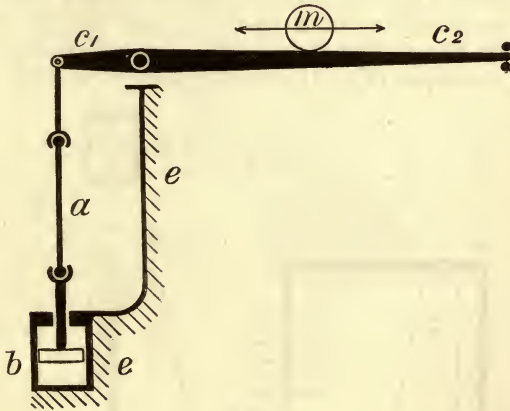
FIG. 5.

Wicksteed's machine* (Fig. 5) is a vertical one with a single lever, $c_1 c_2$, placed horizontally on the top. A movable poise, m, measures the load, pressure being applied to the ram, b, by a screw or pump. The ratio of c_2 to c_1 is 50 : 1. In a 100-ton machine, the weight, m, is 1 ton, so that it balances a pull of 50 tons when at the end of c_2. To carry the load on to 100 tons, m is run back over the fulcrum, and a second weight of 1 ton is hung to the end of c_2. The poise weighs 1 ton, and is moved along the lever by a screw worked by power. Each 3 inches of movement of the poise adds 1 ton to the load on the test-piece, whilst a vernier

* *Inst. Mech. Eng. Proc.*, 1882, p. 384.

B

attached to the poise may be read, on a scale affixed to the lever, to one-hundredth of a ton.

Greenwood's machine (Fig. 6) is in use in the laboratory of Professor Kennedy, by whom the original type has been con-
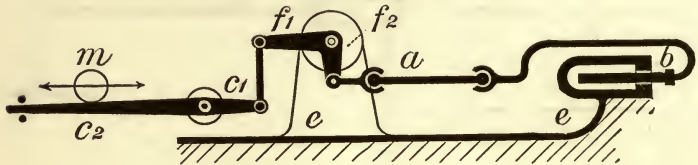
FIG. 6.

siderably improved. It is a horizontal machine with two levers, a knee lever, $f_2 f_1$ (5 : 1), and a steel-yard, $c_2 c_1$ (20 : 1), the total leverage being 100 : 1. The load is applied by the ram, b, and measured by the position of the poise, m, on the steel-yard.

Gollner's machine (Fig. 7) is a double-lever vertical machine,
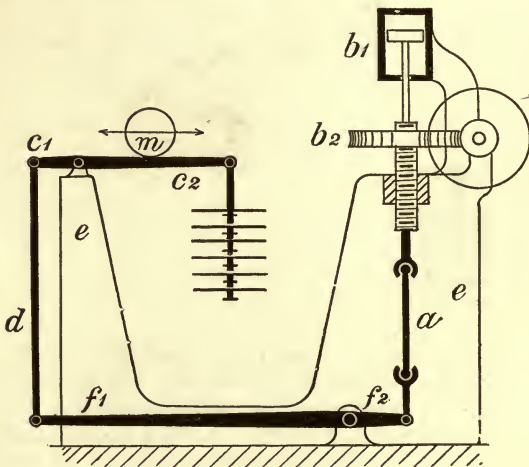
FIG. 7.

working up to 20 tons. Both screw and ram may be provided, with means for changing at once from one to the other. For light tests, the lever, $f_1 f_2$, can be disconnected, and the machine used as a single lever machine. This type of testing machine is that used in the laboratory of the Royal School of Mines, and a

rough perspective sketch of it, in the opposite position to Fig. 7, is given in Fig. 8.
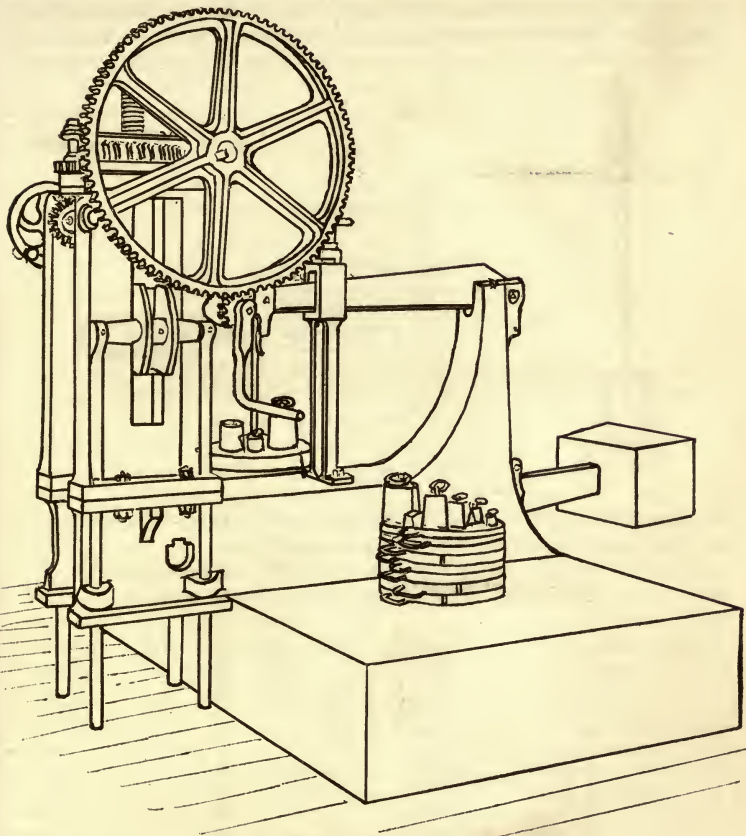
FIG. 8.

In a testing machine it is extremely desirable to have some apparatus by the aid of which the stress-strain diagram of a piece of metal under test may be drawn automatically. The most successful apparatus of this kind is that devised by Wicksteed*

* *Inst. Mech. Eng. Proc.*, 1886, p. 27. For descriptions of American machines consult *Testing Machines: their History, Construction and Use*, by A. V. Abbott. New York, 1884.

(Fig. 9). In this, the motion of the pencil that indicates the load is derived from the pressure in the hydraulic press, and not from the weighing apparatus, a wire attached by clips to the specimen serving to rotate a recording drum by an amount proportional to the elongation. The pencil having an axial motion proportional
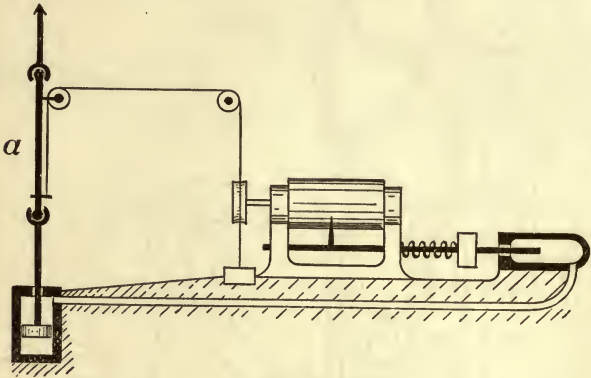
FIG. 9.

to the load, and the drum a rotating motion proportional to the extension, a stress-strain diagram is described.

The following table gives the ultimate tensile strength of a number of metals in lbs. avoirdupois per square inch :—

Copper, cast	.	.	19,000	Steel, low-carbon	.	.	90,000
,,	sheet	.	.	30,000	,, high-carbon	.	.	132,000
,,	bolts	.	.	36,000	Lead, sheet	.	.	3,300
,,	wire	.	.	60,000	Tin, cast	.	.	4,600
Iron, cast, weak	.	.	13,400	Zinc	.	.	{7,000 8,000}
,,	average	.	16,500				
,,	strong	.	.	29,000	Gold, pure, cast	.	.	15,680
Iron, wrought, plates	.	51,000	Aluminium, castings	.	15,000
,,	bars & bolts	60,000	,,	sheet	.	.	24,000
,,	hoop	.	64,000	,,	wire	.	.	30,000
,,	wire	.	90,000	,,	bars	.	.	28,000

Influence of Foreign Elements on the Strength of Metals.—The influence of chemical composition on the mechanical properties of metals is of great importance, and although this has long been recognised it is singular that the subject has been so little investigated. Turn, for instance, to Dr. Percy's classical work on Iron and Steel, published in 1864. It fully represents the information which had been gained at that time, yet it con-

tains the results of but few mechanical tests on the materials with which it deals.

The influence of foreign elements are best shown in the case of iron. The properties of this metal are absolutely changed by the presence of a few tenths per cent. of **carbon**; but it may be doubted whether the exact influence exerted by varying proportions of carbon has been accurately determined. A distinguished authority, Mr. H. M. Howe, thinks that it is not yet known, for, in an elaborate work recently published on the *Metallurgy of Steel* (New York, 1890), which will be of much service to the student, he points out that he has plotted, in a single curve, the results of over 2500 tests, and yet the conclusion he arrives at is, that we are not at present able to quantitatively express the effect of carbon. The fact is, that metallurgists are only beginning to realise that the effect of elements in the presence of each other is very complicated, and that it is absolutely necessary to study the effect of any given element on an absolutely pure mass of the metal to be tested. With regard to iron, the author has shown[*] that the tensile strength of electro-deposited iron, which is as pure as any iron can be, is 2.7 tons per square inch before annealing, and 15.5 tons per square inch after annealing. Even in this case, however, it is doubtful how far the result is influenced by the presence of occluded hydrogen, or by the fact that electrolytic iron is probably an allotropic form of the metal. In studying the effect of carbon, it is very difficult, therefore, to start from pure iron as an absolute basis. It may be sufficient, however, for the student to keep steadily in mind the very useful diagram, represented in Fig. 10, by which Deshayes[†] has indicated the effect of carbon, and incidentally that of manganese, on the tensile strength of iron. The co-ordinates are respectively percentages of carbon and tensile strengths expressed in tons per square inch. The effect of carbon is indicated by the dark continuous line, and that of varying proportions of manganese in the presence of carbon by the thin continuous, and the dotted lines. The effect of a given proportion of carbon is found by producing a vertical line, from the point indicating the percentage of carbon, until it cuts the darker curve, so that the tensile strength will be represented by the length of this vertical line. It may be added that, according to some authorities, the maximum strength would be attained in steel containing 0.8 to 1.0 per cent. of carbon, after which point the line representing tensile

[*] *Journ. Iron and Steel Inst.*, No. i. (1887), p. 74.
[†] *Classement et emploi des Aciers* (Paris, 1880), p. 151.

strength falls rapidly. This is also shown by the dotted curve in Fig. 14, p. 28.

The tenacity of carburised iron is, however, greatly affected by the " mode of existence " of carbon in the iron, as will be shown in Chapter IV., which deals with the thermal treatment of metals. It will therefore be evident that it is only possible for any curve to represent in a very general way the influence of carbon on iron, and this is specially true of the highly carburised varieties of iron known as cast iron.

INFLUENCE OF CARBON & MANGANESE ON IRON.
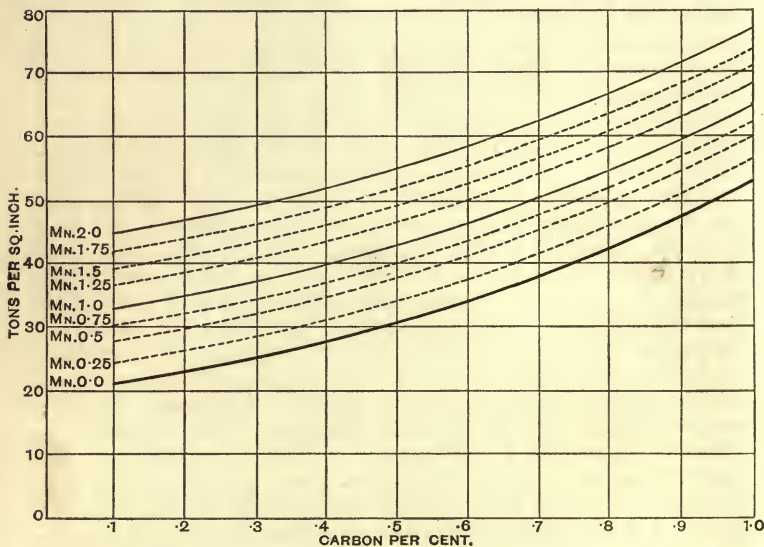
FIG. 10.

Deshayes considers that the modulus of elasticity of all kinds of steel is constant, provided that they have been subjected to identical thermal treatment, and it is safe to conclude that the effect of varying proportions of carbon, within the limits which constitute steel, is probably very slight.

It is difficult to describe briefly the effect of small quantities of manganese on the mechanical properties of carburised iron. Its presence certainly tends to make steel casting sound.

If the effect of the simultaneous presence of **manganese** and carbon is required to be determined, the vertical line must be prolonged until it cuts the particular curve (Fig. 10) indicating the percentage of manganese in question. The foregoing remarks with regard to the action of manganese in the presence of carbon, are only true with amounts of manganese not exceeding 2 per cent. Further additions of manganese give remarkable results. Although steel, if it may be so termed, containing 4 to 6 per cent. of manganese, and less than 0.5 per cent. of carbon, is so brittle that it can be powdered under a hand-hammer, yet by adding twice this amount of manganese, a return in strength is effected; and Hadfield* thus obtained the remarkable substance known as manganese steel. With about 9 to 10 per cent., a cast bar, $2\frac{1}{2}$ inches square, can be bent considerably out of the straight without breaking. The increase in strength continues up to about 15 per cent., when a decrease takes place in actual toughness, though not in transverse strength, and after about 20 per cent. is passed, a rapid decrease again takes place. The singular point connected with these alloys is that they soften by rapid cooling, the very process which hardens ordinary steel, and conversely they recover their hardness by heating to bright redness. Manganese steel, of the best composition, with about 14 per cent. of manganese, and not more than 1 per cent. of carbon, is made very strong and tough by quenching from a white heat. It is free from blow-holes, and rolls and forges well; but it is so very hard that it is extremely difficult to work in the cold. Its electrical resistance is thirty times that of copper and eight times that of wrought iron, and for practical purposes it may be regarded as wholly unmagnetisable.

The influence of phosphorus and of silicon on iron comes next in importance to that of carbon and manganese. Taking the former element first, the diagram (Fig. 11), in which results given by Mr. Howe have been freely used, shows in a very general way the effect on the tensile strength of steel produced by **phosphorus** in the presence of amounts of carbon varying from 0.05 per cent. (line F) to 0.4 per cent. (line A). It is well known that phosphorus makes iron "cold-short," and it is now admitted that the presence of this element tends to increase the tensile strength of iron. Indeed, if the carbon be kept very low, a small quantity of phosphorus, the presence of which would formerly have been considered highly dangerous, is not viewed with disfavour even in rails.

* *Journ. Iron and Steel Inst.*, No. ii. (1888), p. 41. This contains an excellent bibliography of the subject.

It is certain that phosphoric iron and steel is very fragile when subjected to suddenly applied stresses, or, in other words, to "shock." Phosphorus usually increases the limit of elasticity of iron, especially in the presence of carbon.

INFLUENCE OF PHOSPHORUS ON STEEL.

PERCENTAGE OF CARBON.

A	.	.	.	.	.	.	0.40 to 0.50
B	.	.	.	.	.	.	0.30 to 0.40
C	.	.	.	.	.	.	0.25 to 0.30
D	.	.	.	.	.	.	0.20 to 0.25
E	.	.	.	.	.	.	0.10 to 0.15
F	.	.	.	.	.	.	0.05 to 0.10

FIG. 11.
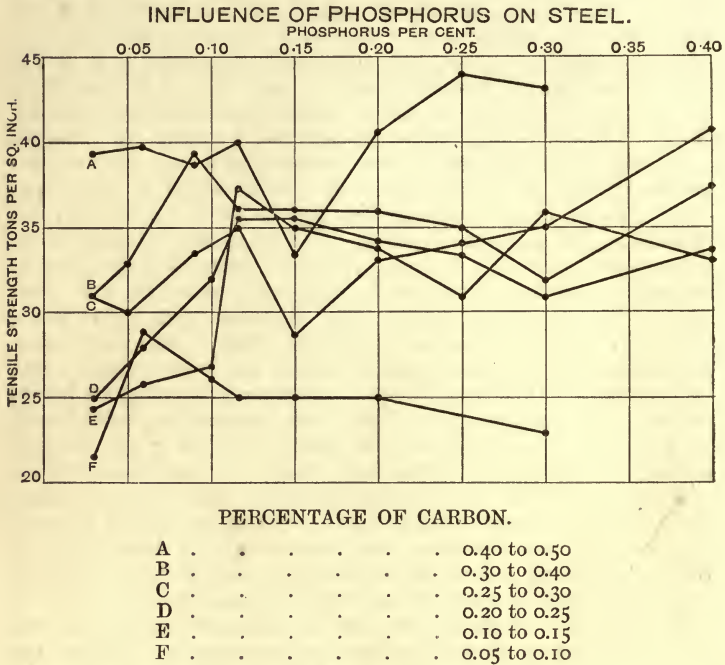
It is very difficult to estimate the influence of **silicon.** It is known that the addition of silicon to molten steel is useful, as it prevents the formation of "blow-holes" in the solidifying mass. Probably the silicon acts by prolonging the solubility of gas in iron until the metal has actually set. The presence of silicon certainly appears to facilitate the separation of graphitic carbon from iron. Mr. T. Turner,* of the Mason College, Birmingham, a former student of the author's, has done excellent work by studying the action of silicon on pig-iron and steel, and his

* *Journ. Chem. Soc.*, 1885, p. 577 and p. 902.

INFLUENCE OF SILICON ON PIG IRON.
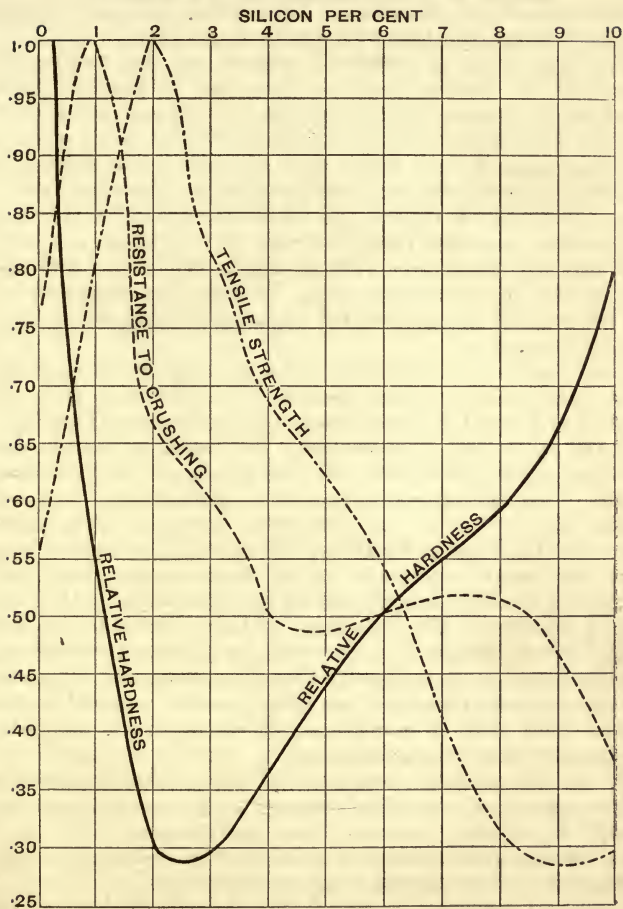
FIG. 12.

results have been conveniently condensed by F. Gautier,* from whose paper the diagram (Fig. 12) has been adapted. The maximum result obtained on the series of samples for each kind of resistance has been taken as unity, and the ordinates are expressed as fractions of this maximum. The datum line of the diagram would, however, fall below the limits of the page.

The chief point of interest is that in pig-iron the maximum resistance to traction (tensile strength), to bending, and to crushing is attained with proportions of silicon varying between 1.5 and 3 per cent. Metal containing between 2 and 3 per cent. of silicon appears to be softer than the rest of the series, whilst the maximum resistance to crushing stress is attained with less than 1 per cent. of silicon. It should be added that the samples of pig-iron examined contained 1.81 to 2.23 per cent. of carbon, and that in the samples rich in silicon the carbon was mainly present in the graphitic state. These also contained about 0.3 per cent. of manganese and a small quantity, about 0.04 per cent., of sulphur.

The results of an elaborate series of mechanical tests by Mr. R. A. Hadfield † on silicon steel in its forged state gave results which are plotted in the accompanying diagram (Fig. 13). In this, the upper pair of curves show the results of tensile tests in tons per square inch, and the lower pair of curves show the results of elongation tests expressed in percentages. Apparently silicon, up to 1.5 or 1.75 per cent., added to iron, although increasing the limit of elasticity, and raising the tensile strength, does not impair ductility. After this, however, the further increase of tensile strength noticed is only obtained with a serious loss of ductility. There appears to be no sharp line of demarcation, but when 1.5 to 2 per cent. is exceeded, further slight increases cause great changes in the characteristics of the material. In this respect, therefore, its action rather resembles that of carbon than that of manganese, of which larger amounts are required to effect similar changes.

In the case of mild steel, it would appear that the presence of silicon increases the tensile strength, but lowers the elastic limit.‡ It will be evident, however, from the diagram (Fig. 13) that when the amount of silicon in mild steel exceeds 2 per cent., the extensibility of the material rapidly diminishes.

It should be borne in mind that larger additions of silicon

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* *Bull. Soc. de l'Ind. Min.*, vol. iii. (1889), p. 91. See also paper read at the Metallurgical Congress, Paris, 1889.

† *Journ. Iron and Steel Inst.*, No. ii. (1889), p. 222.

‡ *Report Brit. Assoc.* 1888, p. 69.

do not cause a return of strength, which is so remarkable in the case of manganese steel. Silicon steel is, moreover, still magnetic with considerable percentages of silicon, and is in this respect unlike both manganese and nickel steels.

Hopkinson states that the electrical resistance of silicon steel is about six or seven times that of pure iron, and Hadfield has recently shown that the influence of silicon closely resembles that of aluminium.

INFLUENCE OF SILICON ON IRON & MILD STEEL.

%C	·14	·18	·19	·20	·20	·21	·25	·26	·04	·08	%C
S₁	·24	·79	1·60	2·11	2·69	3·39	4·18	5·53	7·23	8·83	S₁
M_N	·14	·21	·28	·25	·25	·29	·36	·29		·29	·68	M_N
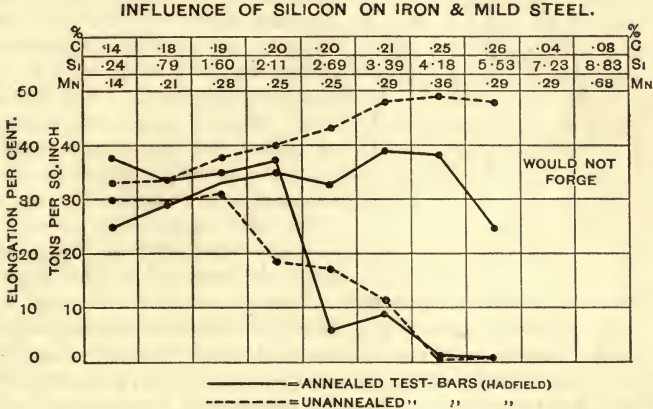
FIG. 13.

The influence of **tungsten** is remarkable. Its presence causes steel to be very hard, and, as Howe points out, although weight for weight, tungsten probably does not increase the hardness of steel as much as carbon, and perhaps not as much as chromium, yet steel may contain a much larger percentage of tungsten—at least 10 per cent—than of carbon, without losing its property of being forged.

Tungsten steel is very fragile to shock, and, as might be anticipated, its extensibility is very low.

Formerly, it was supposed that the presence of **copper** was prejudicial to steel; but it has been urged that the deleterious effects observed arose from the presence of small quantities of sulphur with which the copper was associated, and not from the copper itself.   Dr. E. J. Ball and Mr. A. Wingham * have shown, by some experiments conducted in the author's laboratory, that the presence of copper materially increases the tensile strength of steel.   The results of their experiments are shown in the diagram

(Fig. 14), in which the tensile strength of cupriferous steel is compared with a normal curve for carbon steel, the tensile strength of which is indicated by the dotted line.

INFLUENCE OF COPPER ON STEEL.
CARBON PER CENT.
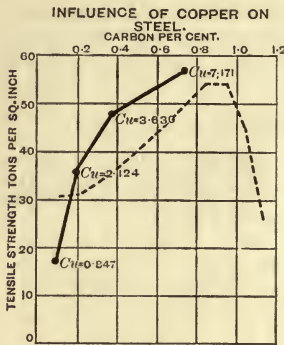
FIG. 14.

The influence of **nickel** on iron is singularly interesting, and the author is indebted to Mr. J. Riley for the diagram (Fig. 15, p. 29), which shows the results of his very important investigation.[*] The material Riley worked with contained from 0.22 to 0.85 per cent. of carbon, and 0.23 to 0.85 per cent. of manganese. Tensile tests were made of steel with contents of nickel varying from 1 up to 49.4 per cent. The curve shows that amounts of nickel up to about 7 per cent. materially increase the tensile strength and the elastic limit of steel, while the extensibility is as rapidly diminished. Amounts of nickel varying from 8 to 15 per cent. appear to produce such intense brittleness that it is not possible to submit the material to the ordinary mechanical tests. The effect of amounts of nickel exceeding 15 per cent. is so evident from the diagram that no description is necessary. It is singular, however, that a rapid rise in extensibility should be produced by adding some 20 per cent. of nickel to iron, especially as the limit of elasticity of this material appears to be greatly reduced by annealing.

A sample of nickel steel wire, containing about 25 per cent. of nickel, was examined by Dr. J. Hopkinson.[†] When heated to over 500°, and then cooled either rapidly or slowly, it lost its magnetic properties, which are, however, restored by cooling it to some point below 0°.

Until quite recently,[‡] the influence of **aluminium** had not been systematically studied. There is no doubt that the presence of a small quantity of aluminium, 0.1 to 0.2 per cent., considerably increases the fluidity of carburised iron. Indeed, it has been urged that its presence lowers the melting point of steel by some 200°. This is, however, not proven, and is improbable, but the remarkable fluidity of cast steel containing aluminium may be due to the fact that the aluminium serves to eliminate the oxygen

* *Journ. Iron and Steel Inst.*, No. i. (1889), p. 45.
† *Proc. Roy. Soc.*, vol. xlvii. (1890), p. 23.
‡ *Trans. Amer. Inst. Min. Eng.*, 1890.

INFLUENCE OF NICKEL ON IRON.

NICKEL PER CENT.

TENSILE STRENGTH, TONS PER SQ INCH
ELONGATION PER CENT ON 4 INCHES.

TENSILE STRENGTH

EXTENSION

ELASTIC LIMIT

ZONE OF BRITTLENESS
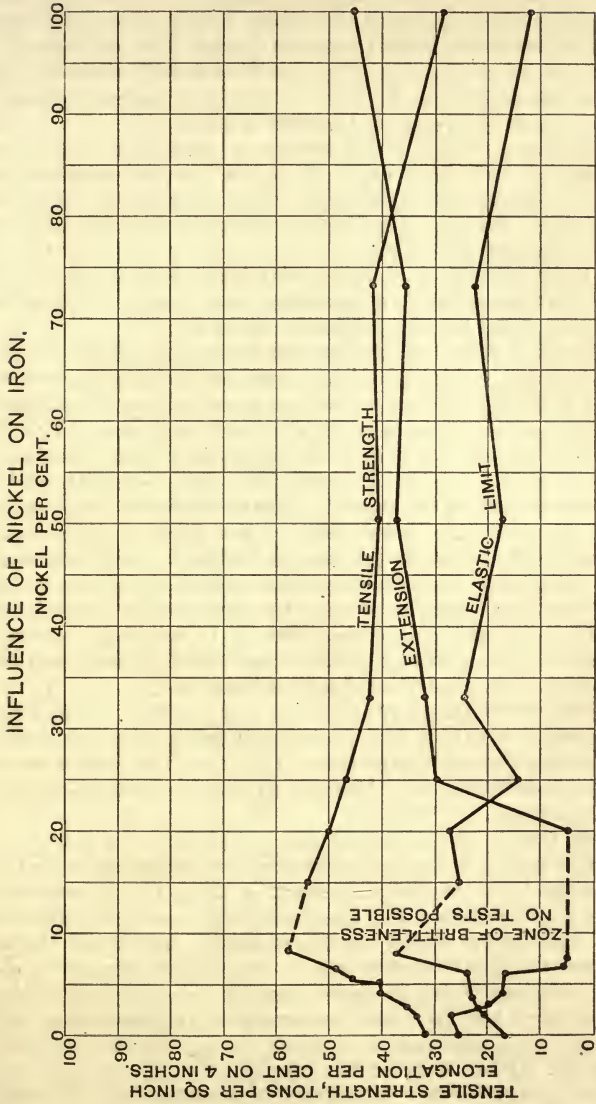NO TESTS POSSIBLE

FIG. 15.

present as oxide of iron. It may, however, be possible to settle this question by analogy, and the author has, by some experiments on gold (as yet unpublished), satisfied himself that the presence of o.2 per cent. of aluminium in the precious metal lowers its melting point considerably. There can obviously be no question of the elimination of oxygen in the case of gold.

The presence of o.1 to o.2 per cent. of aluminium hardens steel; but, on the other hand, the metal may be rendered very soft and extensible by annealing. The presence of aluminium appears, as in the case of silicon, to determine the separation of carbon in the graphitic form.

Mr. F. W. Harbord, a former student of the author's, has shown * that the presence of **arsenic**, even in minute quantities, is very prejudicial to the qualities of the iron.

The alloys of iron and **chromium** have been specially studied by M. Brustlein,† Director of the steelworks of J. Holtzer & Co., at Unieux, France. Very variable proportions may be combined with iron, the maximum appearing to be 82 per cent. With this material chromium steel may be prepared. The influence of chromium on steel is to increase its tensile strength and its resistance to fracture by impact. Chromium steels are, however, difficult to work hot. Steel with 2 per cent. of chromium is somewhat hard to cut in the cold, and when a mass is hardened in the usual way by quenching, the hardness penetrates more deeply than in the case of steel of the same degree of carburisation. There is, moreover, some difficulty in working these steels occasioned by the tendency of the chromium to oxidise and form slag. They consequently weld with difficulty.

The influence of **sulphur** on iron is very marked. This element has the effect of making iron exceedingly brittle at a red heat and of destroying its welding power. As a rule, the action is most marked at a dull-red heat. Manganese counteracts the prejudicial action of sulphur.

To take copper as an example instead of iron, the influence of **tin** on this metal, as far as mechanical properties are concerned, is shown by the accompanying diagram (Fig. 16), in which the upper curves represent the tensile strengths as determined by Mallet and by a board of investigators appointed by the Government of the United States.‡ It may be sufficient to state that the addition of tin to copper rapidly lowers its conductivity for electricity, but increases its strength, the maximum being

* *Journ. Iron and Steel Inst.*, No. i. (1888), p. 183.
† *Bull. Soc. de l'Ind. Min.*, vol. iii. (1889), p. 1.
‡ Report on a preliminary investigation of the properties of the copper-tin alloys. Washington, 1879.

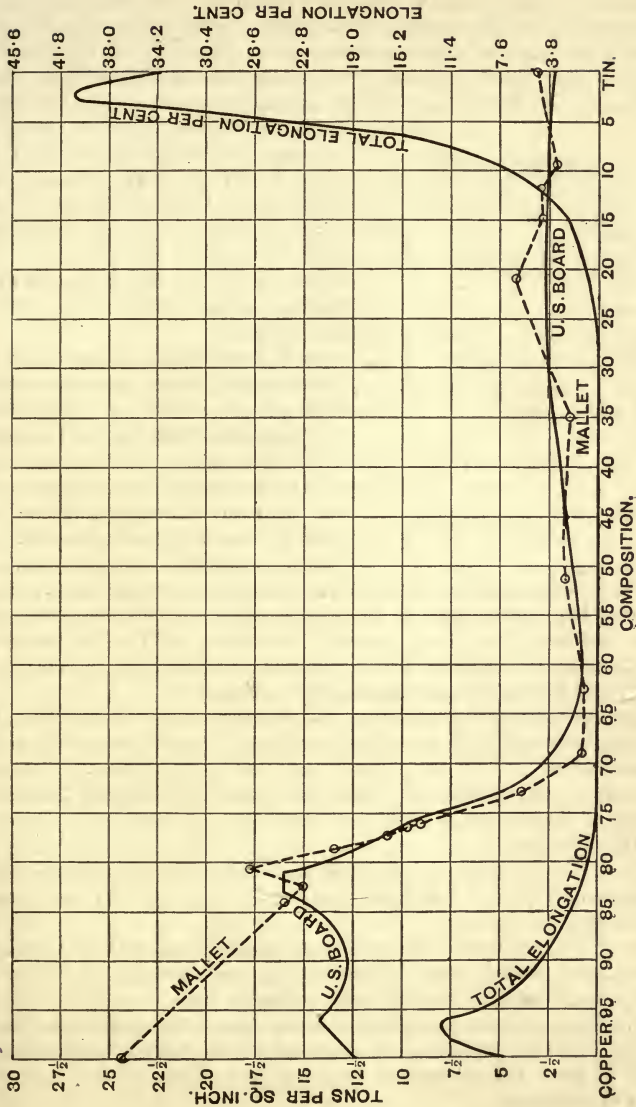INFLUENCE OF TIN ON COPPER.

Fig. 16.

attained with about 7 per cent. of tin. The entire series of copper-tin alloys is very interesting. Two only appear to be homogeneous, and these correspond respectively to the formulæ $SnCu_3$ and $SnCu_4$. Notwithstanding the comparatively small difference in their composition, the appearance of the fractured surfaces of these alloys is quite different, the latter being yellowish grey in colour with a mirror-like fracture, whilst the former is blue with a rough fracture. Having a higher specific gravity than the mean of its constituents, the alloy $SnCu_3$ stands out from the rest of the series.
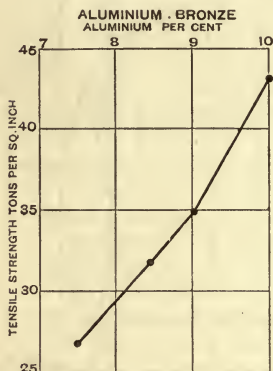
FIG. 17.

An interesting example of the influence of foreign elements on the strength of metals is afforded by **aluminium bronze**, the strongest of all the copper alloys. An alloy of 10 per cent. of aluminium with 90 per cent. of copper, rolled into plates, has a tensile strength of from 100,000 to 120,000 lbs. per square inch, and in castings has a tensile strength of 70,000 to 80,000 lbs. per square inch. This alloy, which was discovered by the late Dr. Percy, closely resembles gold in appearance. The effect of smaller proportions of aluminium on copper is shown in the accompanying diagram (Fig. 17).

In discussing the influence of foreign elements on iron, the terms "cast iron," "wrought iron," and "steel" are used, as this classification is still in general use among engineers. In 1878, however, an international commission at Philadelphia decided to adopt a classification based on the amount of carbon contained in the metal :—

I. *Pig iron* with 2.3 per cent. and more of carbon; melts at a comparatively low temperature (1075° to 1275° C.) and cannot be forged.

a. White pig iron; all the carbon is combined with the iron, the compound is very hard, brittle, white, and is made solely for the purpose of being converted into malleable iron.

b. Grey pig iron; in which more or less of the carbon is present in the form of graphite. The metal is soft, tough, grey to black, and is used for conversion into malleable iron or for the production of castings.

II. *Steel* with 1.6 to 0.4 per cent. of carbon, melts at 1400° C. By sudden cooling of a red-hot mass the hardness is considerably increased.

III. *Weld iron* with less than 0.4 per cent. of carbon, melts at 1600° C. and above. It cannot be appreciably hardened.

The Philadelphia Commission decided that—

1. Every malleable compound of iron, containing the ordinary elements of that metal, which is obtained either by the union of pasty masses of iron or by any process not involving fusion, and which cannot be hardened by the ordinary method, shall be called *weld iron.* This is what has formerly been known as wrought iron.

2. Any analogous compound, which by any cause hardens, shall be called *weld steel.* This has hitherto been termed puddled steel.

3. Every malleable compound of iron, containing the ordinary constituents of that metal, which is obtained and poured in the fused state, but which does not harden by the ordinary methods, shall be known as *ingot iron.*

4. Every compound similar to the last, but capable of hardening from any cause whatever, shall be called *ingot steel.*

Colour.—The colour of metals is influenced by their purity. Thus, iron becomes white by admixture with carbon, silicon, sulphur, phosphorus, and other elements. By the alteration in the colour of a metal it is possible to detect the presence of a very small quantity of impurity, especially in the cases of gold and silver.

The lustre of metals is due to their great power of reflecting light. It varies with the purity and the degree of polish of the metal. It is therefore of great use in detecting the presence of impurities, a notable example of this being afforded by copper.

Fusibility.—All metals are fusible. On account of the difficulty experienced in determining high temperatures, only the melting points of the metals that fuse at temperatures below 1000° have been ascertained with absolute accuracy. The melting points of the more important metals are given in the table on p. 48, 49. Arsenic sublimes at 180°, but it may be fused under the pressure of its own vapour.

When strongly heated, metals pass from a brownish-red to a clear red colour, which gradually increases in luminosity and transparency to a dazzling white. The temperatures corresponding to the different colours have been estimated by Pouillet to be—

C

Incipient red	.	.	.	.	.	$525°$
Dark red .	.	.	.	.	.	$700°$
Incipient cherry-red .		.	.	.	.	$800°$
Clear cherry-red	.	.	.	.	.	$1000°$
White	.	.	.	.	.	$1300°$
Dazzling white .		.	.	.	.	$1500°$

On solidifying from a molten state, metals frequently exhibit excrescences due to the expulsion of absorbed gases. This expulsion often occurs shortly before the solidification, and causes a sudden outburst of metal through the surface. In this way silver, when molten, absorbs oxygen, and expels it on solidification. In the case of steel, the evolution of gas continues long after the metal has solidified on the surface.

When a metal passes from the liquid to the solid state, it either does so suddenly, or it passes through an intermediate pasty stage. This fact is occasionally of great metallurgical importance. Thus, white pig iron is more suitable for dry puddling than is grey pig iron, as the former becomes very pasty, whilst the latter does not.

On solidification after melting, metals usually crystallise. Crystallisation also occurs when metals are condensed from a state of vapour or are deposited by the electrolytic decomposition of metallic solutions. Metals most frequently crystallise in the cubic system. This is the case with platinum, gold, silver, copper, lead, and iron, and probably with tin and zinc. Tin also crystallises in the tetragonal system, and the iron carbide known as *spiegeleisen* crystallises in the rhombic system. Antimony, arsenic, and zinc crystallise in the hexagonal system, whilst bismuth crystallises in rhombohedra resembling cubes. Tin, zinc, and lead are thus dimorphous—that is, they may be developed according to two systems of crystallisation. The crystallisation of metals is of great importance, as the formation of crystals, due to continued vibration, intense cold, sudden alterations of temperature, or the presence of impurities may render a metal absolutely useless. Crystallisation may serve to indicate the quality of the metal, as in the case of foundry pig iron ; to indicate the presence of impurities, as in the case of the film of antimony produced on lead that is refined by steam ; and, lastly, to separate metals on a large scale, as is the case in Pattinson's process of desilverising lead.

Welding is the property possessed by metals which on cooling from the molten state pass through a plastic stage before becoming perfectly solid, of being joined together by the cohesion of the molecules that is induced by the application of an extraneous

force, such as hammering. This property is exhibited in a marked degree by iron and platinum at a white heat. Welding may also be effected, though to a less degree, when two clean surfaces of metal are brought into intimate contact in the cold.

Metals are good conductors of heat and electricity, and may be arranged in the same order as regards both the conductivity for heat and that for electricity.

Iron, nickel, and cobalt may be rendered magnetic. When a small quantity of carbon has converted the iron into steel, the metal readily retains its magnetism.

Certain metals possess acoustic properties. The sound emitted by metals when struck is greatly affected by the presence of impurities. Thus, in the case of lead, the presence of antimony tends to heighten the sound emitted. Owing, it is supposed, to the sliding of the crystal faces over one another, tin, at ordinary temperatures, and zinc, after heating to 160°, emit a sound when bent.

Properties common to Fluids and Solid Metals.— Réaumur, so long ago as 1713, defined with singular clearness the conditions under which metals prove to be ductile. The relation between the behaviour of solid metals and fluids has long been recognised, not in the sense that atomic motion is common to solids and fluids, but from a wider view, for there is much experimental evidence as to the properties that are common to fluids and solid metals, the characteristics of which, at first sight, seem widely separated. A solid has a definite external form, which either does not change, or only changes with extreme slowness when left to itself, and, in order to change this form rapidly, it is necessary to submit it to a considerable stress. A liquid, on the other hand, can be said to have no form of its own, as it always assumes that of the containing vessel; the mobility of its particles is extreme, its resistance to penetration is very small, and its free surface is always a plane when the mass is left at rest. Then there is the colloid condition, which intervenes between the liquid and crystalline solid state, extending into both, and probably affecting all kinds of solid and liquid matter in a greater or less degree. The colloid, or jelly-like body does present a certain amount of resistance to change of shape. Such a substance is well imitated by a sphere of thin india-rubber partly filled with water. Another illustration is probably afforded by iron and other substances which soften under heat, and may be supposed to assume, at the same time, a colloid condition. Last, there is the gaseous condition of matter.

Metals are usually regarded as typical solids; it is easy, how-

ever, to trace the analogies of their behaviour under certain conditions with that of fluids. The transition from the liquid to the solid state is marked by the same phenomena in the case of many metals, as are observed in certain fluids. For instance, metals on solidifying reject impurities, and exhibit the property of surfusion. This leads up to the relations between solid metals and fluids, and the following list shows the classes in which the properties common to fluids and solid metals may be grouped :—

1. Flow under pressure.
2. Changes due to compression.
3. Absorption of gases.
4. Absorption of liquids.
5. Diffusion.
6. Vaporisation.
7. Surface tension.

Water, on passing from the liquid to the solid state, undergoes a partial purification, the ice first formed being sensibly more free from colouring matter or suspended particles than the water from which it separates.

Many metals on freezing similarly eject impurities. In the case of alloys, saturated solutions of one metal in another appear to be formed, and excess of metal ejected, a fact which was studied with much care by Dr. Guthrie (see p. 60). The prominent facts are perhaps best illustrated by reference to a solidified mixture of copper, antimony, and lead. The results of some experiments conducted, in the laboratory of the Royal School of Mines, by Dr. E. J. Ball * show that when a molten mixture of these metals is solidified, a definite atomic alloy of copper and antimony, which possesses a beautiful violet tint, first forms, and, after saturating itself with lead up to a certain point, ejects the rest of the lead, driving it to the centre of the mass so as to form a sharp line of demarcation between the outer violet circle and the grey centre. It thus presents a direct analogy to the comparatively colourless ice which first forms from coloured water. There is yet another remarkable analogy between the freezing of certain fluids and the solidification of some metals. Water may, as is well known, be cooled down to $-8°$ C. without solidification, but agitation immediately determines the formation of ice, and, at the same time, a thermometer plunged in the water rises to zero. Faraday stated,† in 1858, that fused acetic acid, sulphur, phosphorus, many metals, and many solutions would exhibit the

* *Journ. Chem. Soc.*, 1888, p. 167.
† *Experimental Researches in Chemistry and Physics*, p. 379.

same effect. Tin also may be cooled to several degrees below its solidifying point without actually freezing, and Dr. Van Riemsdijk,* of Utrecht, has observed that a globule of gold or silver, in a fused state, will pass below its solidifying point without actually solidifying, but the slightest touch with a metallic point will cause the metal to solidify, and the consequent release of its latent heat of fusion is sufficient to raise the globule to the melting point again, as is indicated by a brilliant glow which the button emits.

It may be well also to remark incidentally that a minute variation in composition is sometimes sufficient to lower the melting point of a metal or alloy, as is instanced by the addition of $\frac{2}{10}$ per cent. of silicon to standard gold, which then softens in the flame of a candle, or at about the melting point of zinc, 412° C., although the melting point of gold, free from silicon, would be over 1000° C.

The result of Raoult's investigations on the lowering of the freezing point of solutions, led him to the conclusion that one molecular proportion of any substance dissolved in 100 molecular proportions of any solvent whatever, lowers the freezing point of that solvent 0.62° C. This had not been tested in the case of solutions of metals in metals, until Heycock and Neville† began an elaborate investigation of the subject. Their research, as far as it has at present been carried, deals, 1st, with the lowering of the freezing points of sodium and tin produced by the addition to them of certain other metals, and, 2nd, with the molecular weights of metals when in solution. The results of their experiments when compared with the empirical laws of Coppet and Raoult may be briefly stated as follows :—

They are in accordance with the law "that for moderate concentration the fall in the freezing point is proportional to the weight of the dissolved substance present in a constant weight of solvent." By making the assumption, that the molecule of zinc, or of mercury, is monatomic when in solution in tin, they confirm the second law, "That when the falls produced in the same solvent by different dissolved substances are compared, it is found that a molecular weight of a dissolved substance produces the same fall whatever the substance is." But the third law which states, "That if a constant number of molecular weights of the solvent be taken, then, the fall is independent of the nature of the solvent," they found to be probably incorrect, and theoretical considerations indeed would lead us to expect this. In the case of silicon in standard gold which has just been mentioned, a long semifluid stage appears to be set up, the metal may contain solidified

* _Ann. de Chim. et de Phys._, t. xx. (1880), p. 66.
† _Journ. Chem. Soc._ vol. lv. (1889), p. 666 ; vol. lvii. (1890), pp. 376 and 656.

particles, and yet be sufficiently fluid to flow readily; this pheno-
menon has not yet been fully investigated.

In a research of much interest, Ramsay * has determined the
molecular weight of a number of metals by Raoult's vapour
pressure method—that is, he ascertained the depression of the
vapour pressure of the solvent, produced by a known weight of
dissolved substance, and he finds that although sodium behaves
irregularly, yet " it would appear legitimate to infer that in
solution, as a rule, the atom of a metal is identical with its
molecule, as the physical properties of those metals which have
been vaporised would lead us to suppose."

Now to pass to solid metals.   It is the common experience that
a counterfeit shilling, consisting principally of lead, does not
" ring " when thrown on a wooden surface.   In 1726 Louis
Lemery observed that lead is, under certain conditions, almost as
sonorous as bell-metal.†   He communicated the fact to Réaumur,
who, being much struck by it, investigated the conditions under
which lead becomes sonorous, and submitted the results to the
French Academy.‡   He pointed out that, in describing a body
which is not sonorous, it is usual to say that it is as "dull as lead,"
an expression which has become proverbial.   Nevertheless, he
adds, under certain conditions, lead has a property both novel and
remarkable, for it emits surprisingly sharp notes when struck with
another piece of lead.   He showed that it was necessary that the
lead should be formed by casting into a segment of a sphere—that
is, mushroom-shaped.   The lead must be free from prominences,
and must be neatly trimmed.   The effect is less marked if the
lead be very pure than if ordinary commercial lead be used, but
it is only a question of degree.   Réaumur showed that the sonorous
lead might be rendered dull by hammering it.   His remarks have
been overlooked in late years.   He was led to the belief that in
cast lead there must be an arrangement of the interior of the
mass which the hammer cannot impart, because lead fashioned by
hammering into the same form as the sonorous cast mass is dull,
and, more important still, he held that the fibrous and granular
structure of the lead is modified in a manner which makes it
probable that the sound is due to the shape of the grains and to
the " way in which they touch each other ; " further, the blows of
the hammer not only change the arrangement of the fibres, but

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* *Journ. Chem. Soc.*, vol. lv. (1889),p. 521.   See also Tammann, *Zeit. für
physikal. Chemie*, 1889, p. 441.
† Hoefer, *Histoire de la Chimie*, ii. p. 374.
‡ *Histoire de l'Académie Royale des Sciences*, *Année* 1726 [vol. for 1728,
p. 243].

they alter the shape of the grains; " the round grains are rendered
flat, they are compelled to elongate and fill the interstitial spaces
which previously existed between them.   The particles are no
longer free to vibrate; hence the lead is dull." These facts acquire
additional interest if they are compared with the observations in
Professor Osborne Reynolds' paper on " Dilatancy in Granular
Matter."   Réaumur's description shows that he fully appreciated
the theoretical importance of the kind of facts depending on the
transfer of metallic matter from one position to another, which
we now consider to be characteristic of the " flow " of metals; at
any rate, Lemery's experiment may be made the starting point of
the remarks which follow.

A solid may be very brittle, and may yet, if time be given to
it, flow from one point to another.   A stick of sealing wax, sup-
ported at its ends, in a few weeks bends at the ordinary atmo-
spheric temperature, although at any given point of its flow it
would have been easy to snap it with a slight application of force.
A tuning-fork may be made from pitch, which will nevertheless
subside into a shapeless mass at the ordinary temperature.   A
much thinner strip of pure lead of the same breadth as the sealing
wax also bends at the ordinary temperature with its own weight,
the ends being supported.   Sir William Thomson has pointed out
that a gold wire, sustaining half the weight which would actually
break it, would probably not rupture in a thousand or even a
million years—that is to say, there would be no " flow " ending in
disruption; if, however, force be suitably applied, metals will flow
readily.   First, examine the case of a metal under force applied so as
to compel it to flow through a hole, as it points to the analogy of an
ordinary viscous fluid.   If a vessel (1, Fig. 18) provided with a
cylindrical hole in its base be filled with lead, the lead will, at the
ordinary pressure, remain there, but if extra pressure be applied the
lead will prove by its behaviour that it is really a viscous solid, as
it flows readily through the orifice; the end of the jet is rounded,
and, as has been shown by the beautiful researches of the late M.
Tresca, of Paris,* all the molecules which compose the original block
place themselves in the jet absolutely as the molecules of a flow-
ing jet of a viscous fluid would.   If the metal has a constant
" head," as it would be termed in the case of water—that is, if the
vessel be kept filled with solid lead up to a certain level—then

* These researches extend through a long series of memoirs; those
relating to the flow of metals are well summarised in the *Proc. Inst. Mech.
Engineers,* 1867, p. 114, and in the Report of the Science Conferences held
in connection with the Loan Collection of Scientific Apparatus (Physics
and Mechanics), London, 1876, p. 252.

there will be a continuous stream, the length depending on the constancy with which the "head" and the pressure are maintained. If, on the other hand, the "head" is diminished so that nearly all the solid lead has been allowed to flow away (2, Fig. 18), there is a folding of the jet, and vertical corrugations, exactly such as would characterise the end of the flow of certain other viscous fluids, and finally the jet forms a distinct funnel-shaped tube concentric with the jet. It is also seen that, when the formation of these cavities takes places, the jet is no longer equal to the full diameter of the orifice, as shown in 2, Fig. 18, the formation of the contracted vein is manifest, and the new analogy is thus obtained between the flow of solids and of liquids.

In punching a disc from a solid plate of metal supported by a die-plate (4, Fig. 18), as in the operation of coining, the portion cut

Transverse Section of Compound Lateral Jet.

Section on A B
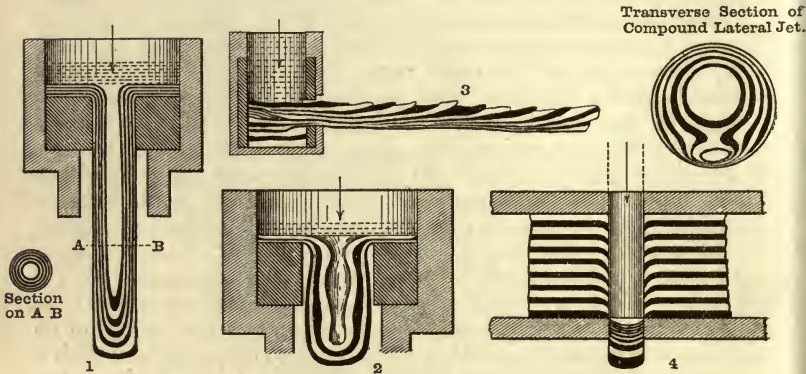
FIG. 18.

out proves to be thinner than the plate from which it has been removed. Since the density of a metal is not increased by pressure except by the obliteration of pores, as has already been stated, it follows that the metal must have flowed in a plastic state laterally from the disc into the plate, the remaining metal becoming so thin that its resistance to shearing is less than the pressure on the punch.

In 3, Fig. 18, the effect is shown of a compound jet of lead flowing through a lateral orifice in a cylindrical vessel.

In the case of planing surfaces of metals by cutting tools, similar effects may be traced, and it is interesting to compare the flow of metal in 4, Fig. 18, which represents the penetration of a

cutting tool through a plate of metal, with the flow of metal under the action of a tool used for planing (Fig. 19). In this case the lines of flow are made evident by the deformation of

lines traced vertically on the side of the block of metal submitted to the tool. The shifting of the material and the connection of the lines, F, in the shaving with those, E, of the original block, will be evident from the diagram. Every artificer knows how complicated in form the shavings may be, and varied problems relating to their production have been studied by M. Tresca.*
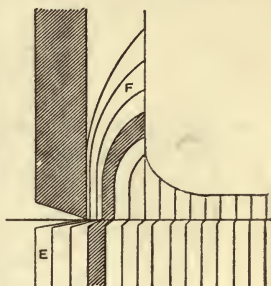

FIG. 19.

The application of this fact, that solid metals flow like viscous fluids, is of great importance in industry, and the production of complicated forms by forging or by rolling iron and steel and other metals entirely depends on the flow of the metal when suitably guided by the artificer. The lines of flow in iron may be well shown by polishing a surface of the metal, and by submitting it to the action of a solution of mercuric chloride, which etches the surface, or, better, to the slow action of chromic acid solution, the result in either case being, that any difference in the hardness of the metal or in the chemical composition, or want of continuity, caused by the presence of traces of entangled slag, reveals the manner in which the metal has flowed. The sketches illustrate the direction of flow in the following cases. Fig. 20 is a section of a forged cross-head, and Figs. 21, 22 are sections of rails.

The experiments of M. Tresca were not made on "cinder-free" metal; it is therefore interesting to compare the etched section of the old rail, Fig. 21, the result of the complicated welding of puddled iron, with a basic-Bessemer rail, rolled from steel which has been cast, and which is therefore free from entangled slag. Fig. 22 represents a section of such a rail.

A very striking illustration of the importance of the flow of metals, when used in construction, is afforded by some observations of Sir B. Baker in a paper on the Forth Bridge.† He says: " If the thing were practicable, what I should choose as the material for the compression members of a bridge would be 34- to 37-ton steel, which had previously been squeezed endwise, in the direction of the stress to a pressure of about 45 tons per

* *Mémoires de l'Académie des Sciences*, vol. xxvii., No. 1, 1880.
† *Journ. Iron and Steel Inst.*, 1885, p. 497.

square inch, the steel plates being held in suitable frames to prevent distortion." He adds : " My experiments have proved that
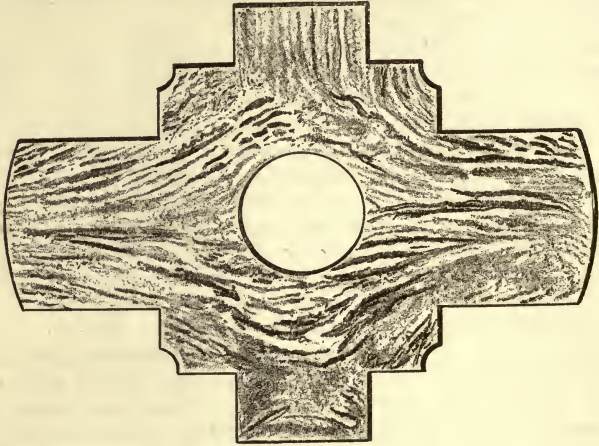
FIG. 20.

37-ton steel so treated will carry as a column as much load as 70-ton steel in the state in which it leaves the rolls—that is to say,
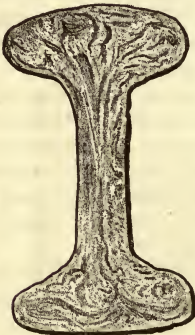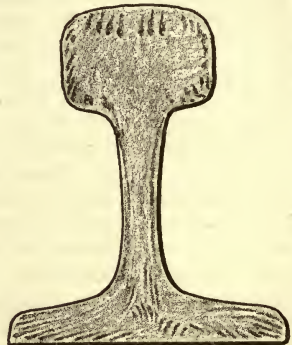

FIG. 21.   FIG. 22.

not previously pressed endwise. . . . . At least one-half of the 42,000 tons of steel in the Forth Bridge is in compression, and the same proportion holds good in most bridges, so the importance of gaining an increased resistance of 60 per cent. without any sacri-

fice in the facility of working, and safety, belonging to a highly ductile material can hardly be exaggerated."

The very ancient mechanical art of striking coin is wholly dependent on the flow of metals. There is a popular belief that the impression imparted to discs of metal during coinage is merely the result of a permanent compression of the metal of which the disc is made. Striking a coin, however, presents a case of moulding a plastic metal, and of the true flow of metal, under pressure, into the sunken portions of the die. A medal struck from a series of discs will serve to show, when the discs are separated, the way the metal flows into the deepest portion of the die. If the alloy used be too hard, or if the thickness of the metal required to flow be insufficient, the impression will always be defective, no matter how many blows may be given by the press.

If one side of the coin be ground away, so as to leave a flat surface, and if the disc be then struck between plain polished dies surrounded by a steel collar, so as to prevent the escape of the metal, the impression on the disc will be driven through the thickness of the metal, and will then appear on both sides. In industrial art the property of flow of metals is very important. The "spinning" of articles in pewter is a familiar instance.

The production of complicated forms, like a jelly mould, from a single sheet of copper under the combined drawing and compressing action of the hammer is a still more remarkable case.

The flow of metals is illustrated very curiously in one phase of Japanese art metal-work, to which reference will be made subsequently.

The flow of metals when submitted to compression has hitherto been alone considered, but the effect of traction has also been examined, for when a viscous metal such as iron or soft steel is submitted to stress by pulling its ends in opposite directions, it stretches uniformly throughout its length, and the metal truly flows when the yield point is reached. The limit of elasticity of a solid body marks the moment at which the body begins to permanently stretch, under the influence of the longitudinal stress to which it is submitted. There are many materials which do not stretch sensibly when their limit of elasticity is reached; in very hard steel, for instance, the breaking point and the limit of elasticity practically coincide. Further, it must be observed that every minute variation in composition is sufficient to change the property of a body, and to cause what was a viscous body to break close to the limit of elasticity.

The particles of a metallic powder left to itself at the ordinary

atmospheric pressure will not unite ; by "augmenting the number of points of contact in a powder" the result may be very different. The powders of metals may weld into blocks, as will subsequently be described, and it will be seen that experiments on the compression of finely divided metals afford important evidence as to the relation between solid metals and fluids. Faraday discovered, in 1850, that two fragments of ice pressed against each other will unite, their tendency to union being considerable when the fragments are near their melting point. Ice owes its movement, in glaciers, not to viscosity, but to regelation, and the union of fragments of ice under compression is also due to regelation. The facts which have been appealed to, and the theories which have been formed, respecting the regelation of ice, are well known ; it may, however, be observed that bismuth, like ice, expands on solidifying, and though Faraday failed to establish the existence of a property similar to regelation in bismuth, Wrightson has satisfied himself, by experimental evidence, that regelation exists in bismuth. In explaining Spring's results (p. 56) there is this difficulty : the union of the particles of the metals, cannot, in all cases, be due to viscosity, because viscous bodies are always capable of being stretched, and we find the welding taking place between the compressed powders of bodies, such as zinc and bismuth, which, when submitted to traction, will not stretch. Spring therefore asks, " Is it possible that regelation may have something to do with the union of the powders ? " and he urges, " Is it safe to conclude that regelation is peculiar to ice alone ? " " It is difficult to believe," he adds, " that in the large number of substances which Nature presents to us, but one exists possessing a property of which we can find only minute traces in other bodies. The sum of our chemical and physical knowledge is against such a belief, and therefore the phenomenon of regelation may be pronounced in ice without being absolutely wanting in other bodies. To ascertain whether this is so, it is necessary to submit other bodies to the conditions under which the phenomenon can be produced." " What," he asks, " are these conditions ? " and he answers, "The pressure supported by the body, a certain degree of temperature, and time."

Helmholtz and Tyndall have shown that when the pressure is weak the regelation of ice is effected slowly. Spring points out that nitrate of sodium and phosphate of sodium, in powder, left to themselves in bottles, become coherent, and if the coherence in these and other chemical compounds is but weak, it is simply because the points of contact between the particles of powder are but few. If, on the other hand, metallic or other powder be submitted to strong compression, the spaces between the fragments

become filled with the débris of the crushed particles, and a solid block is the result. Finally, it may be urged that this union of powders of solid metals under the influence of pressure—that is to say, the close approximation of the particles—can be compared to the liquefaction of gases by pressure. At the first view this comparison may appear rash or strained, but it is not so if the views of Clausius on the nature of gases and liquids be accepted. In a gas the molecules are free, but if by pressure at a suitable temperature the molecules are brought within the limit of their mutual attraction, the gas may be liquified, and under suitable thermal conditions, solidified. The mechanical pulverisation of a metal merely detaches groups of molecules from other groups, because the mechanical treatment is imperfect, but the analogy between a solid and a gas has, in this sense, been established; filing coarsely gasifies the mass, but pressure solidifies it.

It is possible that in some of the compressed metallic blocks, the particles are not actually united by the pressure, which may, nevertheless, develop the kind of "mutual attraction" contemplated by Sir William Thomson as existing between two pieces of matter at distances of less than 10 micro-millimetres.

Occlusion of Gases.—With reference to the absorption of gases by metals, it may be sufficient to point out that Sainte Claire-Deville and Troost discovered that hydrogen would pass through a plate of platinum, prepared from the fused metal or through iron, at a red heat; and it was well known that molten silver had the power of absorbing many times its own volume of oxygen. In Deville's experiments a new kind of porosity was imagined, more minute than that of graphite and earthenware, an intermolecular porosity due entirely to dilatation. Graham * showed that when gas penetrates the substance of the metal there is previous absorption and possibly liquefaction of the gas. Since his time it has been abundantly recognised that the presence of an element which is capable of re-appearing with the elastic tension of a gas must materially affect the mechanical properties of a metal. Palladium is known to possess the power of occluding gas—hydrogen—in the most marked degree. By slow cooling from a red-heat in an atmosphere of hydrogen, palladium foil or wire occludes no less than 900 volumes of hydrogen. Similarly, gold is found to occlude 0.48 of its volume of hydrogen and 0.2 of its volume of nitrogen, silver occludes 0.7 of its volume of oxygen, and wrought copper occludes 0.306 volume of hydrogen.

It is, however, in relation to the metallurgy of iron that the

* *Proc. Roy. Soc.*, vol. xvi. p. 422 : vol. xvii. p. 212, and p. 500; *Trans. Roy. Soc.*, 1886, pp. 399–439.

occlusion of gases is of importance. It is well known that at the conclusion of the Bessemer process, oxygen from the air blown through the metal becomes intimately associated with iron; but the manner in which the oxygen is held, whether as oxide or as dissolved gas, appears to be still obscure, though Müller[*] has given strong evidence in support of the view that gases are dissolved in iron. One thing is certain, that the oxygen may readily be removed from the iron by the action of manganese. Hydrogen is usually present in iron, chiefly as gas, sometimes as ammonia,[†] and in certain cases probably in some non-gaseous state. It does not appear to be in strong chemical combination, as it can easily be expelled. This may happen on solidification of the metal, by heating in vacuo, or by the action of a drill, which appears to release entangled or loosely-held hydrogen. The escape of gas can be prevented by increasing the pressure during solidification, and by the addition, before solidification, of silicon, manganese, or aluminium. The hydrogen probably remains in the cold iron after it is solidified. Cailletet[‡] extracted from electrolytic iron, in which the metal probably exists in a distinct molecular form, nearly 250 times its volume of hydrogen by heating in vacuo. Graham proved that carbonic oxide is dissolved by iron, and that that gas probably plays an important part during the conversion of iron into steel in the ordinary process of cementation. It is certain that the presence of silicon and manganese appears to enable the iron to retain carbonic oxide, as well as hydrogen and nitrogen, in solution.

Another analogy between metals and fluids is presented by the power which certain solid metals possess of taking up fluids, sometimes with a rapidity which suggests the miscibility of ordinary fluid substances. In reference to this, an interesting paper was published, so long ago as 1713, by the Dutch chemist Homberg,[§] " On Substances which Penetrate and which Pass Through Metals, without Melting Them." He enumerates several substances which will pass through the pores of metals without disturbing the particles, and he points out that mercury penetrates metals without destroying them. The rapidity with which mercury will pass through tin is remarkable. A bar 1 inch wide and $\frac{1}{2}$ inch thick will be penetrated by mercury in thirty seconds, so that it breaks readily, although before the addition

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* *Iron*, 1883, p. 115, and p. 244 ; 1884, p. 161.
† Recognised by many observers ; notably by Regnard, *Comptes Rendus*, vol. lxxxiv. (1877), p. 260.
‡ *Comptes Rendus*, vol. lxxx. (1875), p. 319.
§ *Mem. de l'Acad. Royale des Sciences*, 1713 (vol. for 1739, p. 306).

of the mercury the bar would bend double without any sign of fracture.

With regard to the vaporisation of solid metals, Demarçay [*] has shown that *in vacuo* metals evaporate at much lower temperatures than they do at the ordinary atmospheric pressure, and he suggests that even metals of the platinum group will be found to be volatile at comparatively low temperatures. Merget [†] has shown that the solidification of mercury by extreme cold does not prevent the solid metal evaporating into the atmosphere surrounding it.

In relation to surface tension there is an interesting property belonging to a hard drawn rod or thick wire of 13-carat gold, the gold being alloyed with silver and copper in the following proportions:—

Gold	.	.	.	.	.	.	. 54.17
Copper	.	.	.	.	.	.	. 33.33
Silver	.	.	.	.	.	.	. 12.50

100.00

If such a rod be touched with a solution of chloride of iron, or certain other soluble chlorides, it will, in a short time, varying from a few seconds to some minutes, break away, the fracture rapidly extending for a distance of some inches.

The last property to be considered is **diffusion**. The author has shown that in the case of molten metals the interdiffusion may be extremely rapid. In regard to solid metals, some experiments conducted by Abel prove that carbon can pass from a plate of richly carburised iron to one of iron free from carbon against which it is tightly pressed. This passage of carbon appears to take place at the ordinary temperature, and it is difficult to explain the transference of matter without admitting the presence of some action closely allied to the diffusion of liquids.

These facts afford additional evidence as to continuity in the properties of all kinds of matter, and serve as a connecting link with the work of the past, the importance of which is too often overlooked.

This chapter may fittingly conclude with a table of the physical constants of metals.

[*] *Comptes Rendus*, vol. xcv. (1882), p. 183.
[†] *Ann. de Chim. et de Phys.* (4), vol. xxv. p. 121.

PHYSICAL CONSTANTS OF METALS.

	Symbol	Atomic Weight.	Atomic Volume.	Specific Gravity.	Specific Heat.	Melting Point.	Co-efficient of linear Expansion.	Thermal Conductivity.	Electrical Conductivity.
						° C.		Ag = 100.	Hg at 0° = 1.
ALUMINIUM	Al	27.00	10.6	2.56	0.212	625	0.0000231	31.33	31.726
ANTIMONY	Sb	120.00	17.9	6.71	0.051	440	0.0000105	4.03	2.053
ARSENIC.	As	74.90	13.2	5.67	0.081	—	0.0000055	—	2.679
Barium	Ba	136.86	36.5	3.75	0.047	1200			
BISMUTH	Bi	207.50	21.1	9.80	0.031	268	0.0000162	1.8	0.800
CADMIUM	Cd	111.70	12.9	8.60	0.057	320	0.0000306	20.06	13.95
Cæsium	Cs	132.70	70.6	1.88	—	26			
Calcium	Ca	39.91	25.4	1.57	0.170	red heat	—	—	12.46
Cerium	Ce	141.00	21.0	6.68	0.045	between Sb and Ag			
CHROMIUM	Cr	52.40	7.7	6.80	(0.120)	higher than Pt			
COBALT	Co	58.60	6.9	8.50	0.110	1500	0.0000123	—	9.685
COPPER	Cu	63.20	7.2	8.82	0.094	1050	0.0000167	73.6	55.86
Didymium	Di	145.00	22.3	6.54	0.046				
Glucinum	Gl	9.08	5.6	2.07	0.580				
GOLD	Au	196.20	10.2	19.32	0.032	1045	0.0000144	53.2	
Indium	In	113.40	15.3	7.42	0.057	176	0.0000417		
IRIDIUM.	Ir	192.50	8.6	22.42	0.033	2500	0.0000070		43.84

Metal	Symbol								
IRON	Fe	55.90	7.2	7.86	0.110	1600	0.0000121	11.9	8.340
Lanthanum	La	138.50	22.3	6.20	0.045			8.5	4.818
LEAD	Pb	206.40	18.1	11.37	0.031	325	0.0000292	—	10.69
Lithium	Li	7.01	11.9	0.59	0.941	180		34.3	22.57
MAGNESIUM	Mg	23.94	13.8	1.74	0.250	750	0.0000269		
MANGANESE	Mn	54.80	6.9	8.00	0.120	1900			1.000
MERCURY	Hg	199.80	14.7	13.59	0.032	39		1.3	
Molybdenum	Mo	95.90	11.1	8.60	0.072				7.374
NICKEL	Ni	58.60	6.7	8.80	0.110	1600	0.0000127		
Niobium	Nb	94.00	15.0	6.27	?				
OSMIUM	Os	195.00	8.7	22.48	0.031	2500	0.0000065		6.910
PALLADIUM	Pd	106.20	9.2	11.50	0.059	1500	0.0000117		8.257
PLATINUM	Pt	194.30	9.1	21.50	0.033	1775	0.0000089	8.4	11.23
POTASSIUM	K	39.03	45.4	0.87	0.170	62	0.0000841		
Rhodium	Rh	104.10	8.6	12.10	0.058	2000	0.0000085		
Rubidium	Rb	85.20	56.1	1.52	0.077	38			
Ruthenium	Ru	103.50	8.4	12.26	0.061	1800	0.0000096		
SILVER	Ag	107.66	10.2	10.53	0.056	945	0.0000192	100.0	57.226
SODIUM	Na	22.99	23.7	0.97	0.290	95	0.0000710	36.5	18.30
Strontium	Sr	87.20	34.9	2.54	0.074	—			3.774
Tantalum	Ta	182.00	16.9	10.80	?				
Tellurium	Te	126.30	20.2	6.25	0.047	525	0.0000167		0.0004
Thallium	Tl	203.70	17.1	11.85	0.034	288	0.0000302		5.225
Thorium	Th	232.00	20.9	11.10	0.028				
TIN	Sn	117.40	16.1	7.29	0.056	227	0.0000223	15.2	8.237
Titanium	Ti	48.00	—	—	0.130?	higher than Mn			
TUNGSTEN	W	184.00	9.6	19.10	0.033				
Uranium	U	240.00	12.8	18.70	0.028				
Vanadium	V	51.10	9.3	5.50	?				
ZINC	Zn	64.90	9.1	7.15	0.094	415	0.0000291	28.1	16.92
Zirconium	Zr	90.40	21.7	4.15	0.066				

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Notes to the Table of Physical Constants (pp. 48, 49).—For melting points the student must refer to the *Physikalisch-chemische Tabellen*, by Drs. Landolt and Börnstein, Berlin, 1883, p. 81, and to papers by Violle (*Comptes Rendus*, vol. lxxxix. (1879) p. 702), and by Pictet (*ibid.*, vol. lxxxviii. (1879) pp. 855, 1315). The atomic weights and atomic volumes are those given in Lothar Meyer's *Modern Theories of Chemistry*, London, 1888. With regard to electrical conductivity, it is usual in this country to employ pure copper as a standard of reference for industrial purposes. For scientific purposes, it has been usual to refer to pure silver, and to assign to it the value 1000. In view, however, of the fact that it is very difficult to obtain silver of absolute purity, and that the conductivity varies greatly with the thermal and mechanical treatment to which the metal has been subjected, it has been considered better to adopt mercury at 0° as the standard metal, its electrical conductivity being taken as unity. The figures given in the last column of the table may be converted into a series in which silver would be 100, by simply multiplying by 1.75.

CHAPTER III.

ALLOYS.

Early Investigations. — As many valuable mechanical properties are conferred upon metals by associating them with each other, it seldom happens that metals are used in a state of purity when they are intended for industrial purposes, and this fact was discovered at a very early period of metallurgical history. The word alloy originally comes, in all probability, from the Latin *adligo* (alligo), "to bind to," and not, as Sir John Pettus thought, from the Teutonic *linderen*, "to lessen," suggestive as it is of the fact that a precious metal is lessened in value by the addition of a base one.

The distinguished chemist, Dumas, eloquently pleaded, many years ago, against leaving alloys in the oblivion to which moderr chemists consigned them, and there still seems to be a prevalen¹ impression that our knowledge of the phenomena which attend the union of metals is very imperfect, and that it rests upon a slender experimental basis. We are apt to forget the extent and complexity of the subject, and Lupton * has opportunely directed attention to the number of alloys which await examination. He says :—" Hatchett recommended that a systematic examination of all possible alloys of all the metals should be undertaken. He forgot to remind any one who should attempt to follow his advice that if only one proportion of each of the thirty common metals were considered, the number of binary alloys would be 435, of ternary 4060, and of the quarternary 27,405. If four multiples of each of the 30 metals be taken, the binary compounds are 5655, ternary 247,660, and quarternary 1,013,985."

Nevertheless, if the properties of many alloys have yet to be investigated, the study of alloys generally has not been neglected. The modern bibliography relating to them is much more extensive than it is usually supposed to be, and the older writings are very full, and contain the results of far more accurate observation

* *Nature*, Jan. 5, 1888, p. 238.

than they are credited with. In the early days of chemistry, as its history abundantly proves, alloys received much attention, and although the early chemists often failed to distinguish alloys from simple metals, or used them in unsuitable ways, they left an experimental record, the value of which is sadly unappreciated. From this record it is, incidentally, evident that the development of the art of separating metals from their ores, and from each other, was quickly followed by the acquisition of the knowledge that metals possess peculiar properties when re-united in certain proportions, and are thereby rendered more useful than they were in the pure state.

In early times some metals were used unalloyed, although at the present day they have no industrial application except in union with other metals. Antimony, for instance, now only employed as a constituent of certain alloys, was formerly cast and fashioned into ornaments, as is proved by the analyses of Virchow, and by a fragment of a very ancient Chaldean vase, which fragment, when examined by Berthelot, proved to be of pure antimony.[*] The implements and ornaments discovered by Schliemann abundantly show that the early Greeks were familiar with alloys of silver and gold, copper and tin, lead and silver, and with many others, all artificially prepared. Throughout the Middle Ages there seems to have been a belief that the action of metals on gold and silver was, on the whole, corrupting ; and Biringuccio, in 1540, possibly seeing that this was the prevailing view, carefully defined such alloys as being " nothing but amicable associations of metals with each other " ; and he further pointed out that metals must be mixed by weight, and not at random.

Views as to the Constitution of Alloys.—Passing from the sixteenth to the eighteenth century, we find four writers whose names deserve to be specially mentioned, because they seem to have been the first to indicate the direction in which modern investigation has been conducted. These are Réaumur, Gellert, Musschenbroek, and Achard, who respectively studied — 1st (Réaumur), molecular change produced in a metal by heat ; 2nd (Gellert), the relation of fluid metals to each other considered as solvents ; 3rd (Musschenbroek), the cohesion of alloys as shown by certain mechanical properties ; and 4th (Achard), the electrical behaviour of metals and alloys. It is interesting to trace the connection between the older work and the new. Réaumur,[†] in explaining the hardening of steel by rapid cooling from an elevated

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[*] *Ann. de Chim. et de Phys.*, vol. xii., 1887, p. 135.
[†] *L'art de convertir le fer forgé en acier*, Paris, 1722, p. 321.

temperature, comes very near the modern view that a metal may, under certain conditions, pass from one allotropic state to another, for he distinctly contemplates the possibility of molecular change produced by the expulsion by heat of "sulphurs and salts" from the molecules into interstitial spaces between them. He speaks of "molecules and elementary parts of molecules," like a modern writer, and tries to show that when hot steel is rapidly cooled, "sulphurs and salts" cannot return into the molecules, but remain in the interstitial spaces; and that, therefore, the physical properties of hard steel become quite different from those of soft. If it should be urged that the analogy between carburized iron and alloys is over-strained, it may be pointed out that, in 1867, Matthiessen said, after appealing to the fact that in certain alloys the constituent metals are present in allotropic states, "I have always made a comparison between iron and steel (and alloys). This has been done to show that the carbon iron alloys behave in an analogous manner to other alloys, which cannot be looked upon as chemical combinations."[*]

Gellert makes the analogy of certain alloys to solutions very clear, and in his *Metallurgic Chemistry* he gives a table showing the relative solubilities of metals in each other, while in the observations which accompany it [†] he says, to cite one of the cases, he takes as an illustration, "Since copper and silver and copper and gold dissolve one another very readily, the copper cannot be parted from iron by means of gold or silver," probably having in mind a reaction which enables silver to be parted from gold by the action of sulphur and iron. He further clearly shows that, with regard to the solution of metals in a triple alloy, he understood the possibility of a division of a metal between two other metals acting as solvents.

The mechanical properties of alloys were investigated by Musschenbroek, who, working in the early part of the eighteenth century, made some experiments on the tensile strength of metals and alloys. He writes of "the absolute cohesion by which a body resists fracture when acted upon by force drawing according to its length," [‡] and gives the tenacity of several metals, and the alloys, brass and pewter. He shows the importance of such work so clearly that it is remarkable how slowly the mechanical testing of metals developed since his time.

Achard, whose researches were published in 1784, made a very

* *Journ. Chem. Soc.*, 1867, p. 220.
† English translation of his work, London, 1776, p. 186.
‡ *Elements of Philosophy*, translated by John Colson, F.R.S., vol. i., p. 23, 1744.

extended series of experiments on multiple alloys, as well as those of simple metals. He pointed out that the relative conductivities of substances for heat and for electricity are closely related.[*] He devised an appliance for the experimental verification of this fact, and, as he included alloys in his researches, it may fairly be claimed that he led the way for the important generalisation that alloys may be ranged in the same order as regards their power of conducting heat and electricity, which was made by Wiedemann and Franz in 1853-9.

The necessity of metals being pure when added to each other was hardly recognised until the eighteenth century, and Duhamel, who contributed the article on alloys to the *Encyclopédie Méthodique* in 1792, appears to have been the first writer to insist on the necessity for making exact experiments upon alloys with metals which possess a high degree of purity and on effecting their union by heat in closed vessels. He further pointed out that up to his time no chemist had taken these precautions, and it is certain that in conducting some modern experiments they have been neglected.

In the early part of the nineteenth century researches on alloys became more numerous; they were mainly directed to ascertaining the effect on the density of metals produced by alloying them and to determining the effects of slow cooling on alloys with low melting points. Of such a nature was the work of Ermann in 1827 and of Rudberg (1830-1). Ermann called attention to the peculiar behaviour of alloys of lead and tin when solid. Rudberg studied anomalies in these alloys when in the liquid state.

Regnault showed that the specific heats of certain fusible alloys were greater near 100° than the mean specific heat of their constituents, and this fact appears, as Spring has shown,[†] to have induced Person to undertake researches on the latent heat of alloys and on these specific heats.

Undoubtedly one of the greatest works on alloys of the present century was that of Matthiessen, who studied the electrical resistance of metals and alloys, and was led to the conclusion that in many cases metals are present as allotropic modifications——that is, in totally different forms from those in which we ordinarily know them.

It is by no means easy to investigate the molecular constitution of alloys, but evidence may be gathered in the following ways:

* *Sammlung physikalischer und chemischer Abhandlungen*, Berlin, 1784, vol. i.
† *Bull. de l'Académie Royale de Belgique*, 1886 (3), vol. xi.

1. By comparing the properties of an alloy with those of its constituent metals.

2. By studying the behaviour of alloys in passing from the liquid to the solid state, and conversely in passing from the solid to the liquid.

3. By determining the physical constants of solid alloys, such as the melting point, specific gravity, specific heat, electrical resistance, electromotive force, and their mechanical properties, such as tenacity and extensibility.

First we must consider the methods of producing alloys, for the union of metals may be effected in three ways:

1. By fusion—that is, by causing metals to unite by melting them together.

2. By compression of the powders of the constituent metals.

3. By electro-deposition.

Union of Metals by Fusion.—The first method, by fusion, is, of course, the method ordinarily adopted. One of the metals is melted, and the other is added to it, sometimes in the fluid state, but often in the solid. The product—the alloy—will have very different properties from those possessed by either of the constituent metals. Every metal has, of course, a definite melting point, but, apart from the heat initially required to melt a metal, we find that the union of metals is sometimes attended with an evolution and sometimes with an absorption of heat.

The following metals evolve heat when they are united:—aluminium and copper, platinum and tin, arsenic and antimony, bismuth and lead, gold and just-melted tin; while on the other hand, lead and tin when united absorb heat, that is produce cold when their union takes place.

In the case of many metals these effects can only be demonstrated by the aid of delicate instruments. There is, however, a simple case in which the union of metals is attended with a considerable diminution of temperature; it is an experiment we owe to Mohr, and it will be shown subsequently that its explanation is a very complicated one. Take tin, lead, and bismuth in equivalent proportions, as finely divided as possible and mix them with eight equivalents of mercury as rapidly as may be, under conditions in which heat is not transmitted to the mixture from the walls of the containing vessel, and it will be found that the temperature falls from the ordinary temperature of the room + 17° C. to − 10° C., so that if a vessel containing water be placed in the mixture the water will be frozen. The experiment proves that by the union of metals, using mercury as a solvent, a freezing mixture may be produced.

Union of Metals by Compression.—Now turn to the second method by which metals may be caused to unite, that is, by compressing strongly the powders of the constituent metals. Since 1878, the labours of Prof. Walthère Spring, of the University of Liége, have been mainly devoted to the study of the effect of compression on various bodies.*

The particles of a metallic powder left to itself at the ordinary atmospheric pressure will not unite, but by augmenting the points of contact in a powder, the result may be very different. Spring's experiments were made with the aid of a compression apparatus, the general form of the appliance employed being shown in the diagram, Fig. 23. The metallic powder is placed under a short
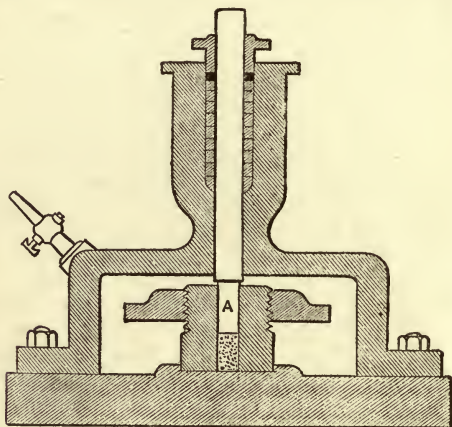
FIG. 23.

cylinder of steel, A, in a cavity in a steel block divided vertically, held together by a collar, and placed in a chamber of gun metal, which may be rendered vacuous. The pressure is applied to a cylindrical rod passing through the stuffing box. Under a pressure of 2000 atmospheres on the piston, or 13 tons on the square inch, lead, in the form of filings, becomes compressed into a solid block, in which it is impossible to detect the slightest vestige of the original grains, while under a pressure of 5000 atmospheres lead

* *Bull. de l'Académie Royale de Belgique* (2), vol. xlv. (1878), No. 6; (2), vol. xlix. (1880), No. 5. See also subsequent papers in the same publication ; in the *Bull. Soc. Chim.*, Paris, and in the *Berichte der Deutsch. Chem. Gesellschaft* (Bildung von Legirungen durch Druck), vol. xv. p. 595.

no longer resists the pressure, but flows, as if it were liquid, through all the cracks of the apparatus, and the piston of the compressor descends to the base of the cylindrical hole, driving the lead before it. The more interesting results were obtained by Spring with crystalline metals. Bismuth, as is well known, is crystalline and brittle, yet fine powder of bismuth unites, under a pressure of 6000 atmospheres into a block very similar to that obtained by fusion, having a crystalline fracture. Tin, when compressed in powder unites, and if it is made to flow through a hole in the base of the compression apparatus, the wire so formed sometimes, though not always, emits the peculiar "cry" of tin when bent. The following table shows the amount of pressure required to unite the powders of the respective metals:—

							Tons Per Square Inch.
Lead .	.	.	.	unites at	.	.	13
Tin .	.	.	.	,,	.	.	19
Zinc .	.	.	.	,,	.	.	38
Antimony .	.	.	.	,,	.	.	38
Aluminium	.	.	.	,,	.	.	38
Bismuth .	.	.	.	,,	.	.	38
Copper .	.	.	.	,,	.	.	33
Lead .	.	.	.	flows at	.	.	33
Tin .	.	.	.	,,	.	.	47

We know that combinations are produced when certain bodies in solution are submitted to each other's action. But do solids combine? Is the alchemical aphorism "That bodies do not react unless they are in solution" true? Experiment proves that such solution is not necessary. Take, for example, two anhydrous salts—iodide of potassium and corrosive sublimate, both in a dry condition. When they are mixed in a mortar they unite, as is shown by the vermilion-coloured iodide of mercury which is produced. But do solid metals combine, in the sense in which chemical combination is possible between metals, when submitted to each other's action under the conditions which prevail when their powders are compressed? Mohr has pointed out* that cohesion is a form of chemical affinity, and the experiment cited, of freezing water by the cold produced by amalgamation, affords valuable evidence in support of his view. It occurred to M. Spring that if there be true union between the particles of a metallic powder when submitted to great pressure in the appliance shown in Fig. 23, it ought to be possible to build up alloys by compressing the powders of the constituent metals, and he urged that the

* *Liebig's Ann.*, vol. cxcvi. (1879), p. 183.

formation of alloys by pressure would afford the most conclusive proof that there is a true union between the particles of metals in the cold, when they are brought into intimate contact.   Experiment proved that this reasoning is correct, for by compressing in a finely divided state, fifteen parts of bismuth, eight parts of lead, four parts of tin, and three parts of cadmium, an alloy is produced which fuses at 100° C.   It is necessary, however, to compress the mixed powder twice, crushing and filing up the block obtained by the first compression because the mechanical mixture of the constituent metals is not sufficiently intimate to enable a uniform alloy to be obtained by a single compression.   The alloy produced fuses in boiling water, actually at 98° C., although the melting point of the most fusible of its constituents, the tin, is 282° C.   It may be urged that by compressing these powders heat is evolved, and that this heat may be sufficient to produce incipient fusion of the metallic powders, or at all events, may exert a material influence on the result obtained.   This objection has been experimentally anticipated by Professor Spring.   First the compression is effected with extreme slowness, and therefore there can be no question as to the sudden evolution of heat, as would be the case if the powders were compressed by impact instead of by slow squeeze; and, to sum the matter up briefly, Spring calculates an extreme case— that if it be granted that all the work done in compressing the powders were actually translated into heat, it would only serve to heat a cylinder of iron 10 mm. in height, and 8 mm. in diameter (the dimensions of cylinder A, Fig. 23, used in his apparatus), 40.64° C.

In order that direct experimental evidence might not be wanting Spring took the organic body, phorone, a hard, crystalline substance which melts at 28° C., and compressed it exactly as in the case of the metallic powders.*   He took the precaution to place a shot of lead on the top of the powder before submitting it to compression.   Only imperfect union of the particles of phorone resulted.   The conclusion of the experiment proved that the shot remained where it had been placed at the top of the column, and, therefore, the 28° necessary to melt the substance had not been evolved, for if it had the shot must have fallen through the fluid mass.   It is, then, absolutely safe to conclude that, in the compression of bismuth, for instance, there can be no question of the evolution of the heat necessary for the fusion of the metal.

It appears to be also quite safe to conclude that it is proven that *solid* metals possess the power of reacting on each other

* *Bull. Soc. Chim.*, vol. xli. (1884), p. 488.

and forming alloys, provided their particles are really in contact.

Union of Metals by Electro-Deposition.—The formation of alloys by the electrolytic deposition of the constituent metals is a subject of great importance, and although the union of metals is usually effected by fusion, fire is not the only agent which can be employed for this purpose. Two or more metals can be deposited side by side by the aid of the electric battery. No statistics as to the amount of precious metals annually employed for electro-deposition in Birmingham, the early home of electro-metallurgy, are available, but it is known that a single works in Paris, belonging to M. Christofle, deposits annually six tons of silver, and it has been estimated that the layer of silver of the thickness actually deposited on various articles would, if spread out continuously, cover an area of 140 acres. Copper and zinc may be deposited by electrolysis so as to form brass, and all the beautiful bronzes and alloys of the Japanese can be obtained by galvanic agency; and, further, by suitable admixture of gold, silver, and copper, red gold, rose-coloured gold, or green gold may be deposited, so that the electro-metallurgist has at his command the varied palette of the decorative artist.

Liquation.—It is now necessary to examine more closely the mutual relations of the metals when united. Metals may be mixed in the fused state, but it by no means follows that they will remain in admixture if they are allowed to cool slowly, or sometimes even rapidly. In fact, a cooling mass of mixed metals often behaves much as water containing suspended matter does in freezing, when the ice first formed rejects the foreign matter, and as has been shown by the classical researches of Levol,[*] the portion of the alloy which first solidifies rejects certain other portions of the constituent metals. This action is called **liquation.** The term is also applied in a somewhat wider sense to the actual isolation of the components of ores or of alloys from each other. For instance, when an ore or mixture of metals is exposed to a degree of heat sufficient only to melt the most fusible member or constituent present in the mass, it flows away from the unmelted residue. In the case of alloys the importance of liquation has been fully recognised. If lead and zinc be thoroughly mixed in the fused state, and slowly cooled in a deep mould, the separation will be almost complete, and it will also be seen that it is easy to break off one corner at the side where the zinc has separated itself, and to flatten out another one, which proves it to be nearly

* *Ann. de Chim. et de Phys.*, vol. xxxvi. (1852), p. 193; vol. xxxix. (1853), p. 163.

pure lead. Take again the case of what was a triple admixture of lead, antimony, and copper, thoroughly mixed when fluid, and cooled in a cylindrical mould. The copper and the antimony unite, but they reject nearly all the lead, and drive it to the centre of the mass, so that the solidified cylinder, when broken across, presents a ring of the purple copper-antimony alloy surrounding a core of lead. Silver and copper alloys behave in a similar manner, but in any mixture of fused silver and copper, one particular alloy of these metals is formed which is driven outward or inward in the cooling mass according to whether silver or copper is in excess in the bath. In all these cases the separation is never complete; the lead retains some 1.6 per cent. of zinc, and the zinc about 1.2 per cent. of lead. The copper and antimony retain a small amount of lead, and the lead a small amount of copper and antimony, as is shown by some very careful experiments of Dr. E. J. Ball, to which reference has already been made. The solid mass in all these cases is a mixture of solidified solutions of the metals in each other.

Dr. Guthrie investigated this side of the problem at some length.* It is difficult to give a brief account of his work, but his conclusions may be stated as follows: He considers that certain alloys in cooling behave as a cooling mass of granite would; clear molten granite would throw off, in cooling, "atomically definite" bodies, leaving behind a fluid mass, which is not definite in composition, as the quartz and the felspar undergo solidification before the mica. In alloys much the same thing happens, for where a molten mass of lead and bismuth or bismuth and tin cools, a certain alloy of the metals falls out, just as the quartz and felspar did, and ultimately the most fusible alloy of the series is left, which Dr. Guthrie calls the eutectic alloy. It is the most fusible alloy of the series, but the proportion between the constituent metals are not atomic proportions, and Guthrie says that "the pre-conceived notion that the alloy of minimum temperature of fusion must have its constituents in simple atomic proportions, that it must be a chemical compound, seems to have misled previous investigators;" but he adds "that certain metals may, and do unite with one another in the small multiples of their combining weight may be conceded; the constitution of eutectic alloys is not in the ratio of any simple multiple of their chemical equivalents, but their composition is not on that account less fixed, nor are their properties the less definite."

Guthrie dealt only with alloys of low melting points, such as

the fusible metals, and it remains to be seen whether the observation will apply to alloys with higher melting points. It does apply, at least, to the silver-copper alloys, which melt below 940°C. For further information upon this point we must wait for the development of Mendeléef's theory of solution. He regards solutions as strictly definite, atomic, chemical combinations at temperatures higher than their dissociation temperatures. Definite chemical substances may be either formed or decomposed at temperatures which are higher than those at which dissociation commences; the same phenomenon occurs in solution; at ordinary temperatures they can either be formed or decomposed.

Liquation is very marked in the case of copper-silver alloys, and it is well known in Mints that when molten alloys of certain metals are cooled, groups of the constituent metals, or even the constituent metals themselves, separate, and thus occasion irregularity in the composition of the solidified mass. The phenomenon has been carefully studied by, amongst others, Lazarus Ercker, and Jars, whilst in more modern times the researches of D'Arcet in 1824, of Mercklein in 1834, of Levol in 1854, have shown that ingots of silver and copper are not homogeneous throughout. Levol cast the alloy to be examined either in a cubical iron mould of 45 mm. side, or in a sphere 50 mm. in diameter. He concluded that the only homogeneous copper-silver alloy was that containing 71.89 per cent. of silver, and he considered this to be a
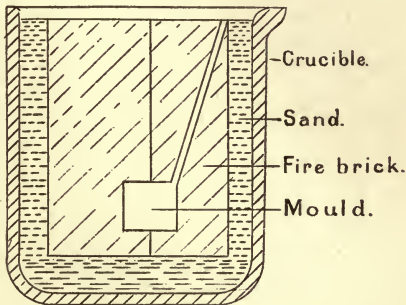
FIG. 24.

definite combination of the two metals, with the formula Ag_3Cu_4 (or Ag_3Cu_2 if 63.34 be taken as the atomic weight of copper). All other alloys of silver and copper he viewed as mixtures of this definite alloy with excess of either of the metals. In 1875 the author[*]

* *Phil. Mag.*, vol. xvii. (1884), p. 462.

repeated many of Levol's experiments, and gave evidence for modifying his view that the only homogeneous alloy of silver and copper is that which contains 71.89 per cent. of silver. The uniformity in composition of the series of copper-silver alloys depends greatly on the method of cooling. By slow cooling many alloys, other than the one mentioned above, may be made as uniform as it, its peculiarity consisting in the fact that its composition is uniform whether it is cooled slowly or rapidly. In order to ascertain whether liquation is modified if the cooling be greatly protracted, cubical moulds, about 4 to 5 millimetres in side, of firebrick (Fig. 24) were employed. These could easily be heated to bright redness, and slowly and uniformly cooled. The following results show that the maximum difference in the composition of an alloy containing 925 parts of silver and 75 parts of copper was only 1.40 per thousand when the alloy was slowly cooled, while it was as much as 13 parts per thousand when the alloy was rapidly cooled :

	Vertical Plane			Horizontal Plane	
$a.$	925.7		1.	924.8
$b.$	925.0		2.	925.0
$c.$	925.0		3.	924.9
$d.$	925.0		4.	924.9
$e.$	925.4		5.	925.0
$f.$	924.3		6.	925.1
$g.$	925.0		7.	925.1
$h.$	925.3		8.	925.1
$i.$	925.3		9.	925.0
$j.$	925.3		10.	925.0
$k.$	924.3			
$l.$	925.3			
$m.$	925.3		$a.$	924.1
$n.$	924.4		$\beta.$	924.1
$o.$	925.0		$\gamma.$	924.1
$p.$	924.3		$\delta.$	924.4
$q.$	925.0		$\epsilon.$	924.0
$r.$	925.3		$\zeta.$	924.2
$s.$	925.0		$\eta.$	924.2
$t.$	924.9		$\theta.$	923.9

Vertical Plane:
a. 925.7
b. 925.0
c. 925.0
d. 925.0
e. 925.4
f. 924.3
g. 925.0
h. 925.3
i. 925.3
j. 925.3
k. 924.3
l. 925.3
m. 925.3
n. 924.4
o. 925.0
p. 924.3
q. 925.0
r. 925.3
s. 925.0
t. 924.9
u. 924.3
v. 924.7
w. 924.9
x. 924.9
y. 925.3

Horizontal Plane:
1. 924.8
2. 925.0
3. 924.9
4. 924.9
5. 925.0
6. 925.1
7. 925.1
8. 925.1
9. 925.0
10. 925.0

Corners:
a. 924.1
β. 924.1
γ. 924.1
δ. 924.4
ε. 924.0
ζ. 924.2
η. 924.2
θ. 923.9

"Dip assay," 924.9.

Maximum difference [between the centre and the corners], 1.40 per thousand.

The diagram (Fig. 25) shows the position in the cube corresponding to the letters and figures given above.

Levol also showed that in solidifying alloys of lead with the precious metals, if the latter are present in small quantity, they are driven towards the centre of the solidifying mass. Gowland

and Koga* have shown that when 984.37 parts of silver and 14.80 parts of bismuth are melted and cast into an open ingot mould so as to give an ingot weighing about 1000 troy oz., the portions of the ingot which remain longest fluid are richer in silver than the others. The entire question has recently been reviewed by Peligot,† who has endeavoured to ascertain, by assaying various parts of an ingot of gold weighing 13 lbs., whether he could detect the effects of liquation. The ingot contained 900 parts of gold in 1000, the alloying metal being principally copper, and he concluded that, within the limits of the errors of observation, there was no evidence of liquation. As this is a question of much industrial importance in relation
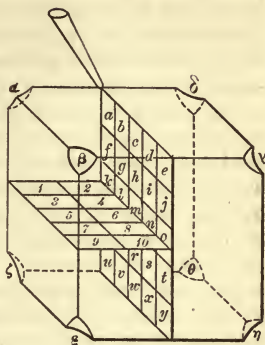
FIG. 25.

to the precious metals, the author has made further investigations into this subject, and in view of the difficulty of obtaining more precise evidence on the point the following experiment was made: A gold ingot of a fineness of 984.7, the alloying metal being silver, was melted and poured into a spherical mould of iron. The temperature of the molten metal was much higher than that of the mould, and probably in this case the position of the metal which solidified last would be situated somewhere above the geometrical centre of the mass. From the sphere of solid gold, which was 3 inches in diameter and weighed 140 oz., a disc, $\frac{3}{8}$ inch in thickness, and of the full diameter of the sphere, was cut in a vertical plane. This disc, which weighed 31 oz., was rolled in two directions at right angles to each other to a convenient thickness for cutting with shears, and assay pieces were cut from points distributed over its entire surface. The results of eighty-two assays afforded no clear evidence of systematic rearrangement, for although there appeared to be an enrichment towards the upper part to the extent of $\frac{8}{100000}$ths, such small differences as existed in the assays made on metal taken from the same horizontal planes could not be regarded as being due to any definite redistribution of the metal. It will thus be evident that gold of high standard does not, like silver, show any marked tendency to reject on solidification the baser metal with which it is

* *Journ. Chem. Soc.*, vol. li. (1887), p. 410.
† *Bull. Soc. d'Encouragement*, vol. iv. (1889), p. 171.

associated.   It is well known, however, that there is a develop-
ment of crystallisation, and that other remarkable changes are
produced in the structure of pure gold by the addition of minute
quantities of lead, bismuth, and certain other metals.   As yet,
there can be said to be no sufficient evidence to show that gold,
alloyed with silver and copper and properly mixed in the molten
state, is not practically homogeneous when solid.

On the other hand, Mr. E. Matthey * has recently shown that
by casting an alloy of gold and platinum containing 900 parts of
gold and 100 parts of platinum, in the identical mould above
described, there is a concentration of platinum towards the centre
of the mass, the gold and platinum being as 900 gold to 98
platinum on the exterior, against 845 gold and 146 platinum at
the centre of the mass.   Consequently, it is evident that gold on
solidifying does tend to free itself from associated platinum,
though no effect of the kind can be detected by careful assay in
the case of associated copper or silver.

It is, however, in relation to the metallurgy of iron and steel
that the question of liquation is of primary importance.   There
can be no doubt that when an ingot of steel slowly cools, phos-
phorus, sulphur, and carbon, and, to a less degree, manganese and
silicon, tend to separate from the mass and to become concentrated
in that portion of the ingot which solidified last.   Of the earlier
researches on this subject, probably the most important is that of
Snelus.†   He cut an ordinary steel ingot into slices parallel to
the base, and analysed borings taken from each slice along a
diagonal line from one corner to the centre, and numbered from
1 to 6, passing from the bottom left hand corner to the centre.
His results are given in the following table, and show that, al-
though the bottom layer is uniform, the carbon, sulphur and
phosphorus are driven towards the centre of the mass :—

	Top.			Bottom.		
	Carbon.	Sulphur.	Phosphorus.	Carbon.	Sulphur.	Phosphorus.
1	0.44	0.032	0.044	0.44	0.048	0.060
2	0.54	0.048	0.060	0.42	0.056	0.062
3	0.57	0.080	0.086	0.41	0.048	0.054
4	0.61	0.096	0.097	0.40	0.048	0.054
5	0.68	0.120	0.111	0.38	0.048	0.058
6	0.77	0.187	0.142	0.37	0.044	0.052

* *Proc. Roy. Soc.*, vol. xlvii. (1890), p. 180.
† *Journ. Iron and Steel Inst.*, 1881, p. 379.

There can be no doubt, therefore, that constituents whose presence is injurious to the mechanical properties of steel, find their way towards the top of the ingot. In steel ingots destined for the manufacture of guns, it is usual to cut off the tops, which are unsound as well as impure. The importance of this procedure has been widely recognised.* It is clear that the action of liquation cannot be neglected in making large castings and forgings, and probably gives rise to fractures that have hitherto been regarded as mysterious.

In the case of pig iron it is possible to isolate products of liquation, as has been shown by M. Lencauchez,† who heated fragments of iron to a temperature of 94° for 100 hours. At the end of this time a number of spherical grains sweated out from the surface of the fragments. Analysis of these exudations showed that they contained from 4 to 6 per cent. of phosphorus, from 0.6 to 0.8 per cent. of silicon, from a trace to 1.5 per cent. of graphite carbon, and from 0 to 1.24 per cent. of combined carbon. The original pig iron contained about 3.5 per cent. of total carbon, 2.6 of silicon, and 1.9 of phosphorus. The composition of these exudations, therefore, is that of pig iron impoverished in carbon and silicon, but considerably enriched in phosphorus.

If lead, tin, and zinc are melted together, and left at rest in a fused condition, no separation takes place if the proportion of tin exceeds a certain amount ; but if the quantity of tin is less than this, the alloy separates into two layers, each layer consisting of a ternary alloy of the three metals. Dr. C. R. A. Wright and Mr. C. Thompson‡ have examined the nature of this separation, and the composition of the alloys under different conditions. The heavier alloy, they found, consists of a saturated solution of zinc in lead containing tin, whilst the lighter consists of lead in zinc containing tin. The two alloys always correspond with two conjugate points on the solubility curves of zinc in lead-tin, and of lead in zinc-tin. The tin is not distributed equally in the two alloys, except when present in a particular proportion, which varies with the ratio of zinc to lead. With less tin than this, the lighter alloy takes up the excess of tin ; with more, the heavier takes up the excess.

Action of Electric Currents on Molten Alloys.—In fur-

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* Maitland, *Min. Proc. Inst. C.E.*, vol. lxxxix. (1887), p. 12. See also Eccles, *Journ. Iron and Steel Inst.*, No. 1 (1888), p. 70, and the discussion on Greenwood's paper on the "Treatment of Steel by Hydraulic Pressure," *Min. Proc. Inst. C.E.*, vol. xcviii., 1889.

† *Mém. Soc. Ing. Civils*, 1887.

‡ *Proc. Roy. Soc.*, vol. xlv. (1889), p. 461.

ther tracing the analogies between alloys and saline solutions, it will be well to see what takes place when a current of electricity is passed through an alloy. Take first the case of a fluid alloy through which a current is passed. We have spoken of alloys as solutions; if they be ordinary chemical solutions it has been urged that an electric current of sufficient strength ought to decompose them, and it becomes a most important question to determine whether an ordinary metallic alloy can conduct electrolytically like a salt solution, or whether it conducts, as a metal would, that is, without being decomposed.

The question therefore arises, can a well-marked alloy, or a quasi-compound, be in the slightest degree electrolysed by an exceedingly intense electric current? Some experiments conducted by M. Gérardin,* in 1861, satisfied him that amalgams of sodium and mercury might be decomposed by an electric current, with partial separation of the constituent metals. The experiments were repeated by Dr. Obach† who employed the apparatus shown in the diagram (Fig. 26). The sodium amalgam is enclosed in the two
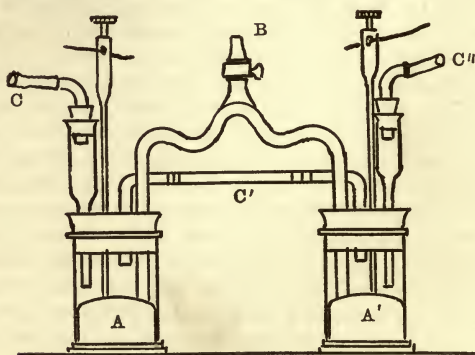
FIG. 26.

glass vessels, A A′, and metallic communication between them is effected by opening the stop-cock, B, and sucking the amalgam into the bent tube. An atmosphere of dry hydrogen is provided, by the tubes, C C′ C″, and the current is transmitted through the amalgam by the battery terminals shown. Subsequent examination of the sodium amalgam proved that no separation had been effected. The composition of the amalgam was unaltered by the

* *Comptes Rendus*, vol. xliii. (1861), p. 727.
† *Poggendorff's Ann. der Phys. u. Chemie*, sup. vol. vii. (1876), p. 280.

passage of the current. He also used a W-shaped tube containing melted alloys, and proved that no decomposition could be observed after the passage of the current.

In 1887, at the request of the Electrolysis Committee of the British Association, the author took up the inquiry* and by employing an intense electric current from secondary cells, showed that no separation took place either in certain alloys of lead and gold, or in alloys of lead and silver, even with so strong a current as 300 ampères. The method employed is indicated by the diagram (Fig. 27). The alloy, C D, under examination was placed in cavities cut in a fire-brick, shown at E, and the cables from a secondary battery were connected by means of copper holders with wrought-iron terminals, A B. The experiments are given in detail in the Report of the British Association for 1887, and it will be sufficient to say here that as the question at present stands, it would seem that fluid alloys conduct just like metals, and not like salt solutions; but, as Dr. Lodge has pointed out with reference to these experiments, " if the question as to the possibility of the
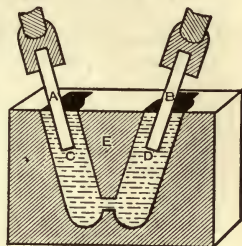
FIG. 27.

electrolytic separation of true alloys of metals should be answered in the negative, there must surely remain a group of bodies on the borderland between alloys proper and electrolytes, among which some gradual change from wholly metallic to wholly electrolytic conduction is to be looked for."

Conduction of Electricity by Alloys at High Temperatures. —It has long been known that the electrical resistance of alloys increases as the temperature is raised, but the want of a simple and accurate pyrometer has hitherto prevented experiments being carried far in this direction. Le Chatelier, however, has shown in a recent paper,† by the aid of his pyrometer, to be hereafter described, that in metals which do not undergo any molecular change before fusion, the increase of electrical resistance is proportional to the temperature. A great number of metals seem, like iron, to undergo sharply defined molecular changes at definite temperatures, and some alloys show progressive changes, all of which facts are clearly indicated by abrupt or gradual change in resistances.

The alloys as yet worked on are brass, German silver, and an

* *Report British Assoc.,* 1887, p. 341.
† *Comptes Rendus,* vol. cxi. (1890), p. 454.

alloy containing :—Copper, 70 per cent.; nickel, 18 per cent.; and iron, 11 per cent. These have been examined at temperatures between the ordinary temperature and their melting points.

Conduction of Electricity by Solid Alloys.—In the case of solid alloys—solidified solutions of metals, that is—the nature of the evidence is very different, for the passage of the electric current through solid alloys reveals the existence (1st) of certain well-defined compounds of the metals, and (2nd) affords abundant proof that in certain alloys the metals exist in allotropic states. And here it is necessary to go back chronologically, and refer to the classical mark of Matthiessen published in 1860.* He showed that the
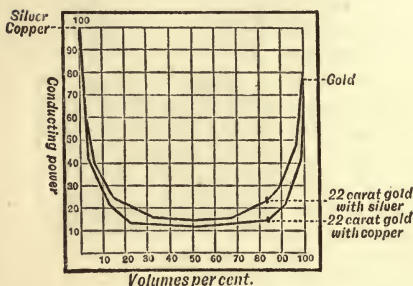
FIG. 28.
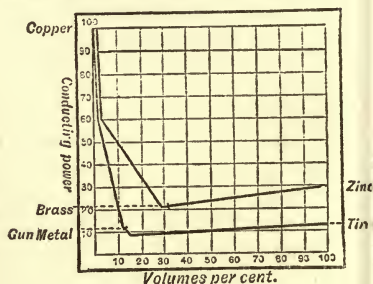
FIG. 29.

electrical conductivity of all alloys may be graphically represented by one or other of three typical curves, which, as the diagrams

FIG. 30.

indicate, are respectively U-shaped (Fig. 28), L-shaped (Fig. 29), or straight lines (Fig. 30). On adding gold to silver, for instance, there is a rapid decrease of conductivity, silver being 100, and the curve gradually turns round and then rises without any break to the point representing the conductivity of gold.
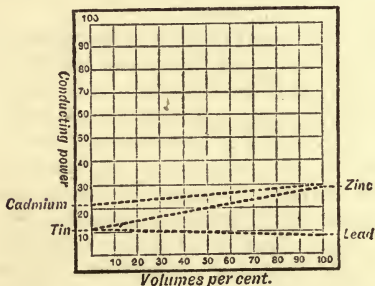
In the case of the silver-copper series, silver being 100 and copper 96, there is a marked break in the U-shaped curve (Fig. 28) corresponding

* *Phil. Trans. Roy. Soc.*, 1860, p. 161.

to the alloy, which contains 71.8 per cent. of silver, and this is probably a definite chemical alloy.

In the case of the L-shaped curve (Fig. 29), representing the conductivity of the copper alloys, $SnCu_3$ and $SnCu_4$ (which contain respectively 61.8 and 68.2 per cent. of copper) are probably definite compounds.* This view is confirmed by Laurie, who has shown quite recently by another † method—by determining the electromotive force of the copper series—that probably $SnCu_3$ is a chemically definite alloy.

The nature of the evidence is as follows:

Laurie finds that if the zinc plate of a Daniell cell be replaced by a compound plate, formed by joining copper and zinc, the cell has the same electromotive force as one in which zinc alone is used. This is true even if the zinc surface be only $\frac{1}{1000}$ part of the copper surface. If the zinc plate be replaced by copper-zinc alloys, no deflection of the electrometer is observed as long as the alloy contains less than 67 per cent. of zinc. At this point however, a considerable deflection, practically equivalent to that given by zinc, is suddenly obtained. This result, in his opinion, may be taken as evidence of the existence of a compound of the two metals of the formula $CuZn_2$. Alloys containing a greater proportion of zinc behave like zinc alone. Similarly in the case of tin-copper alloys, a sudden rise of electromotive force is observed when the proportion of tin in the alloy exceeds that which would be contained in a compound of the formula $SnCu_3$. This result is in harmony with the evidence already obtained by observations of the density and thermal and electrical conductivity of the copper-tin alloys. If an alloy containing a larger percentage of tin than $SnCu_3$, in a state of fine division, be placed in a copper cup and used in place of the zinc in a cuprous chloride cell, the excess of tin is gradually eaten out, leaving approximately the alloy $SnCu_3$. This alloy undergoes no change if the circuit be kept closed.

Various investigators, including Wheatstone, Jules Regnault, Gaugain, Crova, Robb, Lindeck, and Hockin and Taylor, have examined the electromotive force of metallic amalgams in acid and saline liquids, and the latter investigators have shown that 1 part by weight of zinc in 23.6 million parts of mercury is electro-positive to pure mercury in a solution of zinc sulphate. Dr. G. Gore‡ employs two portions of very pure mercury as an electrolyte.

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* See Roberts-Austen, *Phil. Mag.* [5], vol. viii. (1879), p. 551 ; and Lodge, *ibid.*, p. 554.

† *Journ. Chem. Soc.*, 1888, p. 104.

‡ *Chemical News*, vol. lxi. (1890), p. 40.

These are connected by insulated platinum wires with an ordinary astatic torsion galvanometer of 100 ohms resistance, and a sufficiently minute proportion of a very dilute amalgam, of known strength, of one of the particular metals with some of the same mercury is added to one of the portions of mercury, to cause the needles of the instrument to be just visibly deflected whilst being viewed with the aid of a magnifying glass. The following results were obtained:—

One Part of—			1.0 grain of HCl or H_2SO_4 in 120 c.c. of Water— Parts of Mercury.		10 grains of KCl in 120 c.c. of Water— Parts of Mercury.
Mg .	.	.	110,274,000,000	...	13,430,858,806
Zn .	.	.	104,950,000,000	...	18,034,482,758
Cd .	.	.	184,828,432	...	10,404,225
Sn .	.	.	38,900,000	...	8,831,632
Cu .	.	.	15,484,375	...	1,640,160
Bi .	.	.	9,762,300	...	1,621,000
Pb .	.	.	5,651,149	...	1,050,341
Ag .	.	.	905	...	79

The volume of water employed in each electrolyte was 120 c.c.

In the above table the order of voltaic energy of the metals is substantially the same as that of the metals alone and unamalgamated. With each amalgam the amount of energy gradually declined, but recovered on stirring the mixture; the decline was quickest with the most dilute ones.

Allotropic Modifications of Metals when Alloyed.—Of all the researches made by Matthiessen, some thirty years ago, none are of more interest at the present time than those which enabled him to obtain evidence as to the passage of metals from the normal state to an allotropic one, which sometimes attends their union with each other.

Turn, for instance, to the tin-copper curve; he points out that the decrement in the conductivity produced by the addition of a minute quantity of tin to copper is very rapid, and he urges that the amount of tin is far too small to permit the belief to be entertained that true chemical combinations had been formed, and by such reasoning he was led to his great generalisation, that metals may sustain change in their molecular condition by union with each other in a fused state. This is probably the most important generalisation which has hitherto been made in connection with the study of alloys. It may be well to begin the consideration of this question of the molecular change in metals, by a reference to some early views as to their constitution. Consider, therefore, a mass of antimony which is adorned with a

large crystalline star. An attempt to explain the origin of the star led Lemery to the conclusion "that the star doth proceed from the antimony itself; the purification of the metal does serve to lay open the crystals of antimony, and the iron (it contains) by its hardness does expatiate these crystals." This attempt to explain the development of a crystalline structure in a metal by the influence which the presence of a small quantity of a metallic impurity exerts, will serve as a fitting introduction to the class of facts now to be considered, the study of which has been much neglected, notwithstanding their importance in metallurgical industry. All that need be done is to adduce some evidence which may serve to throw light upon the question why a definite material actually employed in the manufacture of, say a bridge, or a weapon, can be depended on to perform the duty entrusted to it, and why a certain other material would be absolutely untrustworthy, although chemical analysis can barely show the difference between the two. It has long been known that the properties of a metal may be influenced by the presence of a minute quantity of another element, even though it is so small as to preclude the possibility of its action being due to the formation of an ordinary chemical compound to which any reasonable formula, based upon atomic proportions, could be assigned. It by no means follows, however, that the atom of the added element does not exert a direct influence, or that its action is not controlled by a well-known law, but it is clear that in the experiment about to be described, for instance, we are not dealing with the union of elements in atomic proportions. Take two ladles containing exceptionally pure bismuth, filled from the same crucible containing the molten metal, and into one ladle introduce a tiny fragment of tellurium. Pour the contents of both ladles into moulds, and when the metal is cold, fracture it. It will be seen that the bismuth to which the tellurium is added has become minutely crystalline, while that which remains pure has crystallised in broad mirror-like planes, and one reflects a ray of light like a mirror, while the other, which contains the tellurium scatters the light. If there were no other guide than that afforded by mere inspection, you would say that the two masses were totally distinct elementary substances, and yet the only difference is that one contains $\frac{1}{2000}$ part of tellurium, and the other does not.

There are many such facts to be met with in practical metallurgy, and the knowledge of them has been steadily accumulating for centuries, but it is only since the end of the last century that it can be said to have been built up on a scientific basis, for it

was not until 1781 that Bergman discovered the wonderful fact that the difference between wrought iron and steel depends upon the presence or absence of a small quantity of carbon. The smallness of the amount of carbon capable of producing such striking effects greatly astonished him, as well as the chemists who followed him, and repeated his experiments, but, strange as it may seem, the promulgation in 1803 of Dalton's atomic theory threw a flood of light upon chemical phenomena, but cast into shade such investigations as those of Bergman, which dealt with influences of traces upon masses, and the authority of Berthollet was not sufficient to save them from neglect. In this eventful year for science, 1803, the latter published his essay on chemical statics, in which he stated, as a fundamental proposition, that in comparing the action of bodies on each other, which depends " on their affinities and mutual proportions, the mass of each has to be considered."*. His views were successfully contested by Proust, but, as Lothar Meyer says, the influence on chemistry of the rejection of Berthollet's views was remarkable. " All phenomena which could not be attributed to fixed atomic proportions were set aside as not truly chemical, and were neglected. The chemists forsook the bridge by which Berthollet had sought to unite the sister sciences, physics and chemistry." Fortunately, however, there was in this country one chemist who had followed up the line of work indicated by the early metallurgists, for in 1803, the same year as that in which Berthollet's essay was published, Charles Hatchett † communicated to the Royal Society the results of a research which he had conducted, with the assistance of Cavendish, in order to ascertain " the chemical effects produced on gold by different metallic substances when employed in certain " (often very small) " proportions as alloys."

The progress of research may show that it is possible, by a sufficiently high temperature, or by a suitable application of heat, to directly modify the chemist's atoms into which a molecule may be split up, and in this way to resolve one elemental substance into another ; at present we only know with certainty that we can change the grouping of the atoms in a molecule, but cannot alter the atoms themselves. That such change in the grouping of atoms is possible has long been known.

It is now recognised that, except in the case of unstable forms of elements, the occurrence of elements in different allotropic states means that, in the respective cases, the atoms are differently arranged in the molecules of which the body is composed.

* English edition, by M. Farrell, M.D., 1804, p. 5.
† *Phil. Trans.*, vol. xciii. (1803), p. 43.

These definitions need not be dwelt upon here; it is only necessary to point out the great industrial importance of the change in the molecular conditions of metals and alloys, produced, as these changes are, by comparatively slight influences.

Chemists have, even to the present day, been very slow to examine the conditions under which a metal, when pure, can exhibit widely different properties, can pass from one allotropic state, as it is termed, to another. Berzelius claimed that the metals osmium and iridium could exist in different allotropic states; and in 1846, Joule and Lyon Playfair,* showed that certain metals in different allotropic states possessed different volumes; and although chemical analysis could detect no change in the composition of a particular metal in either of its different states, its properties were widely different. There are several instances of this. In 1849 Bolley prepared lead by electrolysis. It is similar in composition to sheet lead; but Bolley's lead oxidises rapidly in air, and becomes converted into a yellow powder, and sheet lead does not. There is a form of copper which was first prepared in 1878 by Schützenberger, its specific gravity is less than that of ordinary copper, it oxidises rapidly in air, its behaviour in relation to nitric acid is different from that of ordinary copper, and last, it may be converted into ordinary copper by prolonged contact with dilute sulphuric acid. Similar cases of allotropy are claimed by Fritsche for tin, and by Schützenberger † for silver. It is not necessary to allude specially to Gore's antimony, or to modifications of nickel and palladium, because in their cases the passage from one state to another is determined by the presence or absence of occluded gas, and therefore the phenomenon becomes more complicated than when the composition of the metal is unchanged. It is quite true that in the cases referred to the variations in properties—the allotropy of the same element—are far less marked than the variations which characterise isomerism of organic compounds, but they are nevertheless very real and important, and if we knew the metals mentioned only in their unstable conditions, they would be unfit for industrial use.

Fritsche found that certain ingots of tin, when exposed to the rigour of a Russian winter, fell into powder. This powder was certainly an allotropic form of tin; it was grey and needle-like, but by heating to a point far below its melting point, it became changed into ordinary tin; and Fritsche points out that this property which tin possesses of passing into an unusual condition

led on one occasion to some difficulty. A quantity of buttons, consisting mainly of tin, and intended for the adornment of military uniforms, were safely delivered by the manufacturer and placed in store. On inspection, however, the military authorities, found nothing but a shapeless mass of grey powder, for the tin had assumed its allotropic form, and the buttons had disappeared.

We may now consider the question—Do metals, when they enter into union with each other, preserve their normal conditions, or do they ever assume allotropic states? The experimental evidence that they do assume such states is difficult to obtain, but some facts relating to this subject may be stated.

Evidence is not wanting of allotropy in metals released from solid alloys. Certain alloys may be viewed as solidified solutions, and when such bodies are treated with a suitable solvent, usually an acid, it often happens that one constituent metal is dissolved, and the other released in an insoluble form. For example, if a fragment of an alloy of potassium and gold containing about 10 per cent. of the precious metal, be thrown upon water, the potassium takes fire, decomposes the water, and the gold is released as a black powder; this black or dark-brown gold is an allotropic modification of gold, as there is evidence that it combines with water to form auric hydride. By heating this dark gold to dull redness, it at once assumes the ordinary golden colour. The Japanese use this gold, released from gold-copper alloys, in a remarkable way, for they produce by the aid of certain pickling solutions, a beautiful purple patina on copper, which contains only 2 per cent. of gold, while even a trace of the latter metal is sufficient to alter the tint of the patina.

Joule proved that when iron is released from its amalgam by distilling away the mercury, the metallic iron takes fire on exposure to air, and is therefore clearly different from ordinary iron and is, in fact, an allotropic form of iron. Moissan[*] has shown that similar effects are produced in the case of chromium manganese, cobalt and nickel, when released from the amalgams with mercury.

The best illustration of the change produced in a metal by the action of mercury is afforded by the following experiment. A plate of metallic aluminium would long remain exposed to air without sensible oxidation. Mercury also does not oxidise at the ordinary temperature, when exposed to air, but if the surface of the plate of aluminium be covered with a layer of mercury, then oxidation rapidly ensues, and the plate will soon become covered

[*] *Comptes Rendus*, vol. lxxxviii. (1879), p. 180.

with a white film of alumina, which may be detached in flakes. Clearly the condition of the aluminium has been modified by its union with the mercury.

It has already been stated that water can be frozen by cold produced by the solution of finely divided fusible-metal in mercury. It is not a matter of indifference whether the powders of the mixed constituents of the alloy are employed, or whether the alloy is previously prepared by fusion, and then powdered, which shows that the act of fusion has effected some change in the molecular arrangement of the metals. The explanation of the depolymerisation of the metals when they are united with each other is somewhat complicated. First, Mazetto[*] has shown that there is a similar lowering of temperature, though to a far less extent, when molten tin is mixed with molten lead, so that the lowering of the temperature is by no means confined to the solution of metals in mercury. The next step we owe to Professor W. Spring, of Liége, whose results in building up alloys by compressing the powders of their constituent metals have already been referred to. Spring finds that by determining the amount of heat given out by alloys of lead and tin on cooling from a molten state, that more heat is actually given out than might be expected from the results of calculation ;[†] the difference is so great that it could not be due to errors of observation, for in actual numbers it amounts to many hundreds of calories for a weight of 100 grammes. He concludes that when molten tin is added to molten lead, the atomic constitution of the molecules is simplified—that is, depolymerisation takes place. Let it be assumed that each molecule of molten lead contains an arbitrary number of atoms, say five, and that the molecule of molten tin also contains five atoms. Then, if one molecule of lead be added to three molecules of tin, so as to form the alloy $PbSn_3$, five groups of $PbSn_3$ will be the result, but each molecule of the alloy will contain four atoms instead of five. This molecular change requires heat to effect the re-arrangement in the molten admixture of metals, and as this heat is absorbed cold is produced, and it will therefore be evident that both theory and experiment tend to the view that molecular change may be produced by alloying metals.

Debray[‡] has given a case of an alloy in which a simple elevation of temperature induces allotropic change in the constituent metals. It is prepared as follows :—95 parts of zinc are alloyed by fusion with 5 parts of rhodium, and the alloy is treated with hydrochloric

[*] *Rendiconti del R. Instituto Lombardo* [2], vol. xviii., No. 3.
[†] *Bull. de l'Acad. Roy. de Belgique* [3], vol. xi., No. 5, 1886.
[‡] *Comptes Rendus*, vol. xc. (1880), 1195.

acid, which dissolves away the bulk of the zinc, leaving a rich
rhodium-zinc alloy, containing about 80 per cent. of rhodium.
When this alloy is heated *in vacuo* to a temperature of 400° C., a
slight explosion takes place, but no gas is evolved, and the alloy
is then insoluble in *aqua regia*, which dissolved it readily before
the elevation of temperature caused it to change its state.   We
are thus presented with another undoubted case of isomerism in
alloys, the unstable, soluble modification of the alloy being capable
of passing into the insoluble form by a comparatively slight eleva-
tion of temperature.

**Influence of Varying Quantities of Metals on Each
Other.**—There is, undoubtedly, a firm experimental basis for the
view to which Matthiessen was guided ,nearly thirty years ago, by
a study of the electrical resistance of solid alloys, that when metals
are united to form alloys, in many cases one metal, and sometimes
both metals, assume the allotropic state.   He showed, for instance,
that silver has a conductivity represented by 100, and that the addi-
tion of a small quantity of gold to the silver is attended with a rapid
fall in the conducting power.   The conductivity of pure copper
may be represented by the number 98, the addition of a small
portion of tin greatly diminishes the conductivity, as is proved by
the curves given on p. 68.   He pointed out that the amount of
tin is too small to admit of the possibility of a chemical compound
being formed, and from this fact and other evidence he concludes
that the passage to an allotropic state can alone explain the result.
In this connection the influence of small quantities of one element
on large masses of another may be referred to.   Submarine tele-
graphy will present us with the first case.   The commercial suc-
cess of a submarine cable is measured by the speed with which
messages can be sent through it, and upon this point we have the
testimony of Preece, who tells us that a cable made with the
copper of to-day, when the necessity for using pure copper is
recognised, will carry twice the number of messages that a similar
cable of less pure copper would in 1858, when the influence of im-
purities in increasing the electrical resistance of copper was not
understood.   A paper by Sir William Thomson [*] shows how im-
portant the purity of copper is, and how remarkable is the action
of the impurity.   It is safe to say that the presence of 0.1 per
cent. of bismuth in the copper would, by reducing its conduc-
tivity, be fatal to the commercial success of the cable.

The influence of small quantities of foreign matter is more
marked in the case of iron, but this question may be more con-
veniently studied in the following chapter.

[*] *Proc. Roy. Soc.*, vol. x. (1860), p. 301.

With regard to gold, the addition of 0.2 per cent. by weight of bismuth would, from the point of view of coinage, convert the gold into a useless material, which would crumble under the pressure exerted through the die. Instances of a similar nature might be multiplied indefinitely; it will, however, be sufficent to quote a statement of Sir Hussey Vivian, who says that $\frac{1}{1000}$ part of antimony will convert the best selected copper into the worst conceivable.

In order to explain facts such as these, it is necessary to ascertain what relations may subsist between the atoms of a mass of metal and the atoms of the added impurity. First, as regards the cohesion of a metal, this property may be investigated by the aid of heat, or by submitting the metal to mechanical stress; and, in a research to which the author* devoted much time, tenacity was selected as the property to be tested, with a view to ascertain the effect of the added matter upon a metal or alloy. Gold was chosen as the subject of the experiment for the following reasons :—First, it is a metal which it is possible to purify in a very high degree, it is not liable to oxidation, and the accuracy of the results is not affected by the presence of occluded gases. The purest gold has a tenacity of 7 tons to the square inch, and it elongates about 30 per cent. before breaking. Standard gold, which contains over 91 per cent. of gold, the alloying metal being copper, has a tensile strength of 18 tons to the square inch, and it stretches 34 per cent. before breaking; in fact, when an eminent engineer saw the results of these tests, he expressed an opinion as to the possibility of making a very good gun of standard gold, if the cost of the material were no object. When, however, a small quantity of certain metals, 0.01, 0.1, or 0.2 per cent. is added to the gold, the cohesion of the metal is reduced in a very remarkable way, as Hatchett showed to be the case in 1803. The author has tried the effect of adding to pure gold various metals and metalloids, introducing in each case 0.2 per cent. Some of these elements reduced the tenacity and extensibility of gold to a very low point, while others increased one or both of these properties. Since 1826, when Gmelin called attention to the relations between the atomic weights of elements which have similar properties, chemists have been actively engaged in establishing analogies between the properties of the elements and in arranging them systematically, and the result has been (mainly through the labours of Newlands, Mendeléeff, and Lothar Meyer) the promulgation of the Periodic law. This law states that the properties of

* *Proc. Roy. Soc.*, vol. xliii. (1888), p. 425; and *Phil. Trans.*, vol. clxxix. (1888), A., p. 339.

the elements are a periodic function of their atomic weights.
Lothar Meyer has gone further, and has shown that a remarkable
relation exists between the atomic volumes of the elements. Now,
however tiny the atoms may be, they must possess volume, and
the volume of each element will be peculiar to itself. The
space occupied by one atom cannot yet be measured absolutely,
but relative measurements may be obtained "by taking such
quantities of the elements as are proportional to their atomic
weights, and comparing the space occupied by these quantities."
The relative atomic volumes of the elements are found by dividing
the atomic weights of the elements by their specific gravities. The
atomic weight of gold is 196.2 ; $\dfrac{196.2}{19.3}$ = 10.2 the atomic volume,
or, expressed in the metric system, 196.2 grammes of gold would
occupy a space of 10.2 cubic centimetres. Lead, on the other hand,
would have the large atomic volume of 18.1 and potassium that of
45.1. The question now arises—Does the power to produce fra-
gility, which we have seen certain elements to possess, correspond
to any other of their properties by which they may be classi-
fied ? The facts represented in the Periodic law were, in 1869,
graphically represented by Lothar Meyer in his well-known curve
of the elements. By adopting atomic weights and atomic volumes
as co-ordinates he showed that the elements can be arranged in a
curve representing a series of loops, the highest points of which
are occupied by cæsium, rubidium, potassium, sodium, and lithium,
whilst the metals which are most useful for industrial purposes
occupy the lower portions of the several loops.

An examination of the results the author has obtained shows
that not a single metal or metalloid which occupies a position at
the base of either of the loops of Lothar Meyer's curve diminishes
the tenacity of gold. On the other hand, the fact is clearly
brought out that metals which render gold fragile all occupy
high positions on the curve. This would appear to show that
there is some relation between the influence exerted by the
metallic and other impurities and either their atomic weights or
their atomic volumes. It seems hardly probable that it is due to
atomic weight, because copper, with an atomic weight of 63.2,
has nearly the same influence on the tenacity of pure gold as
rhodium, with an atomic weight of 104, or as aluminium, the
atomic weight of which is 27.0. It will be evident from the fol-
lowing table, which embodies the results of the author's experi-
ments, that metals which diminish the tenacity and extensibility
of gold have high atomic volumes, while those which increase
those properties have either the same atomic volume as gold, or a

lower one. Further, silver has the same atomic volume as gold, 10.2, and its presence in small quantities has very little influence, one way or the other, on the tenacity or extensibility of gold.

Name of added Element.	Tensile Strength. Tons Per Sq. In.	Elongation, Per Cent. (on 3 inches).	Impurity Per Cent.	Atomic Volume of Impurity.
Potassium .	Less than 0.5	Not perceptible	Less than 0.2	45.1
Bismuth .	0.5 (about)	,,	0.210	20.9
Tellurium .	3.88	,,	0.186	20.5
Lead . .	4.17	4.9	0.240	18.0
Thallium .	6.21	8.6	0.193	17.2
Tin . .	6.21	12.3	0.196	16.2
Antimony .	6.0 (about)	qy.	0.203	17.9
Cadmium .	6.88	44.0	0.202	12.9
Silver . .	7.10	33.3	0.200	10.1
Palladium .	7.10	32.6	0.205	9.4
Zinc . .	7.54	28.4	0.205	9.1
Rhodium .	7.76	25.0	0.21 (about)	8.4
Manganese .	7.99	29.7	0.207	6.8
Indium .	7.99	26.5	0.290	15.3
Copper . .	8.22	43.5	0.193	7.0
Lithium . .	8.87	21.0	0.201	11.8
Aluminium .	8.87	25.5	0.186	10.6

These results are shown graphically in the diagram (Fig 31). The tenacity of pure gold is 7 tons per square inch.

INFLUENCE OF IMPURITIES ON GOLD.
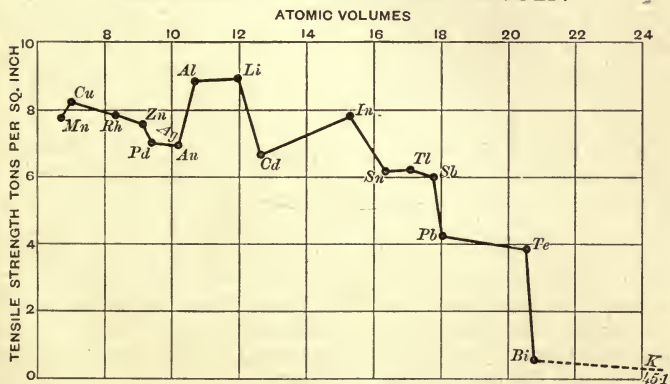
FIG. 31.

Several of the elements, the action of which has been examined, occupy abnormal positions, and any reason for this, except allotropy, remains to be explained. It is difficult to offer any mechanical theory to account for the action of the elements, but it may perhaps be well to give a rough indication of what may take place. If five spheres, representing atoms of a certain volume, are arranged so as to touch each other, it will be evident that the addition of an element with a small atomic volume may improve the tenacity by filling up the central space which would otherwise remain void; with such an arrangement of five atoms the addition of an element with the same atomic volume as themselves will tend to drive them slightly further asunder, and should, therefore, act prejudicially in a five-atom group, although it would exactly fill the space between a six-atom group, but in either case the insertion of a larger atomic volume than that of each member of the group, must tend to drive the members of either the five or six-atom group further asunder, and by so doing would diminish the cohesion of the mass. No doubt, in some cases, condensation takes place, and this may explain some of the abnormal results.

The curve representing the extensibility of the gold to which impurities have been added resembles that shown in Fig. 31. Cadmium exhibits marked irregularity in both curves; but the only striking difference between the two curves is caused by tellurium and bismuth, the former of which seems to be more prejudicial to the elongation of gold than to its tenacity. The influence of cadmium in increasing the extensibility is very remarkable. Aluminium, indium, and lithium occupy somewhat abnormal positions on the curve of tenacity, for they possess high atomic volumes, and yet they appear to increase the tenacity of gold, although they reduce its capability of being elongated. The author has some researches in progress, the results of which appear to enable this abnormal behaviour to be explained.

With regard to the applicability of these generalisations to other metals, it may be observed that recent investigations of Hadfield as to the physical properties of aluminium-steel, show that the part played by aluminium is almost identical with that of silicon, and this fact strongly supports the view above stated, for it is remarkable that the two bodies, aluminium and silicon, of which, when in a free state, the physical and mechanical properties are totally different, should nevertheless when they are alloyed with iron affect it in precisely the same way. Silicon and aluminium have almost the same atomic volume.

Questions of great industrial interest present themselves, espe-

cially in connection with iron. With regard to this metal, the evidence as to the action of other elements upon it tends in the same direction as in the case of gold, although the question is greatly complicated by the relations of iron to oxygen, and by the presence of occluded gases.

In the case of iron, it is difficult to say what property of the metal would be most affected by the added matter; but the author pointed out, in a lecture delivered at Newcastle in 1889, that the direct connection with the Periodic law will probably be traced by the effect of a given element in retarding or promoting the passage of ordinary iron to the allotropic state, a point of much importance, as the mechanical properties of the metal must depend on the atomic arrangement in the molecules. Osmond* has since satisfied himself of the accuracy of this view. He considers, as will be shown in the following chapter, that there are two modifications of iron; the a, or soft variety, which exists in pure iron at temperatures below 855° C., and in iron containing certain other elements, if it has been cooled slowly. There is also the β, or hard modification, which exists at high temperatures or if certain elements be present, in iron which has been rapidly cooled from temperatures above 855° C., or if the iron has been obtained by electrolysis.

The foreign elements, whose action on the critical points of iron has been studied by Osmond experimentally, are ranged as follows in two columns in the order of their atomic volumes :—

I.				II.			
Carbon .	.	.	. 3.6	Chromium .	.	.	7.7
Boron .	.	.	. 4.1	Tungsten .	.	.	9.6
Nickel .	.	.	. 6.7	Silicon .	.	.	11.2
Manganese .	.	.	. 6.9	Arsenic .	.	.	13.2
Copper .	.	.	. 7.1	Phosphorus	.	.	13.5
				Sulphur .	.	.	15.7

The elements in column I., whose atomic volumes are smaller than that of iron (7.2), delay during cooling the change of the β, or hard allotropic variety of iron, into the a, or soft variety, as well as that of hardening carbon into carbide carbon. For these two reasons they tend to increase, with equal rates of cooling, the proportion of β iron that is present in the cooled iron or steel, and consequently the hardness of the metal. Indeed, their presence is equivalent to a more or less energetic hardening. To these elements hydrogen may be added. As is well known, this element renders electro-deposited iron hard and brittle; perhaps

* *Comptes Rendus*, vol. cx. (1890), p. 346.

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it contains the metal, Graham's *hydrogenium*, for hydrogen gas does not appear to have a marked influence on the critical temperature.

The elements in column II., whose atomic volumes are greater than that of iron, tend to raise or at least maintain near its normal position, during cooling, the temperature at which the change of β to a iron takes place. Further, they render the inverse change during heating more or less incomplete, and usually hasten the change of "hardening carbon" to "carbide carbon." Thus, they maintain the iron in the a state at high temperatures, and must therefore have the same effect in the cooled metal. In this way, they would act on iron as annealing does, rendering it soft and malleable, did not their individual properties, or those of their compounds, often intervene and partially mask this natural consequence of their presence.

Thus, foreign elements alloyed with iron either hasten or delay the passage of the iron, during cooling, to an allotropic state, and render the change more or less incomplete, according to whether the atomic volume of the added impurity is less or greater than that of iron. In other words, foreign elements of low atomic volume tend to make iron itself assume or retain the particular molecular form that possesses the lowest atomic volume, whilst elements with large atomic volume produce the inverse effect.

While obeying the general law, carbon possesses on its own account the property of undergoing, at a certain critical temperature, a change, the nature of which is still disputable, although its existence is acknowledged. This property gives carbon a place by itself in the metallurgy of iron.

Whatever may ultimately prove to be the true nature of the molecular change which accompanies the thermal treatment of iron and determines its mechanical properties, there is little doubt but that there is a close relation between the action of foreign elements and their atomic volume. Few metallurgical questions are of greater interest at the present time than those which relate to the molecular structure of metals, and Osmond has shown it to be very probable that the presence of a small quantity of a foreign metal may cause a mass of another metal to pass into an allotropic state. In relation to iron and steel the problems are of great industrial importance, and it is fortunate that we appear to be nearing the discovery of a law in accordance with which *all* metallic masses are influenced by "traces."

The effect of comparatively large quantities of certain elements on the mechanical properties of iron has already been stated in

the preceding chapter, and the subject will be again referred to in Chapter IV.

Colour of Alloys.—It will now be well to examine some effects of uniting metals by fusing them together, and also to consider the direct influence of a minute quantity of one metal in changing the mass of another in which it is hidden, causing it to behave in a different way in relation to light, and consequently to possess a colour different from that which is natural to it. The added metal may so change the chemical nature of the metallic mass that varied effects of colour may be produced by the action of certain "pickling" solutions. This portion of the subject is so large that reference can only be made to certain prominent facts.*

First, with reference to the colour produced by the union of metals. Take, for example, a mass of red copper, and one of grey antimony; the union of the two by fusion produces a beautiful violet alloy when the proportions are so arranged that there is 51 per cent. of copper, and 49 per cent. of antimony in the mixture. This alloy was well-known to the early chemists, but, unfortunately, it is brittle and difficult to work, so that its beautiful colour can hardly be utilised in art. The addition of a small quantity of tin to copper hardens it, and converts it, from a physical and mechanical point of view, into a different metal. The addition of zinc and a certain amount of lead to tin and copper, confers upon the metal copper the property of receiving, when exposed to the atmosphere, varying shades of deep velvety brown, characteristic of the bronze which has from remote antiquity been used for artistic purposes. But by far the most interesting copper-alloys, from the point of view of colour, are those produced by its union with zinc, namely brass. Their preparation demands much care in the selection of the materials.

The colouring power of metals in alloys is very variable. Ledebur† arranges the principal metals in the following order:—

Tin.	Zinc.
Nickel.	Lead.
Aluminium.	Platinum
Manganese.	Silver.
Iron.	Gold.
Copper.	

Each metal in this series has a greater decolorising action than the metal following it. Thus, the colour of the last members is

* A list of books and papers dealing with the colours of metals and alloys, and with the production of coloured patina is given by Professor Ledebur in his work *Die Metallverarbeitung*, 1882, p. 285.

† *Die Legierungen*, Berlin, 1890, p. 47.

concealed by comparatively small amounts of the first members.
A good example is afforded by the alloy used for the continental
nickel coinage. This consists of three parts of red copper with
only one part of white nickel. The comparatively small quantity
of nickel is, however, sufficient to completely hide the red colour
of the copper.

Of the very varied series of alloys the Japanese employ for art
metal-work, the following may be considered the most important
and typical. The first is called *shaku-do*, it contains, as will
be seen from Analyses Nos. I. and II.,* in addition to about 95
per cent. of copper, as much as 4 per cent. of gold. The quantity

						I.		II.
Copper	.	.	.	.	.	94.50	...	95.77
Silver	.	.	.	.	.	1.55	...	0.08
Gold .	.	.	.	.	.	3.73	...	4.16
Lead .	.	.	.	.	.	0.11	...	—
Iron and Arsenic		.	.	.		traces	...	—
Totals .	.	.	.	.		99.89	...	100.01

of gold is, however, very variable, some specimens which have
been analysed containing only 1.5 per cent. of the precious metal.

Another important alloy is called *shibu-ichi*. Analyses of this
alloy gave:—

						III.		IV.
Copper	.	.	.	.	.	67.31	...	51.10
Silver	.	.	.	.	.	32.07	...	48.93
Gold .	.	.	.	.	.	traces	...	0.12
Iron .	.	.	.	.	.	0.52	...	—
						99.90		100.15

There are numerous varieties of it, but in both these alloys, *shaku-
do* and *shibu-ichi*, the point of interest is that the precious metals
are, as it were, sacrificed in order to produce definite results, gold
and silver, when used pure, being employed very sparingly to
heighten the general effect. In the case of the *shaku-do*, we shall
see presently that the gold appears to enable the metal to receive
a beautiful, rich purple coat or patina, as it is called, when treated
with certain pickling solutions; while *shibu-ichi* possesses a pecu-
liar silver-grey tint of its own, which, under ordinary atmospheric
influences, becomes very beautiful, and to which the Japanese
artists are very partial. These are the principal alloys, but there
are several varieties of them, as well as combinations of *shaku-do*
and *shibu-ichi* in various proportions, as, for instance, in the case

* Analyses Nos. I. and III. are by Mr. Gowland, of the Imperial Japanese
Mint at Osaka ; Nos. II. and IV., by Prof. Kalischer, *Dingl. Polyt. Journ.*,
vol. ccxv. p. 93.

of *kiu-shibu-ichi,* the composition of which would correspond to one part of *shaku-do,* rich in gold, and two parts of *shibu-ichi,* rich in silver.

Now, as to the action of pickling solutions.

The Japanese art metal-workers are far ahead of their European brothers in the use of such solutions.

The South Kensington Museum contains a very valuable series of fifty-seven oblong plates, some plain and others richly ornamented, which were specially prepared as samples of the various metals and alloys used by the Japanese. The Geological Museum in Jermyn Street has a smaller, but more instructive, series of twenty-four plates, presented by an eminent metallurgist, the late Mr. Hochstätter-Godfrey. From descriptions accompanying the latter, and from information gathered from certain Japanese artificers, it would appear that there are three solutions generally in use. They are made up respectively in the following proportions, and are used boiling :—

	I.		II.		III.
Verdigris . . .	438 grains	...	87 grains	...	220 grains
Sulphate of copper .	292 ,,	...	437 ,,	...	540 ,,
Nitre	—	...	87 ,,	...	—
Common salt . .	—	...	146 ,,	...	—
Sulphur . . .	—	...	233 ,,	...	—
Water . . .	1 gallon	...	—	...	1 gallon
Vinegar . . .	—	...	1 gallon	...	5 fluid drachms

The most widely employed is No. I. When boiled in No. III. solution pure copper will turn a brownish-red, and *shaku-do,* which contains a little gold, becomes purple. Thus, it is possible to appreciate the effect of small quantities of metallic impurity as affecting the colour resulting from the action of the pickle. Copper containing a small quantity of antimony gives a shade very different from that resulting from the pickling of pure copper. But the copper produced in Japan is often the result of smelting complex ores, and the methods of purification are not so perfectly understood as in the West. The result is that the so-called "antimony" of the Japanese art metal-workers, which is present in the variety of copper called *kuromi,* is really a complex mixture containing tin, cobalt, and many other metals, so that a metal-worker has an infinite series of materials at command with which to secure any particular shade; and these are used with much judgment, although the scientific reasons for the adoption of any particular sample may be hidden from him. It is strictly accurate to say that each particular shade of colour is the result of minute quantities of metallic impurity.

There is one other material to the production of which art-

workmen in this country will, it is to be hoped, soon direct their
attention, as the possibilities of its applications are endless.   It is
called in Japanese *mokumê*, which signifies "wood grain."   It
is now very rare, even in Japan, but formerly the best specimens
appear to have been made in Nagoya by retainers of the Daimio
of Owari.

This diagram (Fig. 32) shows the method of manufacture.
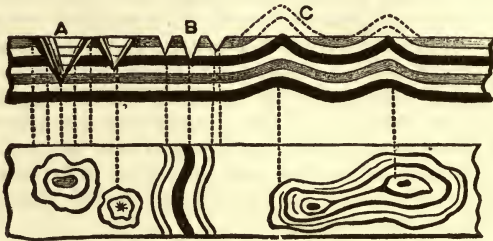
FIG. 32.

Take thin sheets of gold, silver, *shibu-ichi*, *shaku-do*, and *kuromi*,
and solder* them together, layer upon layer, care being taken
that the metals which will present diversity of colour come
together.   Then drill conical holes of varying depth (A) in the
mass, or devices in trench-like cuts of V section (B), and then
hammer the mass until the holes disappear; the holes will thus
be replaced by banded circles and the trenches by banded lines.
Similar effects may be produced by taking the soldered layers of
the alloy, and, by the aid of blunted tools, making depressions on
the back of the mass, so as to produce prominences on the front
(C).   These prominences are filed down until the sheet is again
flat; the banded alloys will then appear on the surface in com-
plicated sections, and a very remarkable effect is produced, espe-
cially when the colours of the alloys are developed by suitable
"pickles."   In this way any device may be produced.   In princi-
ple the method is the same as that which produces the damascen-
ing of a sword-blade or gun-barrel, and depends on the fact that,
under certain conditions, metals behave like viscous solids, and as
truly "flow" as pitch or honey does.   In the case of *mokumê* the
art-workman has a wide range of tinted metals at command.

The Oriental art metal-workers often blend metals and alloys
of different colours by pouring them together at a temperature
near the solidifying point of the more infusible of the metals and

* The following solder was found to answer well :—Silver, 55.5 ; zinc,
26.0 ; copper, 18.5.

alloys to be associated. In this way, by pouring the comparatively fusible grey silver-copper alloy on to fused copper which is just at the point of " setting," the metals unite, but do not thoroughly mix, and a mottled alloy is produced. The Japanese use such alloys in almost every good piece of metal-work.

Alloys of Industrial Importance.—The following tables indicate the composition of some of the more important alloys, which have been selected in order to give the student an idea of the way in which for industrial use metals are associated. The list is, however, necessarily a limited one, and as the properties of an alloy may be greatly modified by a slight variation in its composition, reference should be made for fuller information to the standard treatises, of which a list is appended :—R. H. Thurston, Report on a Preliminary Investigation of the Properties of the Copper-Tin Alloys, Washington, 1879; A. Guettier, *Guide Pratique des Alliages Métalliques*, Paris, 1865; Roberts-Austen, The Alloys used for Coinage (Cantor Lectures, Society of Arts), 1884; A. Ledebur, *Metallverarbeitung*, Brunswick, 1882; Brannt, Krupp, and Wildberger, " The Metallic Alloys," Philadelphia, 1889.

Of recent years, bronzes have come largely into use, in which a minute quantity of a foreign element has been added. The oldest of these bronzes, phosphor bronze, invented by Dr. Kuntzel, is now in general use for the manufacture of machine parts. The presence of phosphorus usually renders bronze brittle, but when added only in sufficient quantity to reduce the oxide contained in the metal, it imparts hardness to the alloy without brittleness. The phosphorus varies up to 2 to 4 per cent., and it has been asserted that the presence of phosphorus is useful in enabling bronzes to be made richer in tin than would otherwise be the case. Manganese bronze has a tensile strength of 29 tons per square inch (annealed rolled rods) to 39 tons (cold rolled). Owing to its non-liability to corrosion it is well adapted for the manufacture of propellers. Silicon bronze is well adapted for telegraphic purposes. The first sample, of which an analysis is given, (telegraph wire) had a tensile strength of $28\frac{1}{2}$ tons per square inch, and a conductivity of 98; the second (telephone wire) a tensile strength of $52\frac{3}{4}$ tons per square inch and a conductivity of 43; the tensile strength of copper being 17 tons per square inch, and its conductivity 100. Delta metal, is a yellow alloy, with a specific gravity of 8.4, and a melting point of 1800° F. Cast in sand it has a tensile strength of 2 tons per square inch, and when hammered or rolled cold it has a tensile strength of 40 tons per square inch.

COPPER ALLOYS.

	Copper.	Zinc.	Tin.	Other Constituents.	Uses and Remarks.
Brass	63 to 72	27 to 34	—		Typical brass.
„	70.29	29.26	0.17	Pb 0.28	Wire. Always brittle if Pb reaches 2 per cent. Tin may vary from 0.1 to 0.5.
Muntz's metal	60 to 62	38 to 40	—		Ships' sheathing.
Sterro metal	55.33	41.80	—	Fe 4.66	Austrian, for ordnance.
Aich's metal	60.00	38.12	—	Fe 1.5	English, Sterro and Aich's metals are remarkable for their great strength, 85,680 lbs. per sq. in.
Mosaic gold	65.00	35.00			
Pinchbeck	83.33	16.76			
Mannheim gold	80 to 88	20 to 12			
Gun metal	91.00	—	9.00		For ordnance.
Bell metal	76.50	—	23.50		
„	75.8	—	25.2		"Big Ben," Westminster.
Speculum metal	70.24	trace	29.11	Fe, Ni, traces	Telescope mirror, Birr Castle, Ireland.
Bronze	66.6	—	33.4		Ross, Atomic proportion.
„	68.1	—	31.9		British bronze coinage.
„	95.0	—	4.0		Japanese art bronze.
Bronze	82.7	1.0	4.7	Pb 9.9	„ „
„	71.4	1.8	5.9	Pb 16.3	Chinese art bronze.
„	74.0	6.0	1.0	Pb 15.0	Prehistoric sword (Ireland).
„	83.5	10.0	5.15	Pb 8.3; Fe 3	Egyptian chisel.
„	94.0	—	5.90	Fe 0.1	Attic coin.
„	88.46	—	10.04	Pb 1.5	Bearings for heavy axles.
„	80 to 90	7.0	18 to 12		Tensile strength, 96,434 lbs. per sq. in.
Aluminium bronze	90.00	—	—	Al 10.0	
Phosphor bronze	82.20	—	12.95	Pb 4.28; P 0.52	Yellowish grey.
Manganese bronze	83.45	—	—	Mn 13.48; Fe 1.24; Co 0.11	Yellowish white.
„	81.03	—	—	Mn 16.86; Fe 1.67; Co 0.06	
Silicon bronze	99.94	—	0.03	Fe, Si trace	Telegraph wire.
„	97.12	1.12	1.14	Fe trace	Telephone „
Delta metal	55.10	43.47	—	Fe 1.08; Pb 0.37; P 0.10	

COPPER NICKEL ALLOYS.

	Cu.	Ni.	Zn.	Other Constituents.	Remarks.
Nickel coins .	75.0	25.0			
Packfong . .	43.8	15.6	40.6	—	Chinese alloy.
English "German silver".	61.3	19.1	19.1		
Berlin argentan	52.0	26.0	22.0		
Sheffield German silver .	57.0	24.0	19.0		
Platinoid . .	—	—	—	A German silver, with 1 to 2 per cent. of tungsten.	High electrical resistance, not changing with temperature.
Ancient coin .	77.58	20.0	—	Fe 1.04; Co 0.54 ; Sn 0.03.	Second century, B.C.

TIN ALLOYS.

	Sn.	Sb.	Cu.	Other Constituents.	Remarks.
Britannia metal	90.62	7.81	1.46		Birmingham sheet.
White metal .	82.00	12.00	6.00		For bearings. The composition of white metal is very variable.
,, .	53.00	10.60	2.40	Pb 33.0 ; Zn 1.0.	
Ashberry metal	77.8	19.4	—	Zn 2.8.	
Pewter . . .	80.0	—	—	Pb 20.0.	
Solder, fine . .	66.6	—	—	Pb 33.3	The melting point increases with the proportion of lead.
,, tin . .	50.0	—	—	Pb 50.0.	
,, plumbers'	33.3	—	—	Pb 66.6	Authorised by the Plumbers' Company.

LEAD ALLOYS.

—	Pb.	Sb.	Sn.	Other Constituents.	Remarks.
Type metal . .	70.0	18.0	10.0	Cu 2.0.	
„ . .	82.0	14.8	3.2	—	For stereotyping.
Bearing metal .	84.0	16.0	—	—	For slowly revolving axles.
„ .	60.0	20.0	20.0		
Shot metal . .	99.6	—	—	As 0.2 to 0.35	

ZINC ALLOYS.

—	Zn.	Sn.	Cu.	Other Constituents.	Remarks.
Antifriction metal . . .	85.0	—	5.0	Sb 10.0	For bearings.
Babbitt's metal	69.0	19.0	4.0	Sb 3.0 ; Pb 5.0.	(Ledebur).

BISMUTH ALLOYS (FUSIBLE METAL).

—	Bi.	Pb.	Sn.	Cd.	Melting Point.
					° C.
Newton's alloy . .	50.0	31.25	18.75	—	95
Rose's „ . .	50.0	28.10	24.64	—	100
Darcet's „ . .	50.0	25.00	25.00	—	93
Wood's „ . .	50.0	24.00	14.00	12.00	66—71
Lipowitz's „ . .	50.0	27.00	13.00	10.00	60

ALLOYS FOR COINAGE.

—	Au.	Cu.	Ag.	Other Constituents.	Remarks.
Gold coin . .	91.66	8.33	—	—	British standard.
„ . .	90.0	10.0	—	—	"Latin Union" and American.
„ . .	1.33	82.73	15.93	—	Roman, Septimus Severus, 265 A.D.
Silver coin . .	0.1	7.1	92.5	Pb 0.2	Roman, B.C. 31, almost same as British silver coin.
Gold coin . .	40.35	19.63	40.02	—	Early British, B.C. 50.
Silver coin . .	—	7.5	92.5	—	British standard.

CHAPTER IV.

THE THERMAL TREATMENT OF METALS.

Annealing, Hardening, and Tempering.—The mechanical properties of metals are often, in a great measure, dependent on the thermal treatment to which they have been subjected. The effect of heat on zinc has already been noticed. There can be no question that the application of heat to a metal may produce a remarkable molecular change in its structure, the nature of the change depending on that of the metal or alloy, and on the treatment it has undergone. It will be well, therefore, to consider carefully what happens when metals are submitted to the three principal operations involving thermal treatment, which are known respectively as **annealing, hardening,** and **tempering.** Usually all three are intimately related. Annealing may be defined as the release of strain in metals which may itself have been produced by mechanical treatment, such as hammering, rolling, or wire-drawing, or by either rapid or slow cooling from a more or less elevated temperature. As an example of the former, it may be mentioned that metals and alloys which have been rendered excessively hard by rolling are heated usually to bright redness and allowed to cool slowly. In the case of copper, it does not appear to be important whether the cooling is slow or rapid, and in recent years much experimental evidence has been accumulated, which tends to show that in the case of certain metals which have been hardened, a more or less prolonged exposure to a low temperature under 100° will sensibly anneal them. On the other hand, the rapidity with which the cooling is effected is very important. Bronze containing about 20 per cent. of tin* is rendered very malleable by rapid cooling, and so are certain alloys of iron with more than 7 per cent. of manganese. It is, however, in the case of iron and steel that thermal treatment is especially important.

Steel, it must be remembered, is modified iron. The name iron is, in fact, a comprehensive one, for the mechanical behaviour of the metal is so singularly changed by influences acting from within

* Riche, *Ann. de Chim. et de Phys.*, vol. xxx. (1873), p. 417.

and without its mass as to lead many to think, with Paracelsus, that iron and steel must be two distinct metals, their properties being so different. Pure iron may be prepared in a form pliable and soft as copper, steel can readily be made sufficiently hard to scratch glass; and notwithstanding this extraordinary variance in the physical properties of iron and certain kinds of steel, the chemical difference between them is comparatively very small, and would hardly secure attention if it were not for the importance of the results to which it gives rise. It is necessary to consider the nature of the transformations which iron can sustain, and to see how it differs from steel, of which an old writer has said:* " Its most useful and advantageous property is that of becoming extremely hard when ignited and plunged in cold water, the hardness produced being greater in proportion as the steel is hotter and the water colder. The colours which appear on the surface of steel slowly heated direct the artist in *tempering* or reducing the hardness of steel to any determinate standard." There is still so much confusion between the words " temper," " tempering," and " hardening," in the writings of even very eminent authorities, that it is well to keep these old definitions carefully in mind. **Hardening** is the result of rapidly cooling a strongly heated mass of steel. **Tempering** consists in re-heating the hardened steel to a temperature far short of that to which it was raised before hardening ; this heating may or may not be followed by rapid cooling. **Annealing,** as applied to steel, consists in heating the mass to a temperature higher than that used for tempering, and allowing it to cool slowly.

This may be shown experimentally in the following manner :— Three strips of steel of identical quality may be taken. It can be shown by bending one that it is soft ; but if it is heated to redness and plunged in cold water it will become hard and will break on any attempt to bend it. The second strip may, after heating and rapid cooling, be again heated to about the melting point of lead, when it will bend readily, but will spring back to a straight line when the bending force is removed. The third piece may be softened by being cooled slowly from a bright red heat, and this will bend easily and will remain distorted.

The metal has been singularly altered in its properties by comparatively simple treatment, and all these changes, it must be remembered, have been produced in a solid metal to which nothing has been added, and from which nothing material has been taken.

* *The First Principles of Chemistry,* by W. Nicholson, London, 1760, p. 312.

The theory of the operation, described above, has been laboriously built up, and its consideration introduces many questions of great interest, both in the history of science and in our knowledge of molecular physics.

History.—First, as regards the history of the subject. The knowledge that steel might be hardened must have been derived from remote antiquity. Copper hardened with tin was its only predecessor, and it continued to be used very long after it was known that steel might be hardened. It would, moreover, appear that a desire to appreciate the difficulties of a people, to whom cutting instruments of hard steel were unknown, seems to have induced experimenters in quite recent times to fashion implements of bronze, and a trustworthy authority states that " Sir Francis Chantry formed an alloy containing about 16 parts of copper, $2\frac{1}{2}$ of zinc, and $2\frac{1}{2}$ of tin, of which he had a razor made, and even shaved with it." * The Greek alchemical MSS., which have been so carefully examined by M. Berthelot, give various receipts, from which it is evident that in the early days the nature of the quenching fluid was considered to be all important. There were certain rivers the waters of which were supposed to be specially efficacious. Pliny, who says that the difference between waters of various rivers can be recognised by workers in steel, also knew that oil might be used with advantage for hardening certain varieties of the metal. It is sad to think how many of the old recipes for hardening and tempering have been lost. Theophilus, writing in the eleventh century, gives very quaint instructions in the art of hardening steel. The belief, however, in the efficacy of curious nostrums and solutions for hardening steel could hardly have been firmer in the third century B.C. than in the sixteenth of our era. Pure cold water is now usually employed for hardening, but it was far too simple a material for many a sixteenth-century artificer to employ, as is shown by the quaint recipes contained in one of the earliest books of trade secrets, which, by its title, showed the existence of the belief that the " right use of alchemy " was to bring chemical knowledge to bear upon industry. The earliest edition was published in 1531,† and the first English translation ‡ in 1583, from which the following extracts may be of interest. " Take snayles, and first drawn water of a red die of which water being taken

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* *Engines of War*, by H. Wilkinson, 1841, p. 194.

† *Rechter Gebrauch d. Alchimei*, 1531. There were many English editions.

‡ " A profitable boke declaring dyuers approoued remedies," &c., London, 1583. See Prof. Ferguson's learned paper " On some Early Treatises on Technological Chemistry," *Phil. Soc. Glasgow*, Jan. 1886.

in the two first monthes of haruest when it raynes," boil it with the snails, " then heate your iron red hot and quench it therein, and it shall be hard as steele." " Ye may do the like with the blood of a man of xxx years of age and of a sanguine complexion, being a merry nature and pleasant . . . . distilled in the middst of May." This may seem trivial enough, but the belief in the efficacy of such solutions survived into the present century, for in a work published in 1810 the artist is prettily directed[*] " to take the root of blue lilies, infuse it in wine and quench the steel in it," and the steel will be hard ; on the other hand, he is told that if he "takes the juice or water of common beans and quenches iron or steel in it, it will be soft as lead." As must always be the case when the practice of an art is purely empyrical, such procedure was often fantastic, but it is by no means obsolete, for probably at the present day there is hardly a workshop in which some artificer could not be found with a claim to possess a quaint nostrum for hardening steel. Even the use of absurdly compounded baths was supported by theoretical views. Otto Tachen,[†] for instance, writing of steel in about the year 1666, says that steel when it is " quenched in water acquires strength, because the light alcaly in the water is a true comforter of the light acid in the iron, and cutlers do strengthen it with the alcaly of animals," hence the use of snails. Again, Lemery[‡] explains in much the same way the production of steel by heating iron in the presence of horns of animals.

These points have been dwelt upon in order to bring out clearly the fact that the early workers attached great importance to the nature of the fluid in which hot steel was quenched, and they were right, though their theories may have been wrong. The degree of rapidity with which heat is abstracted from the steel during the operation of hardening is as important at the present day as it ever was. Roughly speaking, if steel has to be made glass hard, ice-cold water, brine, or mercury is used ; if it has only to be made slightly hard, hot water or oil may be employed ;- while, as Thomas Gill[§] suggested in 1818, both " hardening " and " tempering " may be united in a single operation by plunging the hot metal in a bath of molten lead or other suitable metal, which will, of course, abstract the heat more slowly.

The use of lead and of other metals in hardening steel has,

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[*] *The Laboratory ; or, School of Arts*, sixth edition, 1799, p. 228. There is a later edition of 1810.

[†] *Key to the Ancient Hippocratical Learning*, London, 1690, p. 68.

[‡] *A Course of Chymistry*, second edition, 1686, p. 131.

[§] Thomson's *Annals of Philosophy*, vol. xii. (1818), p. 58.

however, long been known. Réaumur * described in 1722 a method of hardening the points of tools by forcing them when hot into *solid* tin and lead, and he hints at the use of solid masses of gold, silver, and copper as cooling metals. This old work blends curiously into the new, for the cold metallic surfaces suggested by Clémendot † doubtless play an important part in his process of hardening by compression; whilst another process, that of hardening by water spray, of which much has been heard recently in connection with the manufacture of artillery, is at least a century old.‡ In recent years Jarolimek § has studied the conditions under which the process may be practised with success, the vaporisation of the liquid appearing to be all-important.

Probably the earliest reference to the use of mercury as a cooling fluid is that made by Réaumur; but in no direction has the modern development of hardening processes been more important than in connection with the use of baths, in which the fluid, being a molten metal, is not readily vaporised. Lisbonne ‖ has shown what remarkable results as regards resistance to penetration have attended the adoption of the process of hardening armour plates in lead baths, which, as Éverard ¶ shows, must be capacious and not heated above the melting point of lead, his experiments leading to the conclusion that armour-plates so quenched in lead are very difficult to penetrate, and present great resistance to fracture.

Internal Constitution of Steel.—The development of theories relating to the internal constitution of steel must now be traced. The advent of the Phlogistic School with the teaching of Becher and Stahl led to the view that iron gained phlogiston during its conversion into steel. By Phlogiston the early chemists really meant *energy*, but to them phlogiston was represented to be a kind of soul possessed by all metals, which they could lose by burning and regain by the process they called " revivication," " Hardness [in metals] is caused by the jeiunenesse of the spirit and their imparity with the tangible parts," said Francis Bacon ;** while, according to Stahl,†† steel was merely iron possessing, in

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* *L'art de convertir le fer forgé en acier*, Paris, 1722, p. 351.
† *Comptes Rendus*, vol. xciv. (1882), p. 703.
‡ Guyton de Morveau, *Encyc. Méthodique*, Paris, 1786, p. 436.
§ *Oester. Zeit. für Berg. und Hüttenwesen*, 1876, p. 70.
‖ *Génie civil*, vol. xiii. (1888), p. 22.
¶ Paper read at the International Congress of Mining and Metallurgy, Paris, 1889.
** *Sylva Sylvarum*, second edition, 1628, p. 215.
†† *Fundamenta Chemiæ*, part iii., p. 451, quoted by Guyton de Morveau in the article " Acier," *Encyc. Méthodique*, p. 421, Paris, 1786.

virtue of its phlogiston, the characteristics of a metal in a higher degree, and this view prevails in the writings of Henckel, Newmann, Cramer, Gellert, Rinman and Macquer. This opinion survived with wonderful persistence, but it did not influence the teaching of Réaumur,* who, in 1722, was the first to suggest a physical theory which has been in any way justified by modern research. He assumed that when steel was heated "sulphurs and salts" were driven out from the molecules, which he represents diagrammatically, into the interstitial space between them. The quenching of the steel and its sudden cooling prevented the sulphurs and salts from returning into the molecules, which were thus firmly cemented by the matter between them, and hard rigid steel was the result. In tempering, the sulphurs and salts partially returned into the molecules, and the metal became proportionately soft. He used the Torricellian vacuum to demonstrate that the hardening of steel is not accompanied by the evolution of gas, and he concluded that "since the hardening of steel is neither due to the intervention of a new substance nor to the expulsion of air, it only remains to seek its cause in the changes occurring in its structure." Notwithstanding this, the Phlogistic School were not daunted, and this leads directly to the work of Torbern Bergman, the great professor at the University of Upsala, who, in 1781, showed † that steel mainly differs from iron by containing about $\frac{2}{10}$ per cent. of plumbago, while iron does not. Read in connection with modern research his work seems wonderfully advanced. He was so forcibly impressed by the fact that the great difference in the mechanical properties of different specimens of iron is due to the presence of small quantities of impurity, and that the properties of iron do not vary, as he says, unless by chance the iron has gathered foreign matter, " *nisi forte peregrinum paullo uberius inhœreat metallum,*" in which sentence there is even the dawn of the view that, under the influence of small quantities of foreign matter, iron is, as he calls it, polymorphous, and plays the part of many metals. " *Adeo ut jure dici queat, polymorphum ferrum plurium simul metallorum vices sustinere.*"‡ Unfortunately he confounded the plumbago or carbon he had isolated with phlogiston, as did Rinman in 1782, which was strange, because in 1774 the latter physicist had shown that a drop of nitric acid simply whitens wrought iron, but leaves a black stain on steel. Bergman tenaciously held to the phlogistic

* *L'art de convertir le fer forgé en acier,* Paris, 1722, p. 321 *et seq.*
† *Opuscula Physica et Chemica,* vol. iii.; *De Analysi Ferri,* Upsala, 1783, a dissertation delivered June 9, 1781.
‡ *De Analysi Ferri,* p. 4.

theory in relation to steel; it was inevitable that he should. The true nature of oxidation had been explained; no wonder that the defenders of the phlogistic theory should seek to support their case by appealing to the subtle and obscure changes produced in iron by such apparently slight causes. Bergman's view was, however, combated by Vandermonde, Berthollet and Monge,* who showed in a report communicated to the *Académie des Sciences* in 1786 that the difference between the main varieties of iron is determined by variation in the amount of carbon, and further that steel must contain a certain quantity of carbon in order that it might possess definite qualities. Bergman died in 1784, and the report to which reference has been made is full of respect for " this grand chemist," as its authors call him, " whom science had lost too soon."

Kirwan's essay on Phlogiston,† in which Bergman's views were defended, elicited a reply from Lavoisier himself, and brought down the French school in strength to contest almost the last position occupied by the believers in phlogiston.‡

Bergman's was almost the first calorimetric work, and it is impossible to read it without feeling that in paying the just tribute to Lavoisier's genius Bergman has been overlooked. He desired to ascertain whether pure iron, steel, and cast iron contain the same amount of heat. He therefore attacks the materials with a solvent, and notes the heat evolved. He says the solvent breaks up the assemblage of the aggregation of molecules and forms other unions. If the new body demands more heat than the body which has been disunited then the thermometer falls. If, on the other hand, the degree of heat required is less, the environment will be heated, which will result in the rise of the thermometer. In modern language, when a chemical compound is formed, heat is evolved and energy is lost, but if one substance, say a metal, simply dissolves another, the solution is attended with absorption of heat, and the product when attacked by a suitable solvent should evolve practically the same amount of heat, but certainly not less than would be evolved by the individual metals present in solution.§ This is specially interesting from its relation to the calorimetric work of Lavoisier and Laplace in 1780 and of Lavoisier in 1782, which led him to explain the

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* *Histoire de l' Académie Royale des Sciences*, 1786 (printed 1788), p. 132.

† *Essay on Phlogiston and the Constitution of Acids*, 1787, p. 134.

‡ *Essai sur le Phlogistique traduit de l'Anglois de M. Kirwan, avec des Notes de MM. de Morveau, Lavoisier, de la Place, Monge, Berthollet, et de Fourcroy*. Paris, 1788.

§ See French translation of Bergman's work, Paris, 1783, p. 72.

nature of oxidation, and to show that a metal could be as truly calcined or oxidised by the action of a solution as by the action of air at an elevated temperature. Now that the importance of thermal chemistry is beginning to be recognised in relation to industrial chemistry and metallurgy, it is to be hoped that Bergman's merits will be more fully considered. The main point is that he taught that the difference between iron and steel consists in the $\frac{2}{10}$ths to $1\frac{1}{2}$ per cent. of carbon which steel contains.

It was only natural that Black, writing in 1796, should have attributed the hardening of steel to the "extrication of latent heat," "the abatement of the hardness by the temper" being due, he says, "to the restoration of a part of that heat."* Black failed to see that the work of Bergman had entirely changed the situation. The next step was made in France. It was considered necessary to establish the fact that carbon is really the element which gives steel its characteristic properties, and with this object in view, Clouet,† in 1798, melted a little

IRON CRUCIBLE   DIAMOND

PLAN

FIG. 33.

crucible of iron, weighing 57.8 grammes, containing a diamond, weighing 0.907 gramme, and obtained a fused mass of steel. Fig. 33 shows a plan of the iron crucible and diamond from the drawing in Guyton de Morveau's paper.
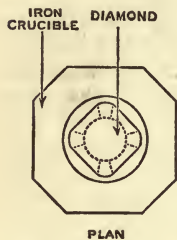
His experiment was repeated by many observers, but the results were open to doubt from the fact that furnace gases could always obtain access to the iron and might, as well as the diamond, have yielded carbon to the iron. The carbon might have been presented to the iron in the form of a gas capable of yielding carbon, and this element would as surely have found its way into the steel.

Margueritte ‡, for instance, in 1865, repeated Clouet's experiment, and showed that although carburisation can be effected by simple contact of iron and carbon, it is nevertheless true that in the ordinary process of cementation the gas carbonic oxide plays an important part, which had until then been overlooked. The discovery of Graham,§ in 1866, of the occlusion of carbonic oxide by iron, gave additional support to this theory.

* *Lectures on the Elements of Chemistry*, vol. ii. (1803), p. 505.
† Experiment described by Guyton de Morveau, *Ann. de Chim.*, vol. xxxi. (1799), p. 328.
‡ "*Sur l'aciération*," *Ann. Chim. et Phys.*, t. vi., 1865, p. 55.
§ *Phil. Trans. Roy. Soc.*, 1866, pp. 399-439.

The question, however, of the direct carburisation of iron by the diamond has never been doubted since 1815, when a working cutler, M. Pepys,* heated iron wire and diamond dust together and obtained steel, the heat being afforded by a powerful electric battery. The absorption of carbon in the diamond form by iron may be made clear by reference to the diagram (Fig. 34), which represents a glass vessel, which may either be rendered vacuous or may be filled with an atmosphere of gas through the tube d. An iron wire, b, placed between the terminals of a battery, c, c', is heated to redness, and remains glowing until it is touched by pure diamond dust, which is effected by raising the cup, a. The iron combines with the diamond dust, and fuses.
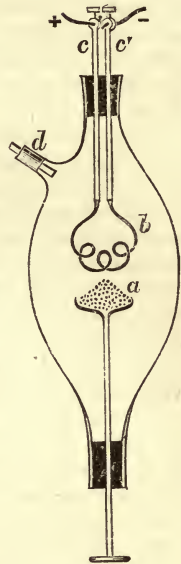
It must not be thought, however, that the steel owes its hardness to the passage of diamond into the iron *as diamond*. Margueritte's form of Clouet's experiment may be repeated by using a vacuum instead of an atmosphere of gas, and employing the form of apparatus shown in Fig. 35, which represents an arrangement for heating the diamond and iron *in vacuo*. A strip of pure iron, b, is placed between two terminals, c, c', which are connected with a dynamo. The vessel (of glass)

FIG. 34.

is rendered vacuous by connecting the tube d with a Sprengel pump. The iron is then heated by the dynamo and maintained
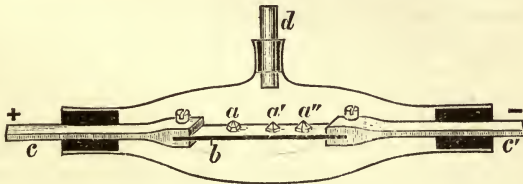
FIG. 35.

glowing until all occluded gas is expelled from the iron, which is then allowed to cool *in vacuo*. Small, pure diamonds, a, a', a'', are then placed on the strip of iron through the orifice into which the

* *Phil. Trans. Roy. Soc.*, 1815, p. 371.

tube d fits. The vessel is rendered vacuous, and when the iron is again heated in contact with the diamonds it fuses and combines with them. The diamond by union with iron has passed partially at least to the other form of carbon, graphite; while treatment with a solvent which removes the iron shows that carbon has entered into intimate association with the iron, a fact which leads us to the next step in the study of the relations between carbon and iron.

Hempel[*] has shown that, in an atmosphere of nitrogen, solid iron appears to assimilate the diamond form of carbon more readily than either the graphitic or the amorphous forms, but directly carbon is associated with *molten* iron it behaves like the protean element it is, and the state which this carbon assumes is influenced by the rate of cooling of the molten mass, or even by the thermal treatment to which the solidified mass is subjected. As carbon is well known to exist in the distinctive forms of diamond, graphite, and soot, it need not be considered strange that carbon should be capable of being present in intimate association with iron, but in very varied forms.

The mode of existence of carbon in soft annealed steel is very different from that in which it occurs in hard steel. Karsten was the first to isolate, in 1827, from soft steel a true compound of iron and carbon; Berthier[†] also separated from soft steel a carbide of iron to which he assigned the formula FeC; and it need only be added that within the last few years Sir F. Abel[‡] has given much experimental evidence in favour of the existence in soft cold-rolled steel of a carbide, Fe_3C, which he isolated by the slow solvent action of a chromic acid solution. His work has been generally accepted as conclusive, and has been the starting-point of much that has followed.

Obviously the microscope should reveal wide differences between the structure of various kinds of iron and steel; and Sorby, in his very delicate investigations into the structure of steel,[§] has shown that this is the case; the point of main importance being the existence of a substance which Sorby called the " pearly constituent " in soft steel. This pearly constituent is closely related to the carbide of iron, Fe_3C, of Abel, and is probably a mixture of Fe_3C and pure iron. Its presence is diagrammatically indicated in Fig. 36. The diagram will serve for the purpose of illustration to indicate the appearance when soft,

[*] *Ber. der deutsch. chem. Gesellschaft*, vol. xviii. p. 998.
[†] *Ann. des Mines*, vol. iii. (1833), p. 229.
[‡] *Proc. Inst. Mech. Eng.*, 1883, p. 56.
[§] *Journ. Iron and Steel Inst.*, No. 1 (1887), p. 255.

hardened, and tempered steel are respectively heated with a solvent which acts gently on the mass.

IRON AND CARBON.
(0·2 to 1·5 per cent of CARBON.)

Heated to bright redness.

Slowly cooled.   Quickly cooled.
"SOFT"   "HARD"

Appearance of metal when etched with a solvent.

Change of carbon takes place rapidly.
Brinell.

CONTAINS 'Carbide-carbon.' Fe₃ C. Mechanically mixed.

CONTAINS 'Hardening carbon.'

Hardened steel reheated to temperatures varying from 200°C. to 400°C. IS "TEMPERED"

Change of carbon takes place more gradually. Brinell.

In annealed steel the carbide is in grey scales.

Tempered at 400°C. the carbide is finely divided.

FIG. 36.

A study of the admirable work of Ledebur[*] will show how complex the relations of carbon and iron really are, but the question arises, Does a change in the "mode of existence" of carbon in iron sufficiently explain the main facts of hardening and tempering? It does not. It is possible to obtain by rapid cooling from a certain temperature steel which is perfectly soft, although analysis proves that the carbon is present in the form which has been recognised as "hardening carbon." No doubt in the hardening of steel the carbon changes its mode of existence;

[*] *Stahl und Eisen*, vol. viii. (1888), p. 742.

but some other theory must be sought which will explain all
the facts, and in order to do this it is necessary to turn to the
behaviour of the iron itself.

In approaching this portion of the subject, a few elementary
facts relative to the constitution of matter must be recalled, and
in doing so a brief appeal to history must again be made.   It is
universally accepted that metals, like all elements, are composed
of atoms of definite weights and volumes grouped in molecules.
In order actually to transmute one metal into another it would
be necessary to discover a method of attacking, not the molecule,
but the *atom*, and of changing it, and this, so far as is known, has
not yet been done ; but it is possible, by influences which often
appear to be very slight, to change the relations of the molecules
to each other, and to alter the arrangement or distribution of
the *atoms* within the *molecules*, and by varying, in this sense,
the molecular arrangement of certain elements, they may be
made to pass into states which are very different from those in
which we ordinarily know them. Carbon, for instance, when
free, or when associated with iron, may readily be changed from
its diamond form to the graphitic state, though the converse
change has not as yet been effected.

Sulphur, again, best known as a hard, brittle, yellow solid, may
be prepared and maintained for a little time in the form of a
brown viscous mass, but this latter form of sulphur soon passes
spontaneously and slowly at the ordinary temperature, and in-
stantaneously at 100°, to the solid octahedral yellow modification
with evolution of heat. The viscous form of sulphur is an
allotropic modification of that element. A few cases of allo-
tropy in metals have already been described in Chapter III.,
and when they do occur they give rise to problems of vast in-
dustrial importance. Such molecular changes in metals are
usually produced by the addition of a small quantity of foreign
matter, and it would appear that the molecular change produced
by the action of *traces* upon *masses* is a widespread principle of
nature, and one which was recognised at the dawn of the science
of chemistry, even in the seventh century, but distorted explana-
tions were given of well-known facts, and gave rise to entirely
false hopes. But students would do well to bear in mind that it
is the same story now as in mediæval times ; the single grain of
powder which Raymond Lully said would transmute millions
of its weight of lead into gold, the single grain of stone that
Solomon Trismosin thought would secure perpetual youth, had
their analogues in the small amount of plumbago which to
Bergman's astonishment in the eighteenth century converted

iron into steel.   By his time it was recognised that the right use of alchemy consisted in the application of its methods to industry, and we still wonder at the minuteness of the quantity of certain elements which can profoundly affect the properties of metals.   The statements are true, and are not derived from poetical literature early or late.   There is no need to fear the taunt of Francis Bacon,* that "sottishly do the chymics appropriate the fancies and delights of poets in the transformation of bodies to the experiments of their furnaces," for, although it may not be possible to *transmute* metals, it is easy so to *transform* them by very slight influences, that as regards special service required from them they may behave either usefully or entirely prejudicially.

The question at once suggests itself, Can iron behave in a similar manner; is an allotropic form of iron known?   Joule afforded experimental evidence for an affirmative answer to this question many years ago, by communicating to the British Association in 1850 a paper on some amalgams.   The result of his experiments, published in detail later,† in a paper which has been sadly neglected, showed that iron released from its amalgam with mercury is chemically active, as it combines readily with the oxygen of the air at the ordinary temperature, and he claims that the iron so set free is allotropic ; but Joule did much more than this.   Magnus had shown (1851) that the thermo-electric properties of hard and of soft steel and iron differ.   Joule, in a paper on some thermo-electric properties of solids, incidentally shows that the generation of a thermo-electric current affords a method of ascertaining the degree of carburisation of iron, and he appeals to the "thermo-electricity of iron in different states" as presenting a "fresh illustration of the extraordinary physical changes produced in iron by its conversion into steel," and he adds the expression of the belief "that the excellence of the latter metal might be tested by ascertaining the amount of change in thermo-electric condition which can be produced by the process of hardening."‡   It is by a thermo-electric method that the views as to the existence of iron in allotropic forms have been confirmed.

Jullien seems to have inclined to the view that iron is allotropic in his *théorie de la trempe*,§ published in 1865, but he

* Preface to the *Wisdom of the Ancients.*
† "On Some Amalgams," *Mem. Lit. Phil. Soc. Manchester*, vol. ii. [3], p. 115.
‡ *Phil. Trans.*, vol. cxlix. (1859), p. 91.
§ *Annexe au Traité de la Métallurgie du Fer*, 1865.

cannot be said to have done much beyond directing attention to the importance of hardening and tempering steel.

The next step was made in Russia, in 1868. Chernoff showed that steel could not be hardened by rapid cooling until it had been heated to a definite temperature, to a degree of redness which he called *a*. Then, in 1873, Professor Tait[*] used this expression in a Rede Lecture delivered at Cambridge : " It seems as if iron becomes, as it were, a different metal on being raised above a certain temperature; this may possibly have some connection with the ferricum and ferrosum of the chemists." He also published his now well-known "first approximation to a thermo-electric diagram," which is of great interest in view of recent work. At about this time those specially interested in this question remembered that Gore[†] had shown that a curious molecular change could be produced by heating an iron wire. Barrett repeated Gore's experiment, and discovered that as an iron wire cools down it suddenly *glows*, a phenomenon to which he gave the name *recalescence*, and these investigations have been pursued and developed in other directions by many skilful experimenters.[‡] In 1879 Wrightson called attention to the abnormal expansion of carburised iron at high temperatures.

The next point of special importance appears to be that recorded by Barus, who, by a thermo-electric method, showed, in an elaborate paper published in 1879,[§] that "the hardness of steel does not increase continuously with its temperature at the moment of sudden cooling, but at a point lying in the dark-red heat state" may suddenly be attained by rapid cooling. Brief reference will again be made to the remarkable series of papers published by Barus and Strouhal,[||] embodying the results of

[*] *Nature*, vol. viii. (1873), pp. 86, 122, and *Trans. Roy. Soc. Edin.*, vol. xxvii. (1873), p. 125.

[†] Gore, *Proc. Roy. Soc.*, vol. xvii. (1869), p. 260. Barrett, *Phil. Mag.*, vol. xlvi. (1873), p. 472.

[‡] G. Forbes, *Proc. Roy. Soc. Edin.*, vol. viii. (1874), p. 363. Norris, *Proc. Roy. Soc.*, vol. xxvi. (1877), p. 127. Tomlinson, *Phil. Mag.*, vol. xxiv. (1887), p. 256; vol. xxv. (1887), pp. 45, 103, and 372; vol. xxvi. p. 18. Newall, *ibid.*, vol. xxiv. (1887), p. 435; vol. xxv. (1888), p. 510.

[§] Barus, *Phil. Mag.*, vol. viii. (1879), p. 341.

[||] Hardness (temper), its electrical and other characteristics : Barus, *Phil. Mag.*, vol. viii. (1879), p. 341; *Wied. Ann.*, vol. vii. (1879), p. 383; Strouhal and Barus, *ibid.*, vol. xi. (1880), p. 930; *ibid.*, vol. xx. (1883), p. 525. Hardness and magnetisation, *ibid.*, vol. xx. (1883), pp. 537, 662. Density and (internal) structure of hard steel and of quenched glass, Barus and Strouhal, *American Journ.*, vol. xxxi. (1886), p. 386; *ibid.*, p. 439; *ibid.*, p. 181. Temper and chemical composition, *ibid.*, vol. xxxii. (1886), p. 276. Temper and viscosity, *ibid.*, p. 444; *ibid.*, vol. xxxiii. (1887), p. 20; Barus *ibid.*, vol. xxxiv. (1887), p. 1; *ibid.*, p. 175. These papers, systemati-

laborious investigations, to which but scanty justice can now be done ; and finally within the last few years Pionchon[*] showed that at a temperature of 700° the specific heat of iron is altogether exceptional, and Le Chatelier[†] has detected that at 700° a change occurs in the curve representing the electromotive force of iron, both experimenters concluding that they had obtained evidence of the passage of iron into an allotropic state. Osmond,[‡] in France, then made the observations of Gore and Barrett the starting-point of a fresh inquiry. Bearing in mind the fact that molecular change in a body is always accompanied with evolution or absorption of heat, which is, indeed, the surest indication of the occurrence of molecular change, he studied, with the aid of a chronograph, what takes place during the slow cooling and the slow heating of masses of iron or steel, using as a thermometer to measure the temperature of the mass a thermo-electric couple of platinum, and of platinum containing 10 per cent. of rhodium, converting the indications of the galvanometer into temperatures by Tait's formulæ.

Figs. 37 and 38 show the actual mode of conducting the experiments. F, Fig. 37, is a piece of steel into which a platinum and

FIG. 37.

platinum-rhodium couple, t, t', is fixed. It is enclosed in a glazed porcelain tube, and heated to bright redness in the furnace S (Fig. 38). This tube, T, may be filled with any gaseous atmosphere. C is a bulb filled with chloride of calcium. The metal under examination is slowly cooled down. The wires from the thermocouple pass to the galvanometer, G. The rate of cooling of the mass, as indicated by the movement of a spot of light from the

cally discussed and enlarged, are embodied with new matter in the Bulletins of the United States Geological Survey—viz., *Bull.* No. 14 (1885), pp. 1–226 ; *Bull.* No. 27 (1886), pp. 30–61 ; *Bull.* No. 35 (1886), pp. 11–60 ; *Bull.* No. 42 (1887), pp. 98–131.

* *Comptes Rendus*, vol. cii. (1886), pp. 675 et 1454 ; vol. ciii. p. 1122.

† *Ibid.*, vol. cii. p. 819.

‡ The reader will find the principal part of Osmond's work in the following papers :—Osmond et Werth, *Théorie cellulaire des Propriétés de l'Acier*, *Ann. des Mines*, vol. viii. (1885), p. 5 ; *Transformations du Fer et du Carbone*, Paris, Baudoin et Cie., 1888 ; *Études métallurgiques*, *Ann. des Mines*, Juillet-Août, 1888. There is also a very interesting paper, *Sur les nouveaux Procédés de Trempe*, which he communicated to the Mining and Metallurgical Congress, Paris, 1889, and another in the *Journ. Iron and Steel Inst.*, No. 1 (1890), p. 38.

galvanometer mirror, M, on the screen, R, is recorded by a chronograph.   The source of light is shown at L.
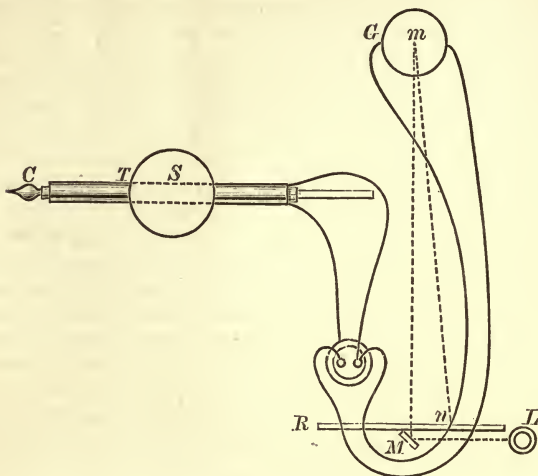
FIG. 38.

The curves given in the diagram, Fig. 39, show how the rate of movement of the spot of light varies with different samples of steel.   The stoppage of the movement of the spot of light of course indicates the evolution of heat from the cooling mass of steel, F (Fig. 37).

It will be seen, therefore, that although the presence of carbon is essential to the hardening of steel, it need not, as has hitherto been supposed, change its mode of existence when soft steel is hardened.

In Fig. 39 the temperatures through which a slowly cooling mass of iron or steel passes are arranged along the horizontal line, and the intervals of time during which the mass falls through a definite number (6.6) of degrees of temperature are shown vertically by ordinates.   See what happens while a mass of electro-deposited iron (shown by a dotted line), which is as pure as any iron can be, slowly cools down.   From 1200° to 870° it falls uniformly at the rate of about 2.2° a second, and the intervals of temperature are plotted as dots at the middle of the successive points of the intervals.   When the temperature falls down to 858° there is a sudden arrest in the fall of temperature; the indicating spot of light, instead of falling at a uniform rate of about
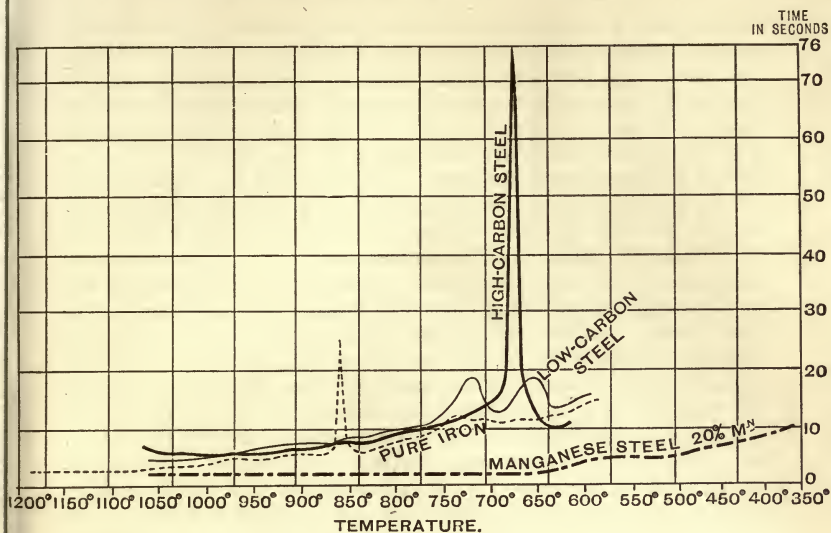
FIG. 39

2° a second, suddenly takes 26 seconds to fall through an interval of temperature which hitherto and subsequently only occupies about 6 seconds. The diagram (Fig. 39) shows what actually happens when the iron contains carbon in the proportion required to constitute it mild steel (indicated by a thin continuous line, Fig. 39), there is not one, but there are two such breaks in the cooling, and both breaks occur at a different temperature from that at which the break in pure iron occurred. As the proportion of carbon increases in steel the first break in cooling travels more and more to the right and gradually becomes confounded with the second break, which, in steel containing much carbon, is of long duration, lasting as much as 76 seconds in the case of steel containing 1.25 per cent. of carbon (thick continuous line, Fig. 39).

Now, it may be urged, as the presence of carbon has evidently an influence on the cooling of steel when left to itself, may it not affect molecular behaviour during the rapid cooling which is essential to the operation of hardening? It is known that the carbon during rapid cooling passes from the state in which it is combined with the iron into a state in which it is dissolved in the iron; it is also known that during slow cooling this dissolved

carbon can re-enter into combination with the iron so as to assume the form in which it occurs in soft steel. Osmond claims that this second arrestation in the fall of the temperature corresponds to the recalescence of Barrett, and is caused by the re-heating of the wire by the heat evolved when carbon leaves its state of solution and truly combines with the iron.

If it is hoped to *harden* steel it must clearly be rapidly cooled before this combination of carbon and iron has taken place, or it will be too late to keep the carbon as hardening carbon. But what does the first break in the curves mean? It will be seen that it occurs in electrolytic iron, which is free from carbon; it must, then, indicate some molecular change in iron itself, accompanied with evolution of heat, a change with which carbon has nothing whatever to do, for no carbon is present, and Osmond argues thus :—There are two kinds of *iron*, the atoms of which are respectively arranged in the molecules so as to constitute *hard* and *soft iron*, quite apart from the presence or absence of carbon. In red-hot iron the mass may be soft, but the molecules are hard : let this be called β iron; cool such red-hot pure iron, whether quickly or slowly, and it becomes soft; it passes to the α soft modification, there is nothing to prevent its doing so. It appears, however, that if carbon is present, and the metal be rapidly cooled, the following result is obtained :—A certain proportion of the molecules are retained in the form in which they existed at a high temperature in the hard form, the β modification, and hard

IRON.

α OR SOFT IRON.

When β IRON cools down from bright redness to 855°C. it changes to α Iron.

β OR HARD IRON.

Pure IRON at temperatures below 855°C. and Iron containing certain other elements if cooled slowly.

IRON at high temperatures or, if certain other elements be present, after being rapidly cooled.
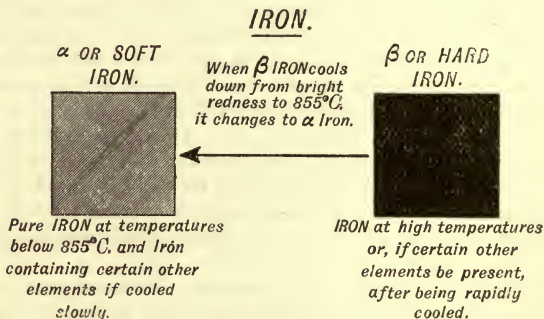
FIG. 40.

steel is the result. The main facts of the case may, perhaps, be made clearer by the aid of the diagram Fig. 40, which shows the relation between α and β iron. This molecular change from β

iron to *a* iron during the slow cooling of a mass of iron or steel is, according to Osmond's theory, indicated by the first break in the curve representing the slow cooling of iron, as is proved by the fact that it occurs alone in electro-iron. A second break, usually one of much longer duration, marks the point at which carbon itself changes from the dissolved or hardening carbon to the combined, carbide-carbon. It follows that if steel be quickly cooled *after the change from β to a* has taken place, but before the carbon has altered its state—that is, before the change indicated by the second break in the curve has been reached—then the iron should be soft, but the carbon, hardening carbon, and, as such, the action of a solvent should show that it cannot be released from iron in the black carbide form. This proves to be the case, and affords strong incidental proof of the correctness of the view that two modifications of iron can exist.

It will be seen, therefore, that, although the presence of carbon is essential to the hardening of steel, the change in the mode of existence of the carbon is less important than has hitherto been supposed. The *a* modification of iron may be converted into the *β* form by stress applied to the metal at temperatures below a dull red heat, provided the stress produces permanent deformation of the iron.*

Barus† has pointed out that since most metals can be similarly hardened by straining, it would follow that there should be *a* and *β* varieties in all cases, even though a molecular change corresponding to recalescence has only been observed in the case of a few metals. He believes, however, that there is reason to be urged in favour of this extreme view. The existence of molecular change in iron may be illustrated by the following experiment:—Take a bar of steel, Fig. 41, containing much carbon.
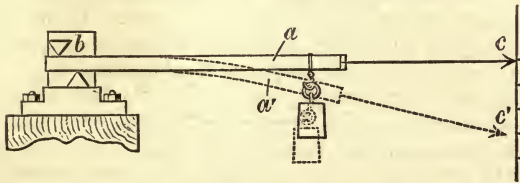
FIG. 41.

In such a variety of steel, the molecular change of the iron itself, and the change in the relations between the carbon and the iron,

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* Osmond, *Etudes métallurgiques*, 1888, p. 6.
† *Nature*, vol. xli. (1890), p. 369.

would occur at nearly the same moment. Heat this bar to red-
ness, one end of the red-hot bar being firmly fixed (Fig. 41),
and sling a weight *not sufficient to bend it* to the free end, which
is lengthened by the addition of a reed to magnify any motion
that may take place. As the bar is red hot, it ought to be at its
softest when it is freshly withdrawn from the furnace, and, if
the weight was ever to have power to bend it, it would be then;
but, in spite of the rapidity with which such a thin bar cools
down in the air and becomes rigid, points of molecular weakness
come when the iron changes from β to a, and the carbon passes
from hardening carbon to carbide carbon; at that moment, at a
temperature much below that at which it is withdrawn from the
furnace, the bar will begin to bend. It has been found experi-
mentally that this is the point at which, according to Osmond's
theory, molecular change takes place. Coffin takes advantage of
this fact to straighten distorted steel axles.*

Barus† traces the connection of this singular minimum of the
viscosity of hot iron and the interpretation given of Maxwell's
theory of viscosity, and he points out that "when iron passes
through the temperature of recalescence, its molecular condition is
for an instant almost chaotic. This has now been abundantly proved
by Hopkinson. The number of unstable configurations, or, more
clearly, the number of configurations made unstable because they
are built up of disintegrating molecules, is therefore at a maximum.
It follows that the viscosity of the metal must pass through a
minimum. Physically considered, the case is entirely analogous
to that of a glass-hard steel rod suddenly exposed to 300°. If all
the molecules passed from Osmond's β state to his a state to-
gether, the iron or steel would necessarily be liquid. This ex-
treme possibility is, however, at variance with the well-known
principles of chemical kinetics. The ratio of stable to unstable
configurations cannot at any instant be zero. Hence the mini-
mum viscosity in question, however relatively low, may yet be
large in value as compared with the liquid state."

Mr. Anderson has recently urged that, "when, by the agency
of heat, molecular motion is raised to a pitch at which incipient
fluidity is obtained, the particles of two pieces brought into
contact will interpenetrate or diffuse into each other, the two
pieces will unite into a homogeneous whole, and we can thus
grasp the full meaning of the operation known as 'welding.'"
It is, however, possible to obtain evidence of interchange of
molecular motion, as has been so abundantly shown by Spring,

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* *Trans. American Soc. Civil Engineers*, vol. xvi. (1887), p. 324.
† *Nature*, vol. xli. (1890), p. 369.

even at the ordinary temperature, while in the case of steel it must take place far below incipient fluidity, indeed, at a comparatively low temperature, as is shown by the following experiment on the welding of steel. Every smith knows how difficult it is to weld highly carburised hard tool steel, but if the ends of a newly fractured $\frac{1}{8}$ inch square steel rod, a (Fig. 42), are covered with platinum foil, b, so as to exclude the air, and if the junction is heated in the flame of a Bunsen burner, c, the metal will weld, without pressure, so firmly that it is difficult to break it with the fingers, although the steel has not attained a red heat.[*]
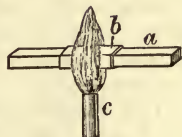
FIG. 42.

The question now arises, what is the effect of the presence of other metals in steel, of which much has been heard recently? Take the case of manganese. This metal enables steel to harden very energetically, as is very well known. If much of it be present, 12 to 20 per cent., in iron, *no break whatever* is observed in the curve which represents slow cooling. (See line marked " Manganese Steel," Fig. 39.) That is, the iron never shows such a change as that which occurs in other cooling masses of iron. Then such a material should be hard, however it is cooled. So it is. There is one other important point of evidence as to molecular change connected with the addition of manganese. Red-hot iron is not magnetic, and Hopkinson[†] has recently stated that the temperature of recalescence is that at which iron ceases to be magnetic. It may be urged that β iron cannot therefore be magnetised. Steel containing much manganese cannot be magnetised, and it is therefore fair to assume that the iron present is in the β form. Hadfield[‡] has given metallurgists wonderful alloys of iron and manganese in proportions varying from 7 to 20 per cent. of manganese. Professor Ewing and others have specially examined the magnetic properties of this material, and Ewing concludes that " no magnetising force to which the metal is likely to be subjected, in any of its practical applications, would produce more than the most infinitesimal degree of magnetisation " in Hadfield's manganese steel. It has been seen that quantities of manganese above 7 per cent. appear to prevent the passage of β iron into the a form. In smaller quantities, manganese seems merely to retard the conversion, and to bring the two loops of the diagram nearer together. With regard to the effect of other elements on

[*] *Trans. American Soc. Mechanical Engineers*, vol. ix. (1888), p. 155.
[†] *Proc. Roy. Soc.*, vol. xlv. (1889), pp. 318, 445, and 457.
[‡] *Proc. Inst. Civil Engineers* vol. xciii. 1888, part iii.

steel, it need only be added that tungsten possesses the same property as manganese, but in a more marked degree. Chromium has exactly the reverse effect, as it enables the change of hard β iron to soft a iron to take place at a higher temperature than would otherwise be the case, and this may explain the extreme hardness of chromium steels when hardened in the same way as ordinary steels.

The disappearance of the magnetic properties of iron on heating is of much interest in relation to the allotropism of the metal. Gilbert appears to have been the first to demonstrate, in his treatise *de Magnete*, published in 1600, that red-hot iron is not magnetic; and nearly half a century later Sir Thomas Browne,* with frequent reference to Gilbert's work, states that masses of iron, " by the fire, omit whatsoever they had received from the earth or loadstone," and he gives evidence of being aware that what is now called the " magnetic permeability " of iron and steel is affected by heating and cooling the metal. These facts have been recognised as being of vital importance in modern research, and they derive new interest from the sharp identification of the loss of magnetism with the temperature at which a molecular change in the iron takes place, and from Hopkinson's recent discovery that an alloy of iron with 25 per cent. of nickel is magnetisable if it be previously cooled (by solid carbonic acid) to a very low temperature.

Working of Steel.—There are a few considerations relative to the actual working of steel which can but briefly be dealt with, notwithstanding their industrial importance. The points a and b adopted in the celebrated memoir of Chernoff, to which reference has already been made, change in position with the degree of carburisation of the metal. It is useless to attempt to harden steel by rapid cooling if it has fallen in temperature below the point (in the red) a, and this is the point of " recalescence " at which the carbon combines with the iron to form carbide carbon ; it is called V by Brinell. In highly carburised steel, it corresponds exactly with the point at which Osmond considers that iron, in cooling slowly, passes from the β to the a modification. Now with regard to the point b of Chernoff (or W of Brinell). If steel be heated to a temperature above a, but below b, it remains fine grained, however slowly it is cooled. If the steel be heated above b, and cooled, it assumes a crystalline granular structure, whatever the rate of cooling may

* *Pseudodoxia Epidemica : or Enquiries into Vulgar Errors.* Second Edition, 1650, p. 45.

be. The size of the crystals, however, increases with the temperature to which the steel has been raised.

Now the crystalline structure, which is unfavourable to the steel from the point of view of its industrial use, may be broken up by the mechanical work of forging the hot mass; and the in-
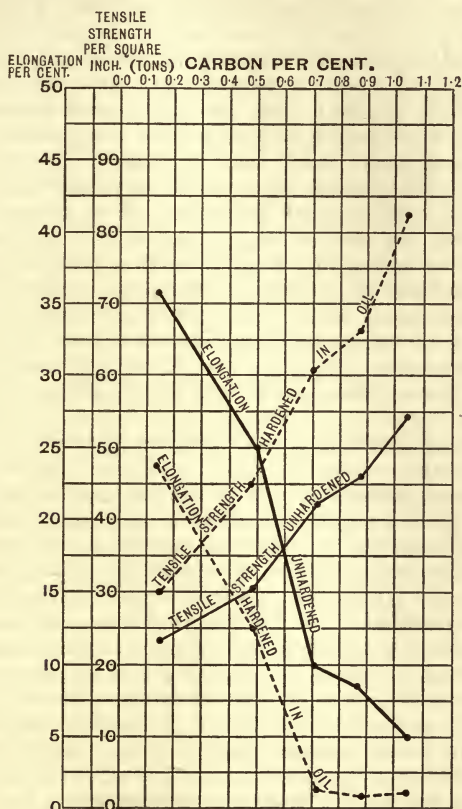
FIG. 43.

vestigations of Abel, of Maitland, and of Noble, have shown how important "work" on the metal is. When small masses of hot steel are quenched in oil, they are hardened just as they would be if water were used as a cooling fluid. The diagram, Fig. 43, shows the way in which the tenacity of steel containing varying

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amounts of carbon is increased by oil-hardening,* while at the same time the elongation rapidly diminishes. With large masses the effect of quenching in oil is different. Such cooling of large hot masses appears to break up this crystalline structure in a manner analogous to mechanical working. If the mass of metal is very large, such as a propeller shaft, or tube of a large gun, the change in the relations between the carbon and the iron, or true " hardening " produced by such oil treatment is only effected *superficially,* that is, the hardened layer does not penetrate to any considerable depth, but the innermost parts are cooled more quickly than they otherwise would have been, and the development of the crystals, which would have assumed serious proportions during slow cooling, is arrested. It depends on the size of the quenched mass whether the tenacity of the metal is or is not increased, but its power of being elongated is considerably augmented. This prevention of crystallisation probably constitutes the great merit of oil quenching, which, as regards large masses of metal, is certainly not a true hardening process.

There has been much divergence of view as to the relative advantages of work on the metal and of oil-hardening, but it will be possible to reconcile these views if the facts so briefly stated be considered.

The effect of annealing remains to be dealt with. In a very complicated steel casting, the cast metal probably contains much of its carbon as hardening carbon, and the mass, which has necessarily been poured into the mould at a high temperature, is crystalline. The effect of annealing is to permit the carbon to pass from the " hardening " to the " carbide " form, and, incidentally, to break up the crystalline structure, and to enable it to become minutely crystalline. The result is that the annealed casting is far stronger and more extensible than the original casting. The carbide carbon is probably interspersed in the iron in a finely divided state, and not in crystalline pallets. It would obviously be impossible to " work "—that is, to hammer—complicated castings, and the extreme importance of obtaining a fine crystalline structure by annealing, with the strength which results from such a structure, has been abundantly demonstrated by Mr. J. W. Spencer, of Newcastle.

The effect of annealing and tempering is, in fact, very complicated, as is shown by the long series of researches which Barus and Strouhal have conducted in recent years. They consider that annealing is demonstrably accompanied by chemical change

* This was well shown in Prof. Akerman's celebrated paper on " Hardening Iron and Steel," *Journ. Iron and Steel Institute,* 1879, part ii. p. 504.

even at temperatures slightly above the mean atmospheric temperature, and that the "molecular configuration of glass-hard steel is always in a state of incipient change . . . . a part of which change must be of a permanent kind." Barus says "that during the small interval of time within which appreciable annealing occurs, a glass-hard steel rod suddenly heated to 300° is almost a viscous fluid,"* and he considers that glass-hard steel is constantly being spontaneously "tempered" at the ordinary temperature, which he says, "acting on freshly quenched [that is, hardened] steel for a period of years, produces a diminution of hardness about equal to that of 100° C. acting for a period of hours."

The nature of the molecular change is well indicated in the long series of researches which led them to conclude that in steel "there is a limited interchange of atoms between molecules under stress, which must be a property common to solids if, according to Clerk-Maxwell's conception, solids are made up of configurations in all degrees of molecular stability."

Barus and Strouhal attach but little importance to the change in the relations between the carbon and the iron during the tempering and annealing of hard steel. They consider that in hardening steel the "strain once applied to steel is locked up in the metal in virtue of its viscosity"; tempering is the release of this molecular strain by heat.

Highly carburised steels harden very energetically by very slight modifications in thermal treatment, and it will be evident that a very hard material is unsuitable for industrial use if the conditions of its employment are such as to render it desirable that the material should stretch.

To turn to the class of steel which does not harden, it is certain that, although wrought iron passes almost insensibly into steel, there can be no question that, not merely the structural, but the molecular aggregation of even steel containing only $\frac{2}{10}$ per cent. of carbon, is profoundly different from that of wrought iron. The class of steel which was formerly employed for weapons and tools belonged to the highly carburised, readily hardening class. It was the "mild steel," containing but little carbon, which was destined to replace wrought iron, and when attempts were made to effect the general substitution of steel for iron, fears as to its character and trustworthiness unfortunately soon arose, so that from about the year 1860 until 1877, steel was viewed with suspicion. This can now be explained. Doubts as to the fidelity of steel, even when it was obtained free from

* *Phil. Mag.*, vol. xxvi. (1888), p. 209.

entangled cinder, arose from ignorance of the fact that, on either side of a comparatively narrow thermal boundary, iron in steel can practically exist in two distinct modifications. The steel was "true" enough, but, from the point of view of the special duties to be entrusted to it, its fidelity depended on which modification of iron had to be called to the front. Artificers attempted to forge steel after it had cooled down below the point a of Chernoff at which recalescence occurs, and they often attempted to work highly carburised steel at temperatures which were not sufficiently low.

Classification of Steel.—From the foregoing remarks, it will be evident that the use of steel depends almost entirely upon its power of being hardened and tempered. It may not be out of place, therefore, to indicate the way in which steel may be classified from the point of view of its industrial use, according to the amount of carbon it contains. Steels may be grouped under certain definite percentages of carbon, ranging from $\frac{2}{10}$ to $1\frac{1}{2}$ per cent. Each class merges into the other, but the members at either end of the series vary very greatly. It would be impossible to make from boiler plate a razor which would cut, and, conversely, a boiler made of razor steel would possibly fracture at once if it were overheated and subjected to any sudden pressure of steam.

Speaking generally, if the steel contains, in addition to carbon, $\frac{5}{10}$ per cent. of manganese, each class of steel would be equivalent, as regards tenacity and hardening properties, to the one above it.

The steel used for naval construction contains 0.15 to 0.2 per cent. of carbon. And when steel faces are used for the armour plates, the material contains 0.7 to 0.8 per cent. of carbon.

It may be mentioned that the latest type of battle ship weighs, fully equipped, about 10,000 tons, there being about 3400 tons of steel in the hull, apart from her armour, which, with its backing, will weigh a further 2800 tons.

With regard to steel used in civil engineering, the most remarkable case is presented by the Forth Bridge. The steel of which the compression members of the structure are composed contains 0.23 per cent. of carbon and 0.69 per cent. of manganese. The parts subjected to extension do not contain more than 0.19 per cent. of carbon.*

Steel for the manufacture of pens contains about 0.3 per cent. of carbon. Steel rails contain from 0.3 to 0.4 per cent. of carbon, and in this class slight variations in the amount of carbon are of

* *Journ. Iron and Steel Institute*, vol. ii. (1888), p. 94.

vital importance, as in certain climates a variation of 0.1 per cent. in the amount of carbon may be very serious. The great benefit which has accrued to the country from the substitution of more durable steel rails for the old wrought-iron ones may be gathered from the statement of Webb, of Crewe, which shows that " the quantity of steel removed from the rails throughout the London and North-Western system by wear and oxidation is about 15 cwts. an hour, or 18 tons a day."

Gun steel contains 0.3 to 0.5 per cent. of carbon, and it may contain 0.8 per cent. of manganese. It is in relation to gun steel that oil-hardening becomes very important. The oil tank of the Saint-Chamond Works (on the Loire) is 72 feet deep, and contains 44,000 gallons of oil, which is kept in circulation by rotary pumps, to prevent the oil being unduly heated locally when the heated mass of steel is plunged into it.

Now with regard to projectiles. The most formidable projectiles belong to the highly carburised class of steel. Shells contain 0.8 to 0.94 per cent. of carbon, and, in addition, some of these have 0.94 to 2 per cent. of chromium. The firm of Holtzer showed in the Paris Exhibition a shell which pierced a steel plate 10 inches thick, and was found, nearly 800 yards from the plate, entire and without flaw, its point alone being slightly distorted. Compound armour plate with steel face, which face contains 0.8 per cent. of carbon, is, however, more difficult to pierce than a simple plate of steel.

Lastly, reference must be made to the highly carburised steel used for the manufacture of dies. Such steel should contain 0.8 to 1 per cent. of carbon and no manganese. It is usual to water-harden and temper it to a straw colour, and a really good die will strike 40,000 coins of average dimensions without being fractured or deformed, but if the steel contain 0.1 per cent. too much carbon, it would not strike 100 pieces without cracking, and if it contained 0.2 per cent. too little carbon, it would probably be hopelessly distorted and its engraved surface destroyed in the attempt to strike a single coin.

The above examples will be sufficient to show how diverse are the properties which carbon confers on iron, but, as Faraday said in 1822, "it is not improbable that there may be other bodies besides charcoal capable of giving to iron the properties of steel." The strange thing is that it is not known with any certainty whether, in the absence of carbon, other elements do play the part of that metalloid in enabling iron to be hardened by rapid cooling. Take the case of chromium, for instance; chromium-carbon steels can, as is well known, be energetically hardened, but

Busek * has asserted that the addition of chromium to iron in the absence of carbon does not enable the iron to be hardened by rapid cooling. Probably by employing the electrical method of heating adopted by Pepys a decision will be arrived at as to the hardening properties of elements other than carbon.

A few words must be devoted to the consideration of the colours which direct the artist in tempering or reducing the hardness of steel to any determinate standard. The technical treatises usually give, not always accurately, as Reiser † has shown, a scale of temperature ranging from 220° to 330°, at which various tints appear passing from very pale-yellow to brown-yellow, purples, and blues to blue tinged with green, and finally to grey. Barus and Strouhal point out ‡ that it is possible that the colour of the oxide film may afford an indication of the temper of steel of far greater critical sensitiveness than has hitherto been supposed. It is, however, at present uncertain how far time, temperature, and colour are correlated.

That the colours produced are really due to oxidation was shown by Sir Humphry Davy in 1813,§ but the nature of the film has been the subject of much controversy. Barus points out that "the oxygen molecule does not penetrate deeper than a few thousand times its own dimensions," and that it probably passes through the film by a process allied to liquid diffusion. The permeable depth increases rapidly with the temperature until, at an incipient red heat, the film is sufficiently thick to be brittle and liable to rupture, whereupon the present phenomenon ceases or is repeated in irregular succession.

Summary.—Looking back over all the facts dealt with in this chapter, it will be evident that two sets of considerations are of special importance—(1) those which belong to the relations of carbon and iron, and (2) those which contemplate molecular change in the iron itself. The first of these has been deliberately subordinated to the second, although it would have been possible to have written much in support of the view that carburised iron is an alloy of carbon and iron, and to have traced with Guthrie the analogies which alloys, in cooling, present to cooling masses of igneous rocks. This view has been developed with much

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* *Stahl und Eisen*, vol. ix. (1889), p. 728.

† *Das Härten des Stahles*, p. 78 (Leipzig, 1881). See also Lœwenherz, *Zeitschrift für Instrumentenkunde*, vol. ix. (1889), p. 322.

‡ *Bull. U.S. Geo. Survey*, No. 27 (1886), p. 51.

§ Sir Humphry Davy, *Thomson's Ann. Phil.*, vol. i. (1813), p. 131, quoted by Turner, *Proc. Phil. Soc. Birmingham*, vol. vi. (1889), part 2.

ability by Howe,* who even suggests mineralogical names such as "cementite," "pearlyte," and "ferrite" for the various associations of carbon and iron.

Such analogies present considerable interest, but the possibility of molecular change in the iron itself, which results in its passage into a distinctive form of iron, is at present the more important subject for consideration, not merely in relation to iron, but as regards the wider question of allotropy in metals generally.

Many facts noted in spectroscopic work will, as Lockyer has shown, have indicated the high probability that the molecular structure of a metal like iron is gradually simplified as higher temperatures are employed. These various simplifications may be regarded as allotropic modifications.

The question of molecular change in solid metals demands continued and rigorous investigation. It is well known what important discoveries have been made in chemistry by the recognition of the fact that the elements act on each other in accordance with the great law of Mendeléef, which states that the properties of the elements are periodic functions of their atomic weights. There is little doubt but that it will be shown that the relation between small quantities of elements and the masses in which they are hidden, is not at variance with the same law. It has elsewhere been shown that this may be true, by a study of the effect of small quantities of impurity on the tenacity of gold, and the probability that it may prove true in the case of iron has also been dealt with in the previous chapter.

The future of steel will depend on the care with which the nature of the influence exerted by various elements on iron is investigated, and by ascertaining the thermal treatment to which it may most suitably be subjected.

Is it not strange that so many researches should have been devoted to the relations between carbon, hydrogen, and oxygen in organic compounds, so few to the relations of iron and carbon, and hardly any to iron in association with other elements? The reason for the comparative neglect of metals as subjects of research arises from the belief that methods which involve working at high temperatures are necessarily inaccurate, but the school of Ste. Claire-Deville has shown that they are not, and there are signs that our traditional love for the study of metals is reviving.

* *Engineering and Mining Journal*, vol. xlvi. (1888), p. 131. See also *The Metallurgy of Steel*, vol. i. (New York, 1890), p. 165.

CHAPTER V.

FUEL.

Classification of Fuel.—The term **fuel** is applied to substances that may be burned by means of atmospheric air with sufficient rapidity to evolve heat capable of being applied to economic purposes. Only those substances that contain a large proportion of carbon and hydrogen can be used economically. In some cases the products of combustion are used for effecting metallurgical reactions; in most cases, however, the fuel is consumed simply for the sake of the heat generated.

Fuels may be of ancient or modern origin, and may be divided into two classes—(I.) Natural fuels and (II.) Prepared fuels.

The first class includes—(1) wood and the various kinds of mineral fuel, (2) turf or peat, (3) lignite, (4) bituminous coal, and (5) anthracite. Besides these, various liquid hydrocarbons, such as petroleum, are found in sufficient quantity to render their employment possible on a large scale. At Pittsburgh in Pennsylvania, and at other localities in the United States, combustible gas occurs naturally, and is largely used for metallurgical purposes.

The second class includes—(1) compressed fuels, which are composed of more or less pulverulent material consolidated into bricks, with or without cementing agents; (2) dried fuels, or those in which the water and a certain proportion of the more volatile constituents have been expelled by heat, examples being afforded by wood, lignite, and peat; (3) carbonised fuels, such as coke and charcoal; and, lastly, (4) liquid and gaseous fuels, obtained (a) by the distillation, partial or entire, of natural fuels, or (b) by their incomplete combustion.

The value of all these fuels depends upon the amount of carbon and hydrogen they contain. The majority of them contain oxygen, nitrogen, sulphur, and phosphorus, as well as a certain amount of inorganic material which ultimately forms the ash. The amount and nature of this ash is of great importance, and it will be evident that, if the fuel can be deprived of its ash-giving

constituents by treatment before combustion, its value will be greatly increased. The hydrogen that is in excess of the quantity required to form water with the oxygen in the fuel is alone available for combustion, and is termed the *disposable* hydrogen. The remainder of the hydrogen is regarded as being already in combination as water, and may be viewed as an actual source of loss, because this water has to be vaporised when the fuel is burned. Cellulose ($C_6H_{10}O_5$) contains no disposable hydrogen, whilst cannel coal contains a considerable quantity.

The temperature at which fuels kindle varies considerably, since an initial temperature is required before combustion is effected. Slow oxidation may, it is true, take place at ordinary temperatures, but in metallurgical practice it is only comparatively rapid combustion that is really useful. Extreme density and, on the other hand, great tenuity equally hinder inflammability. For the former reason, anthracite, diamond, and graphite are ignited with great difficulty. Fuels richest in hydrogen are the easiest to light, the inflammability of resinous wood and of bituminous coal being due to this fact. Combustible gases, however, do not ignite below a cherry-red heat, on account of the extreme dispersion of their molecules.* The inflammability of vegetable charcoal depends upon the temperature at which it is prepared. Thus, when wood is carbonised at 300° to 400°, the charcoal ignites at 60°; and when a temperature of 1200° to 1300° has been employed, ignition cannot be effected below 600° to 800°. This is due to the fact that the hydrogen is driven off almost entirely at the higher temperatures. Peat ignites at 225°; pine wood at 295°; ordinary coal at 325°, the melting-point of lead ; coke, anthracite, hydrogen, and carbonic oxide at a dull-red heat.

The length of flame given by fuel in burning is so important that coals have advantageously been classed as " long-flaming " and " short-flaming." Certain fuels disengage at the moment of combustion a large proportion of volatile matter, and these constitute the long-flaming varieties. The manner in which the fuel is burned, however, has a great effect upon the flame. Charcoal, for example, if burned with free access of air, merely glows ; but if burnt with a limited supply of air in a thick layer so arranged that the products of combustion from the lower portion pass through the upper, carbonic oxide will be formed, which will burn with a blue flame. The volume of the flame depends, amongst other conditions, upon the velocity of the current of air

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* Frankland, *Phil. Mag.*, vol. xxxvi. (1868), p. 309.

by which the combustion is effected, the volume decreasing as the velocity rises.

Calorific Power.—The calorific power of a fuel is the total heat generated by the combustion of a unit of weight of the fuel. The heat is measured in two ways, either by the number of units of weight of water raised $1°$, or by the number of units of water evaporated. The latter method, which was proposed by Professor Rankine, gives numerical results 537 times less than the former. In expressing the calorific power of a fuel, the amount of heat generated on the combustion of carbon to carbonic anhydride is taken as the standard of comparison. This calorific power of carbon is expressed by the number of parts by weight of water capable of being heated from $0°$ to $1°$ by the combustion of one part by weight of carbon. It is found by direct experiment to be 8080 units. The unit of heat varies with the thermometric scale and the unit of weight employed. The unit most largely adopted, the metric unit or *calorie*, is the quantity of heat required to raise 1 gram of water from $0°$ to $1°$ C.; whilst the British thermal unit is the amount of heat required to raise 1 lb. of water one degree Fahr. Thus 1 *calorie* = 3.96832 British units, and 1 British unit = 0.251996 *calorie*. Expressed in equivalent foot-pounds, 1 *calorie* = 1390.

For experimentally determining the calorific power of a fuel, a **calorimeter** is employed. Count Rumford's calorimeter consisted simply of a vessel, filled with water, containing a worm-pipe, through which the products of combustion passed from a funnel outside. In this way they imparted their heat to the water, whose rise in temperature was noted. All calorimeters are similar in principle to Rumford's. In the more modern instruments, however, the vessel in which the combustion takes place is entirely surrounded by water and by an air jacket.[*]

If a fuel consists only of carbon and hydrogen, its calorific power may be calculated by multiplying the weight of each of the elements in one part of the fuel by their respective calorific powers as found by experiment. For example, a fuel consists of 85.71 per cent. of carbon and 14.29 per cent. of hydrogen. What is its calorific power? The calorific powers of carbon and hydrogen are respectively 8080 and 34,462 *calories*, and

$$85.71 \times 8080 = 692536.80$$
$$14.29 \times 34462 = 492461.98$$
$$\overline{1184998.78}$$

* On calorimeters, consult Ganot's *Physics;* Watts' *Dictionary of Chemistry; Zeit. anal. Chem.*, vol. xxiii. p. 453 ; *Journ. Soc. Chem. Ind.*, 1886, p. 635 ; F. J. Rowan, *ibid.;* 1888, p. 195.

which is the heat evolved on the combustion of 100 parts of the fuel. This divided by 100 gives 11,849.98 *calories* as the calorific power of the fuel. So simple a case as this is rarely met with, it being usually necessary to determine the amount of disposable hydrogen in the fuel, and to multiply the result by 34,462.

Scheurer-Kestner[*] has shown that carbon in combination develops more heat than carbon in the form of charcoal. Consequently the calculated values of the calorific powers of coals are, as a rule, too low. In order to obtain results approximating more closely to the truth, it is advisable to employ for carbon the calorific power of 9000 instead of 8080, and for hydrogen 30,000 instead of 34,462 *calories*. Even this correction does not apply to certain bituminous lignites, and actual experiment is the only safe guide for commercial purposes.

Calorific Intensity.—The calorific intensity, or pyrometric effect of a fuel is the highest temperature which the fuel is capable of producing when burnt in air. Measurements of calorific intensity are based on the fact that the heat produced by combustion is transferred to the product of combustion, and it may be determined by calculation on the assumption that the calorific intensity of a simple combustible body burnt in oxygen is equal to its calorific power divided by the product of the relative weight of its products of combustion and the specific heat of those products, or, expressed as an equation,

$$t° = \frac{W \times C}{w \times c}$$

where W represents the weight of the substance, C the calorific power of the substance, w the weight of the product of combustion, and c its specific heat. For example, the calorific intensity of carbon burnt to carbonic anhydride in oxygen, is—

$$\frac{12 \times 8080}{(12 + 32) \times 0.22} = 10015°.$$

The calorific intensity of carbonic oxide burnt to carbonic anhydride is—

$$\frac{28 \times 2403}{(28 + 16) \times 0.22} = 6950°.$$

If the substance is a mixture, the weights and specific heats of

[*] *Revue scientifique*, 1888 ; translation in *Journ. Soc. Chem. Ind.*, 1888, p. 615 ; *Bull. de la Soc. industrielle de Mulhouse*, 1875, p. 241 ; *Comptes Rendus*, vol. lxvi. pp. 1047, 1220 ; vol. lxvii. pp. 659, 1002 ; vol. lxviii. p. 608 ; vol. lxix. p. 412.

the various products of combustion must be introduced. In determining the calorific power of hydrogen, the water obtained is assumed to be in the liquid state. In determinations of the calorific intensity, however, the water is in the form of gas. From the calorific power, therefore, must be subtracted the amount of heat which would be given out on cooling the steam to 0°. For one part of water at 100° this would be 537 *calories*. Again, in raising the product of combustion from 0° to t°, a greater amount of heat will be needed to raise it the first 100° while that product is liquid than would have been required if it had been gaseous. These two amounts of heat are in the proportion of the specific heats of steam and water, that is, as 0.4805 is to 1. Hence the extra quantity of heat to be added to the 537 *calories* is $(1 - 0.4805)$ 100, or 51.95 *calories*. The calorific power must, therefore, be decreased by $(51.95 + 537)$ 9, or 5300.5 *calories*, since 1 part of hydrogen yields 9 parts of water. Hence the calorific intensity of hydrogen is—

$$\frac{1 \times (34462 - 5300.5)}{9 \times 0.4805} = 6743°.$$

The calorific intensity is merely a theoretical quantity, as it is based on the assumptions that the products of combustion of the fuel have constant specific heats for all temperatures, and that they absorb all the heat produced. Neither of these assumptions is true, inasmuch as the specific heats of gases generally increase with the temperature, and as there is also a considerable amount of heat lost by conduction and by radiation, and dissociation limits the temperature. The computation of calorific intensity has consequently but little commercial value.

The calorific intensity of a fuel may be found by direct experiment by means of *pyrometers*. These are thermometers so constructed as to measure high temperatures.

Pyrometry.—This term is applied to the measurement of high temperatures. It is not possible, it is true, to attain as accurate measurements of high temperatures as it is of low ones by the aid of thermometers; nevertheless, very precise determinations have been made, and, as the measurement of high temperatures is of great importance in metallurgy, some attention must be devoted to the principles on which pyrometry is based.

Weinhold[*] has thus briefly set forth the principles on which pyrometers have been constructed :—

* *Pogg. Ann.*, vol. cxlix. (1873), p. 186.

1. Change in the volume of bodies—
    (a) Contraction of a solid body;
    (b) Expansion of solid bodies, or of gases.
2. Change in the physical state of bodies.
3. Conduction of heat by solid bodies.

4. Radiation of heat.
5. Production of thermo-electric currents.
6. Change in the electrical resistance of conductors.
7. Calorimeter methods.
8. Dissociation of chemical compounds.

Carl Barus[*] has given the following more extended classification in an admirable treatise on the thermo-electric measurement of high temperatures:—

1. Dilatation of solids—
    (a) A single solid;
    (b) Two solids acting differentially.
2. Dilatation of liquids.
3. Dilatation of gases—
    (a) Expansion measured in volume, manometrically;
    (b) Expansion measured in pressures, manometrically;
    (c) Expansion measured in volume, by displacement.
4. Vapour tension.
5. Dissociation.

6. Fusion.
7. Ebullition.
8. Specific heat.
9. Heat conduction.
10. Heat radiation.
11. Viscosity—
    (a) of solids;
    (b) of liquids;
    (c) of gases.
12. Spectrophotometry and colour. Rotary polarisation.
13. Acoustics (wave length).
14. Thermo-electrics.
15. Electrical resistance.
16. Magnetic moment.
17. Miscellaneous.

This classification shows that almost every thermal phenomenon has been utilised for pyrometry. It is especially necessary for the student to know what appliances afford a means of estimating high temperatures with sufficient accuracy for the ordinary purposes of a metallurgical works, and are at the same time sufficiently durable to withstand rough usage. For delicate investigations there are several instruments that can safely be adopted. These will be described subsequently.

The simplest methods are undoubtedly grouped in class 6 of Barus "fusion." For instance, the insertion of a fragment of metal of known melting-point in the locality whose temperature is to be tested will often afford at once the required information. Thus, the temperature of the hot blast may be capable of melting a rod of lead (melting-point 335°), though it may fail to melt a similar rod of zinc (melting-point 412°). A strip of pure silver will just

* *Bulletin of the United States Geological Survey*, No. 54, Washington, 1889. This contains an exhaustive bibliography of pyrometry.

melt at a temperature at which zinc boils, and this has been accurately determined as being 942°, and it follows, therefore, that a temperature which will just melt pure silver may safely be taken to be under 950°.

Many appliances, notably such as that devised by Weinhold,* may be purchased, the action of which depends upon the method of mixtures (No. 8 in Barus' scheme). In such appliances a " carrier " of platinum, iron, or clay transfers heat from the furnace to a known weight of water, the increase in temperature of which affords a means of calculating the unknown temperature. The method of mixtures has even been applied to gases. The hot blast supplied to a furnace is cooled with a known amount of cold air, of which the increase in temperature may easily be ascertained by means of an ordinary thermometer, and the temperature of the hot blast calculated.

For rapid determinations of high temperatures in works the pyrometer of Carnelly and Burton † (class 9 of Barus) may advantageously be used. It is cheap, and does not readily get out of order; moreover, when once placed in position, it requires little or no manipulation except the reading off of a couple of thermometers and a reference to a table. The principle on which it is based is as follows :—If a current of water of known temperature be allowed to flow at a constant rate through a coiled metallic tube, placed in the space the temperature of which is required, then the increase in the temperature of the outflowing water will be greater the higher the temperature of the space.

Fig. 44 illustrates the form of the new pyrometer and the method of using it. A is a coil of copper tubing placed in the space, M, of which the temperature is required. A current of water flows from the cistern C, through the coil A, into the glass tube B, and out at the nozzle f. The tube F attached to the water-main, feeds the receptacle at such a rate as to maintain a small but continual overflow through the tube G, which is connected with the waste-pipe. In this way a uniform head of water is obtained, so that the current flows through the coil at a constant rate. The effluent branch of the copper coil projects such a distance into the tube B, that the issuing water flows directly on to the bulb of the thermometer D. The two thermometers, E and D, serve to determine the temperatures of the inflowing and outflowing water. They are graduated to $\frac{1}{5}$°, so that temperatures can easily be read off to $\frac{1}{10}$°. The copper tube has an

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* *Pogg. Ann.*, vol. cxlix. p. 209.
† *Journ. Chem. Soc.*, vol. xlv. (1884), p. 237.

internal diameter of 6 millimetres. The coil, which has five complete turns, is 8 centimetres high, and has an external diameter of 8 centimetres. The head of water in the receptacle C, above the outflow f, was 20 centimetres in the inventors' experiments, the average flow of water at a temperature of 80° being 813 cubic centimetres per minute measured at a temperature of 10°.
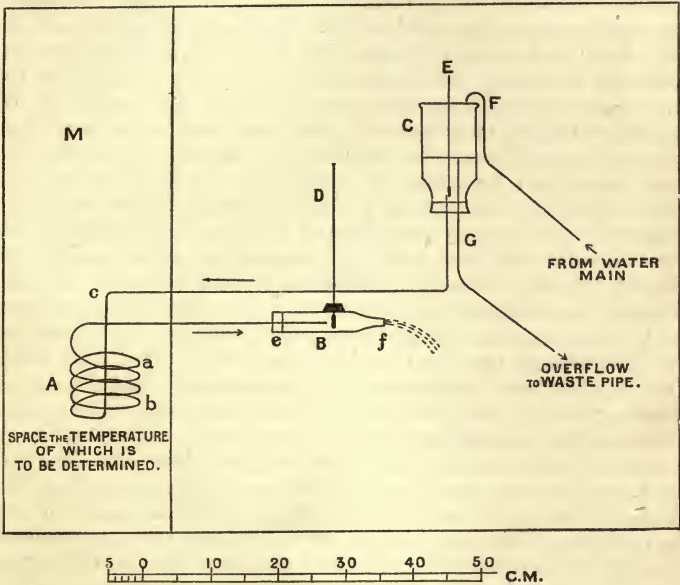
FIG. 44.

From a number of experiments made for the purpose of graduation, Carnelly and Burton deduced a mean curve showing the relation between the temperature of the furnace and the increase in temperature of the effluent water. When once the pyrometer is placed in position in any given furnace, a certain increase in the temperature of the effluent water will always indicate to the operator that a desired temperature has been reached, independently of any knowledge of what that particular temperature may be as measured on an ordinary thermometric scale. Each instrument and every variation in the head of water will of course require a distinct table; but when once the

instrument is fixed, and supplied with a constant head of water, one table will be all that is necessary. As, however, in most metallurgical operations the actual temperature in so many degrees is not necessarily required, it will be sufficient for the workman to know the increment in temperature of the out-flowing water, and he would soon accustom himself to represent all the different states of the furnace in terms of this increment. The Siemens electrical pyrometer * (class 15 of Barus) occupies an intermediate position between the appliances that are specially useful for industrial purposes and those which are adapted for scientific research. The measurement of temperatures by this instrument depends on the increase which takes place in the resistance offered by a metallic conductor to the passage of an electric current when the conductor is heated, and on the law, that when two branches, or conductors, are substituted for a single conductor in part of a circuit through which an electric current is passing, the intensities of the separate currents in the two branches will be inversely proportional to the resistance offered by each branch. Excellent as the Siemens electrical pyrometer is for certain purposes, it is an expensive instrument, and, as the resistance of platinum varies with continued heating, the instrument has been said to deteriorate after long usage. On the other hand, in an admirable monograph on the practical measurement of temperature,† H. L. Callendar states that a standard for measuring temperatures should always give the same indications at the same temperature, should be free from secular change of zero, and should possess the widest possible range. The results of his elaborate experiments at moderate temperatures have led him to the conclusion that the self-con-sistency of the platinum pyrometer has been abundantly verified in all the experiments undertaken with it. If the wire is pure to start with, and care is taken not to alloy it with silicon, carbon, tin, or other impurities, and to subject it to strain (such as in-crease of length), its resistance is always the same at the same temperature.

The optical pyrometer of Mesuré and Nouel ‡ has been tested by the author, and may also be recommended for approximate deter-minations. It belongs to class 12 of Barus, and depends on the partial rotation of polarised light by a quartz plate. The rota-tion varies with the intensity of the light; and, as this can be

* Drawings of this pyrometer are given by Percy, *Fuel* (1875), p. 176 ; Galloway, *Fuel* (1880), p. 78.
  † *Phil. Trans.* (A), vol. clxxviii. (1888), p. 161.
  ‡ *Industries*, vol. vi. (1889), p. 331.

measured, the temperature of the substance which emits the light can be determined. In the instrument a quartz plate is placed between the polarising and analysing prisms, the latter being turned until a definite neutral tint between green and red is produced. The angle is measured, and the corresponding temperature derived from a table.*

For really accurate measurements in scientific research the following methods may safely be adopted :—

(1) The modification of the air thermometer devised by Deville and Troost, and (2) the thermo-electric method perfected by Le Chatelier. With regard to the former of these, modifications of the air thermometer in which glass bulbs were replaced by metal were adopted by Prinsep and others early in the present century. The great advance Deville and Troost made was the substitution of bulbs of porcelain for those of metal. The following is an outline of their experimental method :—

Their apparatus consists of a globular flask of Bayeux porcelain of 280 or 300 cubic centimetres capacity, with a neck 11 centimetres long and 4 millimetres in internal diameter. A quantity of iodine is put into the flask, and the neck is nearly closed by a small plug of porcelain, which lies loosely in the opening. When the flask is now exposed to a high temperature, the iodine is vaporised, and the greater part escapes by the neck, driving out at the same time nearly the whole of the air. After the flask has been exposed for about twenty minutes to the temperature that is to be measured, the flame of an oxy-hydrogen blowpipe is allowed to play for an instant on the porcelain plug lying in the neck; the plug is thus melted, and closes the flask hermetically. When cold the flask is cleaned and carefully weighed; the end of the neck is broken under boiled water or mercury, and the flask is weighed, together with the water or mercury which enters; it is then completely filled with water or mercury and weighed again; lastly, the flask is weighed when empty. From the weights thus obtained it is easy to calculate the capacity of the flask and the volume of the residual air, that is, air which has not been expelled by the iodine vapour. The first weighing gives directly the excess of weight of the flask and iodine vapour over that of the empty flask. The observations which require to be made in each experiment are the following :—

* Descriptions of pyrometers for measuring hot-blast temperatures will be found in *Journ. Iron and Steel Inst.*, 1884, pp. 195, 240; 1885, p. 325; 1886, p. 207; 1888, No. 2, p. 110; *Proc. Inst. M.E.*, 1852, p. 53; *Journ. Soc. Chem. Ind.*, 1885, p. 40.

Temperature of the balance . . $t°$
Pressure of the atmosphere . . h millimetres
Excess of weight of sealed flask
and iodine vapour at end of ex-
periment over that of the empty
flask . . . . . . i grms.
Capacity of flask . . . . v cubic centimetres
Residual air . . . . . a ,,   ,,

In order to be able to calculate the exact temperature at which the flask was sealed the following constants are necessary :—

Weight of 1 c.c. air at 0° and 760 mm. pressure = 0.001293 grm.
Density of iodine vapour referred to air as unity = 8.716 grms.
Co-efficient of expansion of air for 1° C. . . = 0.00366 grm.
Co-efficient of cubical expansion of the porcelain
for 1° C. . . . . = 0.0000108 ,,

The required temperature may then be calculated in the following manner :—

Let $I_w = \left(\dfrac{(v-a)0.001293}{(1+0.00366\,t)} \dfrac{h}{760} + i \right)$ be the total weight of iodine

vapour contained in the flask at the moment of sealing; then

$$\frac{I_w}{0.001293 \times 8.716} \quad \frac{(1+0.00366\,T)\,760}{h} = I_v$$

will be the volume of the vapour at the same moment; but

$$I_v + \frac{a(1+0.00366\,T)\,760}{(1+0.00366\,t)\,h} = v(1+0.0000108\,T),$$

and from this equation, in which T, the temperature required, is the only unknown quantity, its value is easily found.

Owing to the belief that the molecule of iodine undergoes dissociation at high temperatures, this method has been modified, atmospheric air being used in place of iodine.

Barus has devised a form of appliance which he considers to be superior to that used by Deville for determining the boiling-points of metals. As shown in Fig. 45, it consists of a glazed tube of porcelain, d, passed through a hole in the base of a crucible, a. The zinc or other metal whose boiling-point is to be determined is shown at k. In this case a thermo-couple is used as a pyrometer, and it is inserted into the porcelain tube d. A reducing atmosphere of gas may be introduced through the tube h. The whole is enclosed in a Fletcher gas furnace, F. Gas enters through A, and the products of combustion escape at D.

The most trustworthy thermo-electric pyrometer is that devised in 1886 by Le Chatelier, who has greatly improved the appliance which had been used by previous experimenters. As early as

1836 Pouillet* suggested the use of an iron-platinum couple for measuring high temperatures. Solly, in 1841, suggested the employment of a copper-iron couple, and Joule, between the
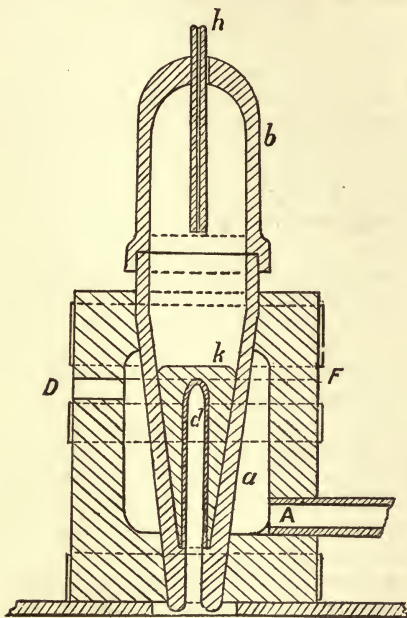
FIG. 45.

years 1843 and 1859, actually used such a couple in some memorable researches. Becquerel† made great advances in pyrometric measurements, and obtained trustworthy results with couples of platinum and palladium, but Le Chatelier‡ has pointed out that couples of platinum with iron or palladium are not satisfactory, as it is impossible to render these metals sufficiently homogeneous. In 1886 this distinguished physicist adopted a couple consisting of platinum and platinum alloyed with 10 per cent. of rhodium. The arrangement he proposed has already been described; but the

* *Comptes Rendus*, vol. iii. (1836), p. 782.
† *Ann. de Chim.*, vol. lxviii. (1863), p. 49.
‡ *Bull. Soc. Chim. Paris*, vol. xlvii. (1886), p. 2 ; *Journ. de Physique,* vol. vi. (1887), p. 23.

diagram, Fig. 38, shows the couple arranged for determining the temperature of a cooling mass of steel in a research to which reference has been made in Chapter IV. of this volume.

The deflections of the galvanometer may be converted into thermometric degrees by Tait's formula—

$$E = A (T_1 - T_0) + B (T_1^2 - T_0^2),$$

in which E is the electro-motive force in terms of the absolute temperature T_1 and T_0 of the two elements of the couple. It is only necessary to introduce into this formula the values of E corresponding to two fixed points, in order to determine the co-efficients A and B, and to construct a table of ordinary temperatures corresponding to each millimetre of the scale. Le Chatelier, however, showed that the second term of the equation (a parabola) ceased to be of importance with the platinum, platinum-rhodium couple for high temperatures, and that between 300° and 1200° the equation becomes approximately that of a straight line: $E = a + bt,$
in which E is the electromotive force, t the observed temperature, and a and b numerical co-efficients.[*]

The graduation, in thermometric degrees, of the scale traversed by the spot of light is effected by heating the couple in proximity to substances of known melting-points, and fortunately these are more numerous than is generally supposed. Volatile metals must, however, be avoided, as their vapours combine with the platinum and destroy it. Some years ago, Carnelly [†] determined the melting-points of certain substances by the method of mixtures, and used them, when enclosed in capillary tubes of glass, to ascertain at what temperatures substances of unknown melting-points actually fuse. Le Chatelier [‡] has since tested, with the aid of his thermo-couple, the accuracy of Carnelly's experiments, and has obtained in many cases very concordant results, as is shown in the following table :—

[*] For a further development of this formula, see Osmond, *Transformations du Fer et du Carbone* (Paris, 1888), p. 16.

[†] *Journ. Chem. Soc.*, vol. xxxiii. (1878), pp. 273, 281 ; vol. xlv. (1884), p. 237.

[‡] *Bull. Soc. Chim. Paris*, vol. xlvii. (1887), p. 300.

TABLE OF MELTING-POINTS.

	Le Chatelier.	Carnelly.
Potassium chloride	740°	734°
Sodium „	775	772
Calcium „	755	719
Barium „	847	772
Tin (SnCl₂) „	840	812
Sodium carbonate	810	814
Barium „	795	
Potassium „	885	834
Sodium sulphate	867	861
Barium nitrate	592	
Potassium sulphate	1015	
Potassium bichromate	975	
Sodium phosphate	957	
Potassium chlorate	370	359
Cuprous sulphide	1100	
Pure white pig-iron	1135	
Grey pig-iron	1240	
Grey forge pig-iron	1220	
Nickel	1420	

The melting-points of silver, 945°, of gold, 1045°, and of palladium, 1500°, may be conveniently remembered in connection with the above table.

The student is thus placed in possession of a number of melting-points which may safely be trusted.

I. NATURAL FUELS.

1. **Wood.**—When dry, wood consists of 96 per cent. of woody tissue (cellulose, $C_6H_{10}O_5$) and 4 per cent. of sap. A small proportion of inorganic matter is also present, and, when recently felled, all wood contains a large proportion of water. The mean composition of well-dried wood is—

Carbon.	Hydrogen.	Oxygen.	Nitrogen.
50.0	... 6.0	... 42.0	... 2.0

or, roughly, 50 per cent. of carbon and 50 per cent of chemically combined water. Air-dried wood contains 40 per cent. of carbon, 40 per cent. of chemically combined water, and 20 per cent. of hygroscopic water. The proportion of ash-giving constituents varies from 1.2 to 2.3 per cent., the average percentage being 1.5. The ash consists of about 70 per cent. of calcium carbonate, 20 per cent. of alkaline carbonates, together with varying amounts

of alkaline sulphates and chlorides, silica, phosphoric anhydride, magnesia, ferric oxide, manganous oxide, and alumina. The specific gravity of wood varies considerably. Air-dried woods, with 20 per cent. of moisture, having a specific gravity of more than 0.55, are classed as *hard ;* with a lower specific gravity they are classed as *soft*. After the air has been completely expelled from the pores of the wood, the specific gravity is in all cases nearly the same, varying only from 1.48 to 1.53. The calorific intensity of wood is small, but its combustibility and the amount of flame it gives are very great. The large percentage of hygroscopic water renders wood unsuitable as a fuel in cases where high temperatures are required, and the rapid demolition of forests tends to increase its cost.

2. **Peat.**—Peat or turf is the product of the slow decay of plants under conditions in which the supply of air is limited. It is formed chiefly from the mosses *Sphagnum* and *Hypnum,* with other plants. It may be classed, according to the localities where it has been produced, as highland and lowland peat, according to its age as recent peat, and as old peat with only traces of organic texture, and, lastly, according to the mode in which it has been extracted, as " cut peat " or " dredge peat."

Peat deposits are widely distributed throughout the world. In Ireland it is estimated that the peat area is not less than one-seventh of the island. That of Great Britain covers six million acres, with an average depth of 12 feet. Extensive deposits are met with in Russia, where peat is of metallurgical importance, in North Germany, Austria, and Scandinavia.

The composition of peat is extremely variable, the proportion of water and of ash-giving constituents having so great an influence that it is almost impossible to estimate its average composition. The best air-dried peat still contains 25 per cent. of hygroscopic water. From numerous analyses, the composition of pure peat, exclusive of moisture, has been found to be as follows :—

Carbon.	Hydrogen.	Oxygen.	Nitrogen.
49.6 to 63.9	4.7 to 6.8	28.6 to 44.1	0.0 to 2.6

in which the ratio of the oxygen (with the nitrogen) to the hydrogen is as 5 or 6 : 1.

The mean composition of good air-dried peat is approximately—

Hygroscopic Water.	Water.	Hydrogen.	Carbon.
25.0	28.5	1.5	45.0

The proportion of ash-giving constituents, however, varies from

1 to 30 per cent. and more, being rarely below 10 per cent. The ash consists chiefly of lime, ferric oxide, and silica, together with phosphoric acid, sulphuric acid, and carbonic acid, and, in inconsiderable quantities, alkalies, alumina, and magnesia. Raw peat also frequently contains iron pyrites. The high percentage of ash and of water, together with its bulk, are the main objections to the use of peat as fuel. For an equal evaporative power, its bulk is from 8 to 18 times that of coal.

Numerous methods have been adopted for freeing peat from ash and moisture. They consist chiefly in the subdivision of the peat into minute fragments. These are washed, and dried, with or without compression.

The calorific power of peat varies inversely as the amount of water and ash it contains. For peat without ash and water, the calorific power is 5237 *calories*, whilst for ordinary air-dried peat it does not exceed 3000 *calories*.

The specific gravity of peat varies, with the proportion of ash and the mode of preparation, from 0.113 to 1.039.

3. **Lignite.**—Brown-coal or lignite occupies an intermediate place between peat and true coals, there being no abrupt break in the compositions. Indeed, the transition from woody tissue to anthracite is gradual, as is well shown by the following tabular statement, in which the carbon is represented as a constant quantity :—

	Carbon.	Hydrogen.	Oxygen.
Wood	100	12.18	83 07
Peat	100	9.85	55.67
Lignite	100	8.37	42.42
Bituminous coal . . .	100	6.12	21.23
Anthracite	100	2.84	1.74

(*Percy.*)

The term lignite is used by British and American writers as synonymous with the brown-coal of the Germans. It is usually applied to those varieties of coal which are older than peat and more recent than the coals of carboniferous age. Many writers, however, erroneously confine the term lignite or brown-coal to coals of the Tertiary epoch. Four fairly distinct types of lignite may be distinguished—(1) Fossil wood, fibrous brown-coal, the lignite of the Germans, which has a distinct ligneous texture ; (2) Earthy lignite, without structure and earthy in fracture ; (3) Conchoidal lignite, without any distinct vegetable structure and

with a conchoidal fracture; (4) Bituminous lignite, a black shiny fuel sometimes resembling anthracite, and having a conchoidal or earthy fracture. For metallurgical purposes, the first three types only are of importance, the fourth type being used more frequently as material for the production of tar than as a fuel.

When recently raised from the mine, lignites contain as much as 33 per cent. of moisture, and even more. When air dried, however, they lose half this amount. The proportion of ash varies from 3 to 30 per cent. The ash contains lime, alumina, and silica, together with magnesia, some alkalies, and ferric oxide, and an appreciable quantity of sulphuric acid, but as a rule no phosphoric acid. The mean percentage composition of lignite is as follows :—

Variety.	Carbon.	Hydrogen.	Oxygen.
1. Fibrous	57 to 67	5 to 6	28 to 37
2. Earthy	45 to 70	5 to 6	25 to 30
3. Conchoidal	65 to 75	4 to 6	21 to 29
4. Bituminous	70 to 80	6 to 8	12 to 24

Lignite burns with a long smoky flame. The calorific power varies considerably, the mean calorific power of the four varieties being—(1) 5000, (2) 5700, (3) 6500, and (4) 7000 *calories* respectively. The value of lignite as fuel would thus appear to be considerable, but in practice complete desiccation is hardly attainable, and a high percentage of moisture is always retained. The only practical method of increasing the calorific power of lignite is by removing this moisture, and for this purpose drying in air, heating in kilns, or compression has been attempted with considerable success.[*]

4. **Coal.**—Coals, formed previously to the Cretaceous period, are distinguished from lignites by their deep-black colour, great density, and friability. The fracture is more lamellar, the ligneous texture having disappeared. When subjected to dry distillation, they yield a greater amount of carbonaceous residue, and the condensed products contain less water than is the case with fuels of more recent age. Coals contain very little water, and when dried at 100° they are considerably less hygroscopic than wood and lignite. The specific gravity of pure coal, with a low percentage of ash, varies from 1.2 to 1.4, the density being in direct proportion to the percentage of carbon. A cubic yard of coal averages

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[*] Zincken, *Physiographie der Braunkohle*, Hanover, 1867–71.

18 cwt. in weight. The proportion of coke left on distillation varies from 50 to 90 per cent., and the composition of coal varies within the following limits:—

Carbon.		Hydrogen.		Oxygen.
75 to 93	...	6 to 4	...	19 to 3

With the oxygen is included 1 to 2 per cent. of nitrogen. In coals the ratio of the oxygen (with the nitrogen) to the hydrogen varies between the wide limits of 1 : 1 to 4 : 1.

Coals may be classified according to the length of the flame, and the character of the residue which is left when they are subjected to dry distillation. The old classification, based solely on the character of the coke produced, divided coals into two classes, *caking* and *non-caking*, according as the coke produced formed a compact or pulverulent mass. Percy classed coal into three varieties—(1) non-caking or free-burning, rich in oxygen; (2) caking; (3) non-caking, rich in carbon. This classification is based on the chemical composition of the coals, and therefore on their calorific power. Gruner was led to adopt a more detailed classification, in which five types are distinguished—

(1) *Non-caking Coals with Long Flames.*—These coals, which most closely approach lignites, when subjected to dry distillation yield 55 to 60 per cent. of pulverulent coke, the evolution of volatile gases giving rise to a long smoky flame. The composition varies within the following limits:—

Carbon.		Hydrogen.		Oxygen and Nitrogen.
75 to 80	...	4.5 to 5.5	...	15.0 to 19.5

the ratio of the oxygen to the hydrogen being 3 : 1, or 4 : 1. The calorific power varies from 8000 to 8500 *calories*, and the evaporative factor, or number of times its weight of water evaporated by a unit weight of coal from 6.7 to 7.5. Coals of this type are of common occurrence in Scotland, Derbyshire, and Staffordshire.

(2) *Caking, Long-flame Gas-coal.*—Coals of this type contain:—

Carbon.		Hydrogen.		Oxygen and Nitrogen.
80 to 85	...	5 to 5.8	...	10 to 14.2

the ratio of the oxygen to the hydrogen being 2 : 1, or 3 : 1. They yield on slow distillation 60 to 68 per cent. of caked, but very friable and porous, coke, and 32 to 40 per cent. of volatile matter, of which 17 to 20 per cent. is gas. The calorific power varies from 8500 to 8800 *calories*, and the evaporative factor from 7.6 to 8.3.

(3) *Bituminous or Furnace Coal.*—These coals are black, not

very hard; they burn with a smoky flame, at the same time softening and intumescing in the fire.   They contain—

Carbon.		Hydrogen.		Oxygen and Nitrogen.
84 to 89	...	5 to 5.5	...	5.5 to 11

the ratio of the oxygen to the hydrogen being 1 : 1.   They yield 68 to 74 per cent. of caked and swollen coke, and 15 to 16 per cent. of gas.   The calorific power varies from 8800 to 9300 *calories*, and the evaporative factor from 8.4 to 9.2.

(4) *Caking Coals with Short Flame.*—These contain—

Carbon.		Hydrogen.		Oxygen and Nitrogen.
88 to 91	...	4.5 to 5.5	...	5.5 to 6.5

the ratio of the oxygen to the hydrogen being 1 : 1.   They yield 74 to 82 per cent. of caked and very compact coke, and 12 to 15 per cent. of gas.   The calorific power varies from 9300 to 9600 *calories*, and the evaporative factor from 9.2 to 10.

(5) *Anthracitic Coals.*—These burn with a short flame, and have the following composition :—

Carbon.		Hydrogen.		Oxygen and Nitrogen.
90 to 93	...	4 to 4.5	...	3 to 5.5

the ratio of the oxygen to the hydrogen being 0.5 : 1.   These coals form the transition to true anthracites.   On coking, they yield 82 to 92 per cent. of pulverulent or fritted coke, and 12 to 8 per cent. of gases.   The calorific power varies from 9200 to 9500 *calories*, and the evaporative factor from 9 to 9.5.   Coals of this type are met with in South Wales and in Pennsylvania.

The percentage of ash yielded by the several varieties of coal ranges from 1 to 30, but seldom exceeds 7.   The ash consists mainly of silica, with alumina, lime, magnesia, ferric oxide, and manganic oxide.   Sulphuric acid is also frequently present; but the proportion of phosphoric acid is usually inconsiderable.

5. **Anthracite.**—This is the ultimate product of the conversion of vegetable matter into coal.   Its colour is jet black, with a vitreous lustre; its structure homogeneous, and its fracture conchoidal.

The mean of a large number of analyses gave the following as the composition of true anthracite, free from ash :—

Carbon.		Hydrogen.		Oxygen and Nitrogen.
93 to 95	...	2 to 4	...	3.0

The proportion of nitrogen varies from 0.55 to 2.85 per cent., and that of sulphur from 0.63 to 1 per cent.; ratio, 1 : 1 to 1 : 0.5.

Anthracite burns almost without flame, and the carbonaceous residue remaining after distillation shows no signs of caking. The anthracite of Pennsylvania is employed on a large scale in the manufacture of pig-iron. In the United Kingdom this is not the case, as the anthracites will not stand a high temperature without disintegration.

It must be borne in mind that " coal " is a popular rather than a scientific name, as it is frequently applied, not only to beds of fossilised vegetation, but to all mineral substances capable of being used as fuel. According to Frémy,* true coal may be distinguished from lignites by its insolubility in hypochlorites, and its very imperfect solubility in nitric acid.

Coals having widely different properties may be proved by analysis to contain exactly the same amounts of carbon, hydrogen, and oxygen, so that in the respective cases the grouping of these elements must vary greatly. Coals, in fact, may be isomeric.

It is found that the calorific power of true coal and lignites increases with the proportion of coke left by distillation, and the student will do well to bear in mind that the calorific value of a coal may be better estimated by weighing the coke left after strongly heating the coal in a covered crucible than by calculations based on a chemical analysis of the sample. The class to which the coal belongs may also be best determined by this method of distillation in a closed vessel, which enables the relative amounts of water, bituminous matter, and coke to be ascertained. The method of coking in a covered crucible also gives valuable information as to the nature of the coke.

6. **Liquid Fuels.**—Under the general term of *petroleum* is included a series of natural hydrocarbons. These usually occur in nature impregnating clay, marl, sand, and schist, sometimes sufficiently to render the rock combustible. The high percentage of ash in such fuels prevents them from being used direct, and, as a rule, renders it necessary to subject them to distillation, which yields tar products, oils, and gases. The so-called " Boghead mineral," a bituminous schist of the Scotch coal measures, yields—

Ash.		Fixed Carbon.		Combustible Gases.
19.60	...	10.13	...	70.10

Cannel coal is a fuel of a similar character, but with a low percentage of ash. It burns with a long smoky flame, and has the following percentage composition :—

Carbon.		Oxygen.		Hydrogen.		Ash.
85.0	...	8.0	...	5.0	...	2.0

* *Comptes Rendus*, vol. lii. (1861), p. 114.

It yields 42 per cent. of volatile matter. The mineral *jet* is a bituminous lignite. When the bituminous constituents of these rocks occur in sufficient quantity, naphtha and petroleum springs, or deposits of solid asphalt, are formed. At Baku in the Caspian Sea, and in Pennsylvania, mineral oils are obtained in enormous quantities by means of deep bore-holes. The oil regions of Pennsylvania alone have a productive area of 364 square miles, and the total output from 1859 to 1884 was 260,990,035 barrels, each of 42 gallons.

Petroleum contains a very high proportion of hydrogen, which in the case of the solid bituminous materials may reach 15 per cent. On distillation, from crude petroleum a product is obtained containing 79.82 to 88.5 per cent. of carbon and 11.5 to 20.18 per cent. of hydrogen. The boiling-point of petroleum varies from 110° to 280°, and the calorific power of the crude oil is 10,000 *calories*, a calorific power which is greater than that of refined oil.

The oil is employed in practice by burning it in a trough, by effecting its combustion in a spray or finely divided form by injecting it with a jet of steam or air, or by converting it into gas before combustion.*

7. **Natural Gas.**—In the oil regions of Pennsylvania and of the adjoining States, natural gas issues from the strata at a depth of 500 to 2000 feet below the surface; and when bore-holes are sunk to the accumulated gas, it rises under a pressure of some 200 lbs. per square inch. When first reached, the gas is sometimes evolved at the enormous pressure of 1000 lbs. per square inch. Compared with air the gas has a density of 0.45 to 0.55, and varies in volumetric composition within the following limits:—

CH_4.	H.	N.	C_2H_6.	C_3H_4.	CO_2.	CO.
60 to 80	5 to 20	1 to 12	1 to 8	0 to 2	0.3 to 2	trace

It has a calorific power of 14,000 to 15,600 *calories*, and a calorific intensity of 2745° to 2765°. Natural gas has long been used in Pennsylvania to a limited extent for heating purposes. Since 1883, however, it has attained a remarkably rapid development for industrial purposes, and is now largely used in Pittsburgh in the blast furnace, and for other metallurgical purposes.

The territory containing the source of natural gas includes a section of country extending from Western New York, through Pennsylvania, into West Virginia and Ohio. It is estimated that

* On petroleum, consult Crew, *Practical Treatise on Petroleum*, Philadelphia, 1887.

in 1884 as much as £292,000 worth of coal was supplanted by natural gas, about two-thirds of this amount representing the consumption of the Pittsburgh district. The freedom of the gas from sulphur has been an important element in its metallurgical value.*

II. Prepared Fuels.

1. **Compressed Fuels.**—Numerous attempts have been made to prepare a good fuel by mixing some binding material with small coal in proportions sufficient to enable the particles to cohere so as to be pressed into a block or *briquette*. Potato-meal, soluble glass, asphalt, and turpentine have been used as binding materials, but abandoned, whilst coal-tar, pitch, and even treacle have been successfully used for the purpose.†

2. **Dried Fuels.**—The advantages derived from the expulsion of the water and a certain proportion of the more volatile constituents of wood, peat, and lignite have already been pointed out.

3. **Carbonised Fuels.**—On heating fuels without access of air, their constituents re-arrange themselves in the form of solid, liquid, and gaseous compounds. For metallurgical purposes, the object of this operation is often only to obtain the solid constituent, charcoal or coke, which consists of carbon with subordinate amounts of hydrogen, oxygen, and ash-giving constituents, and which has a high calorific intensity. At the same time, the by-products obtained during the carbonisation are frequently utilised. The carbonised fuels to be considered are—(*a*) charcoal and (*b*) coke.

(*a*) **Charcoal.**—This name is given to the carbonised residue remaining after the dry distillation of wood. When wood is heated to 200° without access of air, it remains unaltered; at 220° it becomes brown; and at 270° to 300° it suffers decomposition, torrefied wood (*Rothholz*) being formed. At 350° it is resolved into a fixed residue, or charcoal, and volatile products. Good charcoal prepared at a temperature of 350° to 400° retains the structure of the wood from which it was derived, the volume being less. It is black, porous, and burns without smoke, and, in separate pieces, without flame. The specific gravity of porous charcoal varies from 0.28 to 0.54 according to the nature of the original wood, and the temperature at which it was made.

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* On natural gas, consult Phillips, *Rep. Second Geol. Surv. of Pennsylvania*; Carnegie, *Journ. Iron and Steel Inst.*, 1885, p. 168; Ashburner, *Trans. Amer. Inst. M.E.*, vol. xiv. p. 428.

† Compare Preissig, *Die Presskohlenindustrie*, Freiberg, 1888.

Charcoal prepared at 350° is considerably lighter than that prepared at the melting-point of platinum.   Hard woods give a dense and heavy charcoal, whilst soft woods give soft and friable charcoal.   The chemical composition also varies considerably, the percentage composition of charcoal prepared at 340° (I.), and at the melting-point of platinum (II.), being as follows :—

	Carbon.		Hydrogen.		Oxygen and Nitrogen.
I.	75.20	...	4.41	...	19.96
II.	96.52	...	0.62	...	0.94

The ash of the first charcoal was 0.48, and of the second 1.94 per cent.   On an average, dry charcoal contains 90 per cent. of carbon, 3 per cent. of hydrogen, and 7 per cent. of oxygen and nitrogen.

The charcoal used in metallurgical operations is prepared by various methods, which may be divided into two groups—viz., methods of coking (1) in the open air and (2) in closed chambers. For charcoal burning in the open air, a suitable site is necessary. This should be dry, and sheltered from any prevailing wind. Water should be at hand for quenching the charcoal when made. The wood employed must be mature, cut while free from sap, barked, and air dried for some months.*

When the charring is effected in *circular piles*, or meilers, the bed is made to slope from the circumference to the centre at an inclination of 1 in 15.   Three stakes, 10 to 15 feet high, are driven in near the centre, so as to form a central triangular chimney.   Around this, the timber, cut into suitable lengths, is stacked horizontally and radially.   The mass is then covered with a mixture of fine charcoal and clay, and then with sods with the grassy side inwards.   To keep this covering up, wedges are driven in, and props put in so as to form hoops around the lower part of the pile.   Brushwood is then thrown down the chimney, and ignited, vents being made near the top of the pile.   This causes a cone, with the apex downwards, of the pile to be charred, and, by opening vents lower down, the angle of the cone is enlarged.   This process is continued until the base is reached.   When the smoke issuing from the pile is seen, by its blue colour, to be free from aqueous vapour, the charring is complete.   The charcoal is then drawn from the bottom of the pile and in small quantities quenched with water or dust.   Small piles are carbonised in six to

* On charcoal burning, consult G. Svedelius' *Handbook for Charcoal Burners*, translated from the Swedish by R. B. Anderson and W. J. L. Nicodemus (New York, 1875).

fourteen days; but if the diameter be more than 30 feet, the process occupies a month.

Logs as much as 24 feet in length may be charred in *rectangular piles*. They are laid together in the form of a wedge, of which the breadth is limited by the length of the logs. The heap is 20 to 30 feet long, and 7 to 9 feet high at the upper end, and only 3 feet high at the lower end. It is surrounded on all sides with a layer of sods and charcoal dust, and by a wooden covering supported by vertical stakes. On the top is placed a roof of twigs, leaves, and charcoal dust. At the lower end, a horizontal chimney is left. Vents are opened at the opposite end so as to give planes of charring. Rectangular piles are used in Sweden and in Austria. In China the carbonisation is effected in pits provided with a chimney communicating with the bottom.

Experiments, on a large scale, on the amount of charcoal yielded gave the following results :—In France, with circular piles of 2120 to 3180 cubic feet, the yield by weight was 17 to 21.3 per cent.; in Belgium, on charring wood fifteen to twenty years old, half hard, half soft, the yield at the ordinary rate was 15 to 17 per cent., but when charred more slowly, 20 to 22 per cent.; in Sweden, from pine wood, the yield was 20 to 28 per cent. By volume, the yield of charcoal varies from 50 to 75 per cent.

By using closed ovens or kilns, the yield of charcoal may be somewhat increased, but as about 5 per cent. is required for heating the oven or retort, the advantages presented are very slight. Peat may be charred, like wood, in heaps or in kilns. Peat-charcoal, however, on account of its lightness, friability, and its high percentage of ash, is not adapted for metallurgical purposes, and its application has not advanced beyond the experimental stage.

(*b*) **Coke.**—Coke is the carbonaceous residue left on the dry distillation of coal. Good coke should possess sufficient strength to withstand the pressure in a blast furnace without crushing. For this reason, only those coals which give on dry distillation a coherent residue can advantageously be used. The coals of the second, third, and fourth groups of Gruner's classification are suitable for coking. A high percentage of ash has a detrimental influence on the coke produced, and must therefore be removed by subjecting the coal to a preliminary washing.

Coke varies considerably in its external characters. It may be porous and light, or compact and heavy; black and dull, or light-grey and bright, with a semi-metallic lustre. The porosity of coke induces a tendency to absorb gas : for example, Belgian locomotive coke contains—

Carbon.		Hydrogen.		Oxygen.
97.33	...	0.35 to 0.50	...	2.18 to 2.32

Like charcoal, coke is hygroscopic, absorbing 1 to 2.5 per cent. of water from air at the ordinary temperature. When dipped in water, coke will absorb 20 to 50 per cent. The calorific power of coke, free from ash, is 8000 *calories*, or almost equal to that of pure carbon.

The earliest method of preparing coke was by carbonising coal in the open air in heaps, without any external covering. A more economical method is by carbonising the coal in mounds, piled round a central octagonal chimney. The mound is ignited at the top, and the operation proceeds exactly as in charcoal burning. The mounds are usually 12 to 21 feet in diameter, and 9 to 15 feet high. The yield after five days' coking is 65 per cent. of the theoretical quantity.

In Upper Silesia, rectangular kilns have been used for coking for many years. They are cheap, easy to work, and give a large output, but, like the mounds, they do not yield a uniformly coked product. They are chiefly used for coking coal slack. These kilns, or Schaumburg coke-ovens, Fig. 46, have two fixed parallel
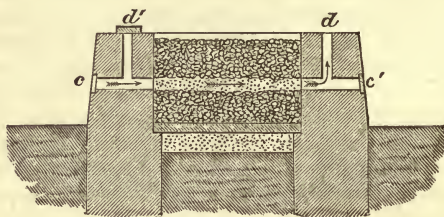
FIG. 46.

walls 18 yards long and 5 feet high. The walls are 8 feet apart, and are provided with a series of square openings 2 feet apart and 1 foot above the sole, the apertures, *c*, in one wall being opposite those in the other. From each aperture ascends a vertical flue, *d*, which may be closed with a tile. In order to charge the kiln one of the open ends is bricked up, and moistened coal slack is stamped-in up to the level of the apertures. From the apertures in one wall wood stakes are placed across, the ends passing into the corresponding apertures on the opposite side, and the whole kiln is filled with moistened slack, and covered with loam. On withdrawing the stakes, the passages formed communicate with the horizontal apertures and with the vertical flues in the side

walls. The process consists merely in regulating the air current in the flues, and is complete in about six days. The flues are then closed, and the coke, after cooling for two days, is withdrawn at the open end.

These wasteful methods of coking are now generally superseded by coking in ovens of brick or stone, in which carbonisation is effected mainly by the heat resulting from the combustion of the volatile products evolved during the process, the aim of the coke-burner being to bring air into contact with these gases, but to prevent its contact with the coke formed.

The coke-ovens that have been introduced to obviate the loss of heat occurring in heaps and kilns are of very various types. The simplest form resembles a beehive or a baker's oven. This is a sort of covered-in mound or meiler. It is lined with fire-bricks, and air is admitted through a doorway closed with loosely piled up fire-bricks. There is thus, as in the cases of the mound and kiln, partial combustion in the coking space itself, and so some coke is burnt. The cavity of the oven is 6 to 12 feet in diameter, and $4\frac{1}{2}$ to 9 feet in height. The doorway is about $2\frac{1}{2}$ feet square, and the coke is drawn through it and quenched in the open air. In some cases the coke is cooled in the ovens before it is drawn by watering it by means of a hose. This quenching, by double decomposition, removes some of the sulphur from the coke in the form of sulphuretted hydrogen. Sometimes the ovens have the form of a rectangular chamber 10 feet deep, 12 feet wide, and 10 feet high. The working of the ovens is very simple. On the base, heated from the last charge, or on a layer of slack, the coal ($1\frac{1}{2}$ to $4\frac{1}{2}$ tons) is charged in. The door is then closed, and carbonisation commenced. If the oven was cold, before shutting the door, fire is introduced, and the lower holes in the doorway are left open. The coking proceeds from the top downwards, the draught-holes being successively stopped as the level of the carbonisation sinks. The coking lasts twenty-four to forty-eight hours.

In the improved forms of coke-ovens, air is not admitted into the coking space, but into side flues, so as to mix with the gaseous products passing through openings in the oven walls into the side flues. In this way, use is made of the heat afforded by the ignited gases which are, in the older forms of oven, allowed to pass directly into the chimney or into the open air; there is complete combustion of all the gaseous products, and the ovens are heated without any coke being actually burnt.

All ovens for coking without access of air have a prismatic form, with a quadrilateral section. They may be classed, accord-

ing to the position of the principal axis, into three types—(1) those with a horizontal axis, (2) those with a vertical axis, and (3) those with an inclined axis.

Numerous varieties of ovens with horizontal axes have been introduced, and worked with more or less success. In all these ovens, the object sought is to utilise the gases to the highest possible degree by effecting the coking by their combustion. At first, this led to the adoption of complicated constructions, which have recently been greatly simplified, and the main differences in the system of heating and in the arrangement of flues depend on whether the gases from one coking chamber play on its own walls and floor, or whether the gases from two adjacent ovens are united for heating both chambers, the object being to mix the products of distillation and combustion from coal which has been newly introduced with those from coal which has been longer in the oven.

Of ovens with horizontal axes, the Coppée coke-oven is that most generally in use. It is designed for coking finely divided coal. The Coppée ovens are usually built in series of thirty or forty, and are worked in pairs. The ovens, which are 30 feet long, 18 inches wide, and 4 feet high, have each twenty-eight vertical flues leading from the top through the partition-wall common to two ovens, to the horizontal flues that pass underneath the chambers in the direction of their length. In these horizontal flues, the gases from a freshly charged oven mix with those from one in which the coking is nearly complete, and combustion is effected by air admitted through three small openings. At each end of an oven are two metal doors. The coke is removed from the oven by means of a ram propelled by a cogged driving-wheel worked by a small portable engine. When the coking is complete, the engine and ram are placed opposite the end of the oven, and the coke is pushed out, the operation lasting about two minutes. A jet of water is then applied to the coke. At the same time the lower doors of the oven are closed, and coal is fed in through three openings in the roof, the openings being then covered by sliding doors. The coal is then levelled by means of rakes, and the upper doors are then closed. The whole operation, from the opening to the closing of the doors, lasts only eight minutes. At Dowlais there are thirty of these ovens, numbered consecutively; those with odd numbers are drawn in the morning, and the even twelve hours later, the coking occupying twenty-four hours.

Only one oven, with a vertical axis, has been successfully adopted. This was invented in 1856 by the brothers Appolt,[*]

* *Annales des Mines*, vol. xiii. (1858), p. 417.

and is now largely used on the Continent. It consists of twelve or more vertical coking chambers of brickwork, arranged in rows, the series being surrounded by walls of brickwork. The ovens are rectangular in plan; they are tapered, measuring, at Saarbrücken, 4 feet 1 inch by 1 foot 7 inches at the lower, and 3 feet 8 inches by 1 foot 2 inches at the upper end, and 16 feet in height. Each oven is surrounded by an air space 10 inches in width, and is provided above with a lid, and below with a door opening downwards into a vault where the coke may be received in an iron waggon. As the charging is also effected by waggons on the top of the furnace, the working is extremely simple. The brickwork of the ovens is separated by air spaces which communicate with one another, and with the interior of the ovens themselves. The products of combustion are carried off to the chimney by means of flues, which have fire-brick dampers for regulating the draught, and in which there are openings to allow of their being cleaned out. The gases from the coal pass into the air spaces surrounding the retort, where they mix with air introduced through flues in the wide sides of the ovens. As in all coke-ovens, the process is conducted by first heating the ovens to redness. They are then filled, and the process may be carried on uninterruptedly. The charge in each chamber is 1 ton 4 cwt. to 1 ton 8 cwt., so that the whole oven cokes about 17 tons of coal in twenty-four hours. The Appolt coke-oven presents the advantage of a very great heating surface in proportion to its capacity, which is easily explained by the fact that each chamber is completely surrounded, with the exception of the two end planes, by fire. Thus, much less heat is lost by cooling from without. Dürre estimates the internal area of the walls at 50 to 58 square feet per cubic yard of capacity, and Kerpely states that the heating surface is more than 1 square foot per 20.5 lbs. of charge. In either case the ratio is double that in the case of horizontal coke-ovens. The average yield of coke is 70 to 80 per cent. with caking coal, and very good results have been obtained with a mixture of caking and non-caking coals. The vertical position of the compartments presents the advantages of occupying less space than other ovens; the coke in dropping down exerts no injurious amount of wear on the sides, and the pressure of the column of coal produces a coke of greater density than that obtained in other ovens. On the other hand, the Appolt coke-oven has the disadvantage of high initial cost, which is double that of any horizontal coke-oven. The cost of an Appolt coke-oven with eighteen chambers is £1500 to £2000. Repairs, too, are effected with much difficulty.

Coke-ovens with inclined axes are used to some extent in the Saarbrücken district. The complicated character of their construction has, however, prevented their general adoption.

Many attempts have recently been made to collect the by-products—ammoniacal liquors and tar—produced during the carbonisation of coal. Henry Simon* calculates that in the British ironworks alone, which produce annually some seven million tons of coke, by the collection of by-products an annual saving of £1,350,000 might be effected. Of the methods in practical operation for collecting the by-products from coke-ovens, that of Simon-Carvès has been most largely adopted. The construction of this coke-oven is somewhat similar to that of the Coppée. There are charging holes, a, a', a'', in the roof of the oven. The gases are drawn off through a pipe, b, b', b'', which is provided with a regulating valve. From here the gases pass into a system of pipes common to 30–50 ovens, and kept cool by jets of water, so that the tar and ammoniacal liquors are condensed. The lower open ends of the pipes dip into a collector for the products of condensation similar to that employed in many gas-works. The gases from the condenser are then passed through scrubbers filled with moistened coke, where the last traces of ammonia are removed. The uncondensed gases pass onwards to the oven for heating purposes, entering through a horizontal aperture, c, c', in the basal flue of the oven above a grate, d, that is filled with ignited coke-dust, whilst the air for combustion enters from below through the grate. Under the base of the oven the burning gases pass to and fro once, then rise between two adjacent ovens to the uppermost of the side flues, e, e', e'', and pass gradually downwards to a large flue, f, which conveys them to the chimney or under steam boilers. The ovens are 2 to $2\frac{1}{2}$ feet broad and $5\frac{1}{2}$ to $6\frac{1}{2}$ feet high. A greater breadth has not been found to answer. The duration of coking with the smaller oven is from sixty to seventy-two hours. The yield is about 75 per cent. The coke produced possesses sufficient resistance to render it suitable for blast-furnace use. In 1879, at the Bessèges Ironworks, in France, the amount of coke produced from ninety-six ovens of this type was 33,092 tons, together with 1099 tons of tar and 4399 tons of ammoniacal liquor. The consumption of coke-dust on the grate did not exceed 35 lbs. per ton of coke produced.

In the recent Carvès oven, the fireplace and grate are dispensed with, and the oven is fired exclusively by the gases escaping con-

* *Journ. Iron and Steel Inst.*, 1880, p. 137.

Horizontal section on E-F

Section on A-B

Section on C-D
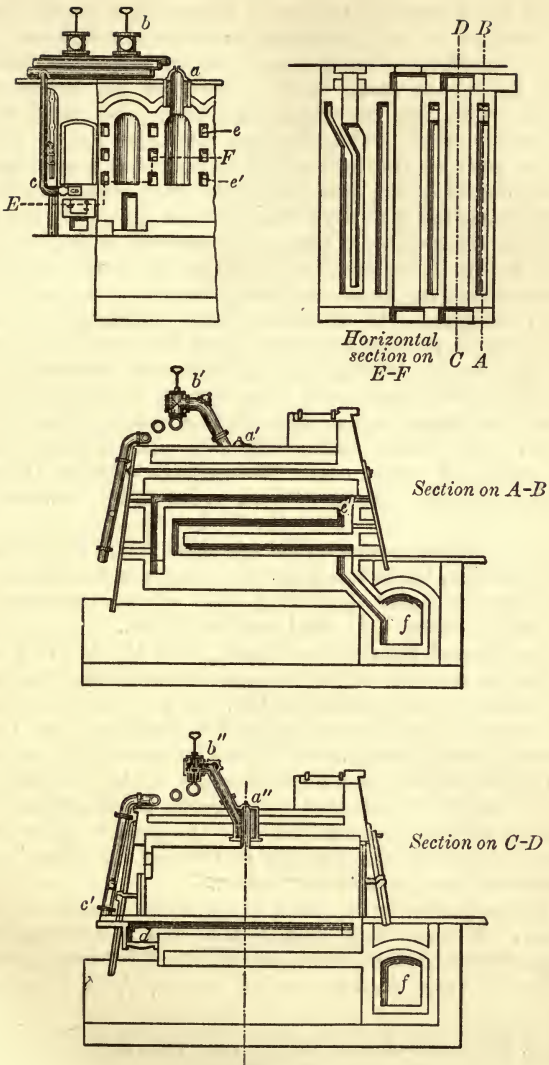
Fig. 47.

densation, these entering the lower flue at the place where the
hearth used to be, whilst air is forced in through an annular
pipe.   In the Simon-Carvès oven* the air introduced receives a
previous heating to some 500° or 600° by its being brought
into contact with the hot flues conveying away the spent fire-
gases from the ovens.   The two lower flues are thrown into one,
and, at the part of the bottom flue where the greatest heat is
sustained, the walls are lined with the best silica bricks.   The
heated air admitted into the bottom flue is purposely insufficient
for complete combustion of the gas introduced there, the further
supply of hot air being admitted into the side flues of the oven.
The arrangement for thus admitting the air is completely con-
trolled by dampers.   At the Bear Park Colliery, Durham, fifty
of these ovens have been erected.   Each is charged with $4\frac{1}{2}$ tons
of coal, the time for coking being a little over forty-eight hours.
At Messrs. Pease's collieries, near Crook, Durham, there are
twenty-five of these ovens, each 23 feet long, 6 feet 6 inches
high, and $19\frac{1}{2}$ inches wide, with side and bottom flues, the
capacity being $4\frac{1}{4}$ tons of coal.   The average cost of an oven of
this description, if a hundred were erected, is calculated to be
£180.

The Pernolet coke-oven (Fig. 48) differs but little from the
ordinary beehive, but it has a fireplace and grate, and the gas is
carried into the upper collecting tube a, and returned to the
bottom flue, b, where it is fired with solid fuel.

At the Almond Ironworks, Falkirk, Mr. H. Aitken† adapted
means for the recovery of by-products to the beehive oven.   The
Aitken coke-oven, as shown in Fig. 49, is a beehive oven fitted
with two pipes, a, a', for conveying the blast and gas from the
condensers through small openings in the roof distributed equally
round the circumference, whilst channels, b, b', b'', in the floor of
the oven conduct the collected by-products to an external pipe, c,
which leads them to the condensers.   The main body of the oven
measures 5 feet from the opening in the roof for filling in coal to
the floor, and has a diameter of 9 feet.

The Jameson coke-oven ‡ is another improvement on the bee-
hive oven.   It is shown in cross-section and in sectional plan in
Fig. 50.   In the bottom of the ordinary beehive oven, a, channels
are formed, covered with perforated tiles, b, b', b'', connected out-

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* *Journ. Iron and Steel Inst.*, 1883, p. 494; 1885, p. 108.
† *Trans. N. Eng. Inst. M.E.*, vol. xxix. (1879).
‡ *Journ. Soc. Chem. Ind.*, vol. ii. (1883), p. 114; *Journ. Iron and Steel
Inst.*, 1883, p. 504.
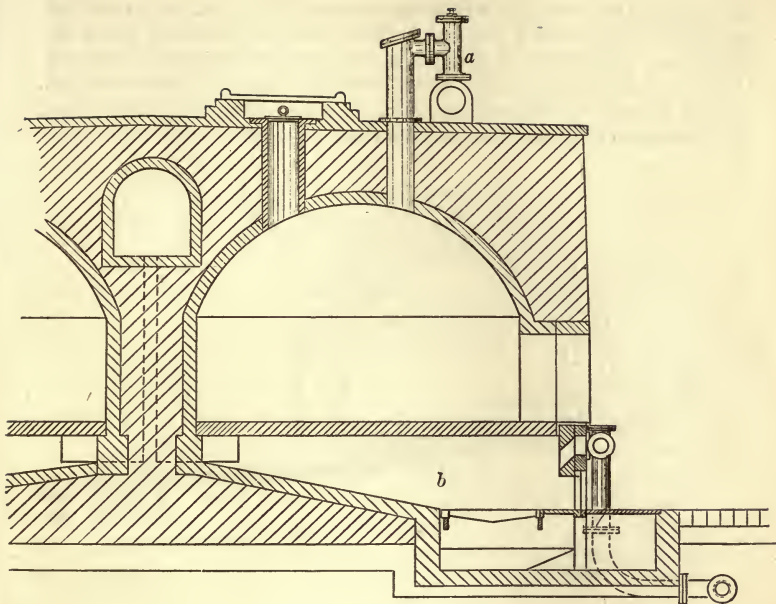
FIG. 48.
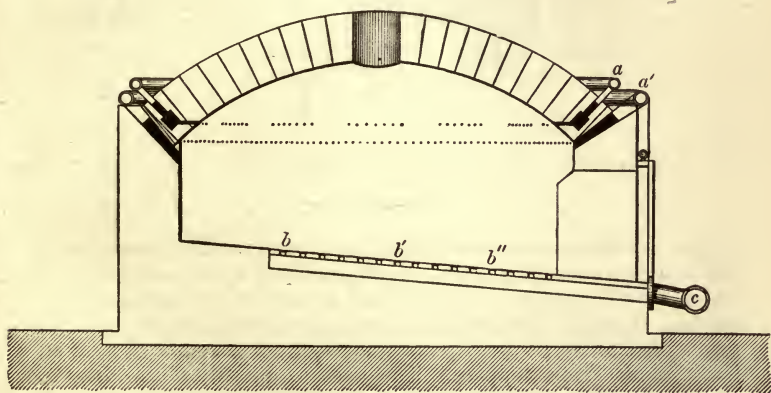
FIG. 49.

side the oven with pipes leading to apparatus, c, c', for producing a slight suction and for discharging the by-products when required. The cost of applying this process is small, and the results of a series of trials show that the average yield of coke is 65.49 per cent., the average yield of ammonium sulphate and of oil being 4.6 lbs. and 6.1 lbs. per ton respectively.
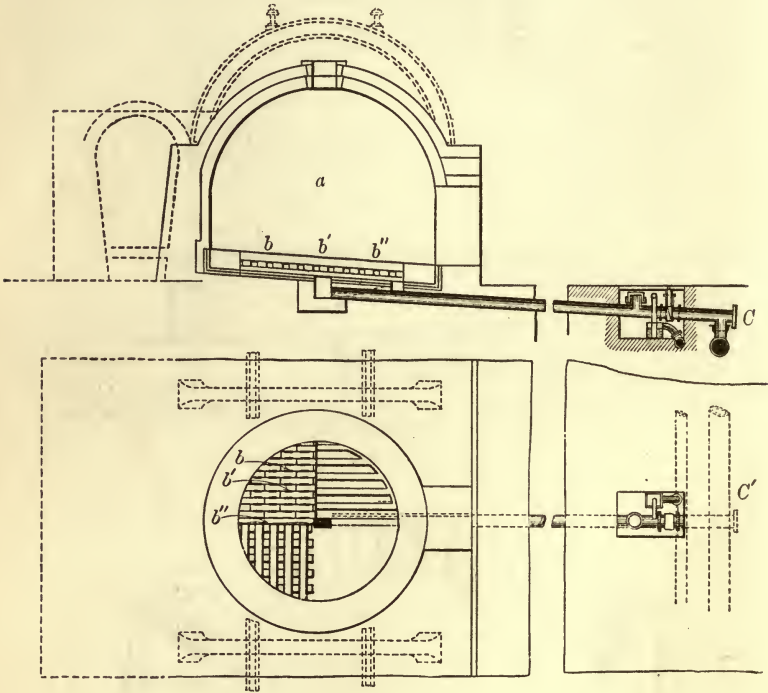
FIG. 50.

The Lürmann coke-oven (Fig. 51) works continuously, and yields a good compact coke. It consists of a large chamber, a, which may be either a huge tunnel or arched as shown in the figure. Opening into this are a number of coking chambers, b, b', into which fine coal is fed continuously by a piston-feed, worked by a crank, from hoppers. The gaseous products pass into a, and, if required to be collected, they are drawn off at an aperture at the top, and thence conducted into the spaces, c, c', under the

retorts b, b', where they are burnt by means of air admitted for the purpose. The coke as it falls from the ends of b, b', is received in a, and is removed at intervals. A great advantage presented by this coke-oven is that it does not need special fire-bricks.

4. **Gaseous Fuel.**—The use of gaseous fuel in metallurgical operations has effected a great saving in coal. Besides this advan-
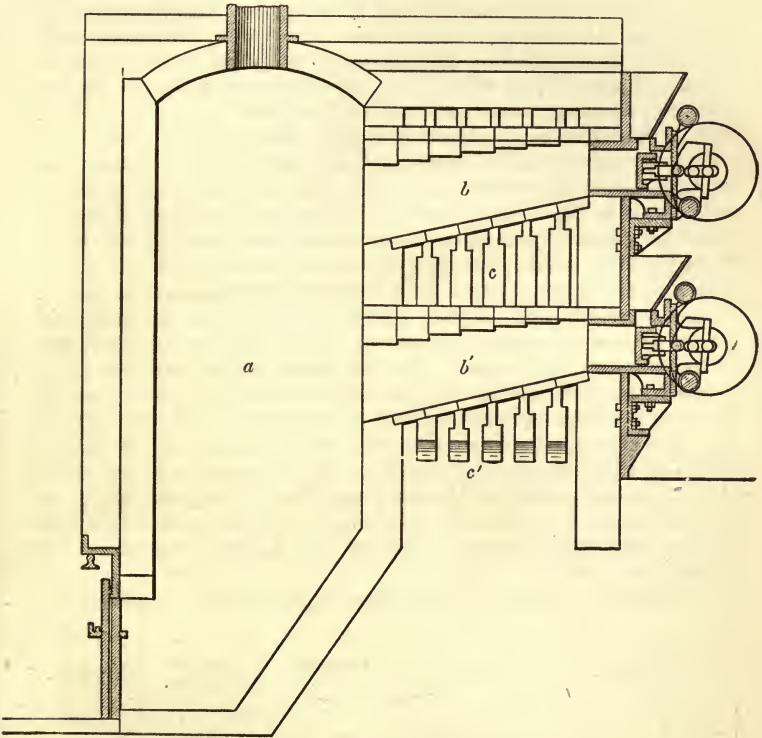
FIG. 51.

tage, there are two circumstances that must lead to its more general adoption; these are the possibility of employing inferior fuels and waste products, and the high temperatures attainable by the use of such fuel. The method of gas-firing is, however, still far short of a universal adoption, but it may be predicted that, as the sub-

ject becomes more widely understood, the examples of any other method of treating fuel will become rare.

The use of gas as fuel is based on the principle that at one place all the fuel is converted into combustible gas, which is consumed by admixture with the necessary amount of air at another. These gases are produced by burning the fuel in a long column, whereby most of the carbon is burnt to carbonic oxide, whilst the hydrogen either remains free or is converted into carburetted hydrogen. Directly above the grate carbonic anhydride is formed, but this is converted into carbonic oxide on passing through the column of heated fuel above it. The reaction is shown by the following equation :—$CO_2 + C = 2CO$. As a rule, the finer the fuel, that is, the more compactly it lies, the lower is the column required for the reduction of the carbonic anhydride. Besides the products of combustion mentioned above, distillation products are formed in the upper layers of the fuel and mix with the combustible gases. Amongst these, heavy carburetted hydrogen (C_2H_4) is that which principally increases the value of the gas as fuel, and the drier the fuel used the more of this gas is produced.

The decomposition of fuel into combustible gas is effected in special apparatus, termed *producers*, from which it is conducted to the furnace, and burnt. For the formation of producer-gases a certain temperature is required, which must not be exceeded. This temperature is dependent on the amount of air introduced. If this is large, complete combustion is effected, and the desired object is only imperfectly attained. If, however, it is too small, the heat is not sufficient for the formation of carbonic oxide, and the evolution of gas ceases. The exact amount of air that should be introduced into a gas-producer can only be determined by experiment.

The composition of producer-gases is, by weight, as follows :—

Fuel Used.	Nitrogen.	Carbonic Oxide.	Carbonic Anhydride.	Hydrogen.
Wood . . .	53.2 to 55.5	21.2 to 34.5	11.6 to 22.0	0.7 to 1.3
Charcoal . .	64.9	34.1	0.8	0.2
Peat . . .	63.1	22.4	14.0	0.5
Coke . . .	64.8	33.8	1.3	0.1

The gas-producer first assumed importance in 1856, on the introduction of the Siemens regenerative system. In 1861 the well-known Siemens gas-producer was patented. It consists of a chamber lined with fire-brick, with one side sloping at

an angle of 45° to 60°, with the grate at the bottom. The grate thus resembles the step-grate largely used on the Continent. The fuel is charged in at the top of the incline, and falls in a thick bed upon the grate, where air is admitted. Passing from the top of a brick shaft or up-take, 8 to 10 feet high, placed above the producer at the back, there is a cooling tube, having not less than 60 square feet of surface per producer. Its object is to cool the gases issuing from the producer, thus giving them increased density, causing an onward movement towards the furnace, and rendering it unnecessary to place the producer at a much lower level than that of the furnace. This cooling, however, results in a condensation of tar, and, to overcome this annoyance, modifications have been adopted in the producer and its working. In the new type of Siemens producer the volatile products of distillation are obliged to descend through highly heated fuel, thus causing the tar to undergo decomposition.

The principal forms of gas-producers are described by Rowan.* Since the introduction of the regenerative principle, many designs for furnaces have been proposed, without separate gas-producers. One of the most successful of these is the Boëtius furnace, largely used for zinc-smelting.

The Wilson gas-producer (Fig. 52), working under a slight pressure, presents the advantage of burning fine slack coal. Fuel is introduced in the chamber A, through a hopper, h. The ashes are drawn by two small doors, c, at the bottom every twenty-four hours, the operation occupying about twenty minutes. During this time the production of gas is stopped. The producer represented in the figure has a diameter of 8 feet, and is constructed to burn 4 cwt. of small coal per hour. Air is injected into the chamber by two steam jets, b, each having a diameter of $\frac{1}{8}$ inch.

Analyses of gas from the Wilson producer gave the following results :—

	I.	II.	III.
Carbonic oxide	26.89	23.41	23.60
Marsh-gas	1.45	2.22	3.05
Hydrogen	11.55	13.82	10.55
Nitrogen	56.11	55.86	57.55
Carbonic anhydride	4.00	4.69	5.25
Totals	100.00	100.00	100.00
Percentage of combustible gas . .	39.89	39.45	37.20

* *Min. Proc. Inst. C.E.*, vol. lxxxiv. p. 2.

I. is from a producer using Durham coal. II. is an average of six samples of gas taken over a time of one hour from a producer working on fine slack from a Yorkshire colliery. III. is from a producer working with coal of the Jemmapes district, near Mons, Belgium.

In 1814 Aubertot first used the waste gases of blast furnaces for roasting ore, burning lime, and similar purposes, and these
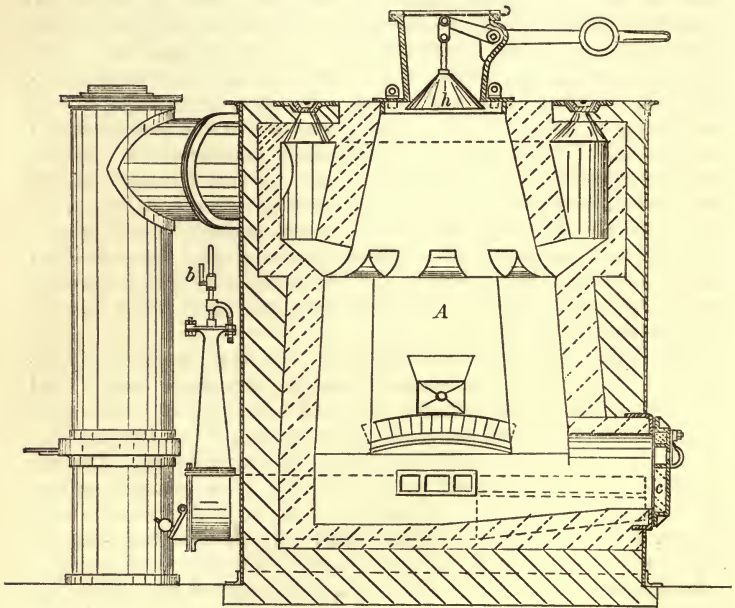
FIG. 52.

gases are now largely used when a very high and uniform temperature is not required. The composition by weight of the waste gases, according to the fuel used in the blast furnace, is as follows :—

	N.	CO.	CO_2.	CH_4.	H.	C_2H_4.
Charcoal . .	59.7–63.4	20.2–29.6	5.9–19.4	0.3–1.0	0.1–0.4	—
Coke . . .	64.4	34.6	0.9	—	0.1	—
Coal . . .	56.3	21.5	15.2	4.2	1.0	1.8

Water-gas.—The gaseous fuel known as water-gas is made in the following manner:—An iron cylinder is lined with fire-brick, and provided with the necessary apparatus for introducing the coke. When this has been lighted, a current of air is forced in until the mass is brought to a high temperature. The blast is then stopped, the charging aperture is closed, and a jet of steam is passed through the incandescent carbon. The steam is decomposed; its oxygen burns the carbon into carbonic oxide, setting free the hydrogen. The resulting mixture is known as water-gas. It consists of one volume of hydrogen and one volume of carbonic oxide, the weights being in the proportion of 2 to 28.

If, by burning one unit of carbon, it were possible to generate one unit of hydrogen, the exchange effected in the water-gas apparatus might be a very profitable one. Such a condition of things is, however, shown by Sir Lowthian Bell[*] to be directly opposed to the known facts of the case, for 25 per cent. only of the carbon used is burnt to the condition of water-gas, whilst the other 75 per cent. is converted into producer-gas, containing 68 per cent. of inert nitrogen. From 25 parts by weight of carbon there will be generated 62.5 parts of water-gas, containing 4.16 of hydrogen and 58.34 of carbonic oxide. The producer-gas from the remainder (75 parts) of the carbon will weigh 551.19 parts, of which 376.19 will be incombustible nitrogen and 175 carbonic oxide. The following estimate gives the quantity of heat generated by the combustion of the two gases:—

Water-gas .	.	4.16 of H	from steam × 29400	= 122304	
		58.34 of CO	,, × 2400	= 140016	
		——			262320
		62.50			
Producer-gas	.	175.00 of CO	× 2400		420000
		376.19 of N			
		551.19	*Calories* .	.	682320

Had the 100 parts of carbon been burnt direct, the heat generated would have been 800,000 *calories*. The loss is thus 14.71 per cent. Besides this, as coke was used, there is the loss of combustible matter which is incurred at the coke-oven, and the labour in conducting the process of coking.

Sir Lowthian Bell calculates that the relative values of coal, producer-gas, and water-gas are as follow:—

Coal .	.	.	.	.	.	.	.	. 83.93
Producer-gas	.	.	.	.	.	.	.	71.14
Water-gas and its producer-gas	.	.	.	.	78.80

[*] *Journ. Iron and Steel Inst.*, 1889, No. ii. p. 139.

Bibliography.—For fuller information on fuel the student is referred to the following standard treatises :—Percy, *Metallurgy*, vol. i. London, 1861; second edition, 1875 ; Galloway, *Treatise on Fuel*, London, 1880 ; Schwack-höfer and Browne, *Fuel and Water*, London, 1885 ; Phillips and Bauerman, *Elements of Metallurgy*, London, 1887, pp. 16–107 ; Mills and Rowan, *Fuel and its Applications*, London, 1889; Gruner, *Traité de Métallurgie*, Paris, 1875, vol. i. pp. 36–161 ; Kerl, *Grundriss der allgemeinen Hüttenkunde*, Leipzig, 1879, pp. 36–198 ; Muck, *Grundzüge der Steinkohlen-Chemie*, Bonn, 1881 ; Fischer, *Chemische Technologie der Brennstoffe*, Leipzig, 1887. Schnabel, *Lehrbuch der Allgemeinen Hültenkunde*, Berlin, 1890.

CHAPTER VI.

MATERIALS AND PRODUCTS OF METALLURGICAL PROCESSES.

Ores.—This term is applied by the metallurgist only to those minerals from which, on a large scale, metals may be obtained with profit. The ores must be supplied to the works in a suitable condition for smelting, the preliminary washing and dressing operations being carried out at the mine. *Gangue*, vein-stuff, or matrix is the extraneous earthy matter associated with the ore.

Ores contain the metals—(1) in the native or metallic state (examples—gold, silver, copper, mercury); (2) in combination with oxygen as oxides (for example, ferric oxide, tin oxide); (3) as oxides in combination with water (limonite, $Fe_2H_2O_4$); (4) in combination with halogens (silver chloride); (5) in combination with sulphur, arsenic, and antimony (galena, PbS); (6) in combination with acids as salts (anglesite, $PbSO_4$); ores also occur in nature in a state of mixture; (7) as various combinations of the same metal (for example, azurite, $2CuCO_3 + Cu(HO)_2$); (8) as various combinations of more than one metal in one mineral species (for example, pyrargyrite, $3Ag_2S,Sb_2S_3$); lastly, (9) as several mineral species occurring together in the ore-deposit, galena and blende, spathic iron ore and iron pyrites.

The value of an ore depends upon the nature of the metal it contains and the difficulty with which its extraction is attended. Thus, iron ores containing less than 30 per cent. of metal are rarely smelted. Ores of iron, lead, or zinc are not considered rich unless they contain 50 per cent. of metal. Copper ores are rich when they contain 25 per cent. of metal, whilst ores yielding a few ounces of gold per ton are extremely valuable.

Fluxes.—In order to separate the extraneous matter usually contained in a furnace charge of ore and reducing agent, certain materials must be added to form slag. These materials are known as fluxes.

In the smelting processes earthy, alkaline, and metallic sub-

stances are used as fluxes. The alkaline fluxes are expensive, and are rarely used except in refining processes. The following are the principal earthy fluxes in use :—

1. Lime, which acts as a powerful base for removing silica. Lime is used in a pure state or as carbonate. As a rule, limestone is used, especially if the furnace is large. Limestone is largely used in iron smelting, as most iron ores contain unsaturated silica. Dolomite, the carbonate of lime and magnesia, is specially useful.

2. Fluorspar (calcium fluoride), which is a useful flux for ores containing silica, barytes, or gypsum. With the two latter it easily fuses. It has also been used for removing phosphorus from iron ores in the blast furnace, but on account of its expense its employment, though advantageous under all conditions, is limited. The greater portion of the fluorspar is found unchanged in the slag; it facilitates the fusion, and increases the fluidity of the mass.

3. Barytes, which acts as a powerful base. It is a good sulphurising agent, for example, in the concentration of nickel speise, the copper present with the speise being removed and a regulus formed.

4. Alumina-bearing rocks, such as clay-slate, are used in smelting ores very rich in lime. As a rule, however, the charge is so mixed that argillaceous and calcareous ores are present in suitable proportions.

5. Siliceous materials, such as quartz, natural silicates, siliceous slags, are used when the ores contain an excess of basic materials that have to be removed.

Metallurgical Agents.—The metallurgical agents chiefly used are—1. Metals, either for decomposing the combinations of other metals, or as a means of concentration. Thus, iron is used for decomposing galena, zinc for desilverising argentiferous lead, and mercury for concentrating gold.

2. Metallic oxides are used for purifying the raw metal in refining processes. Thus, iron ore or hammer-scale is used for refining iron.

3. Slags serve to increase the fluidity of the furnace charge; or mixtures of slags may be used for recovering the metals they contain, and lastly for preventing " scaffolding " or choking of the furnace when pulverised ores are smelted. Their chemical action varies with their composition ; basic slags are able to take up a large proportion of silica, while acid slags readily absorb bases. Alkaline slags are rarely used except in crucible processes, as in assaying.

4. Iron pyrites (FeS_2) and magnetic pyrites (Fe_7S_8) exert a reduc-

ing action on oxides by giving up sulphur and forming sulphurous anhydride. Certain sulphides, such as zinc sulphide, infusible alone, may be rendered fusible by the addition of iron pyrites.

In the roasting of ores in furnaces or in piles the following chemicals are used :—(1) Salt for the formation of silver chloride in the treatment of silver ores; (2) Lime for the absorption or separation of the acids formed on roasting copper regulus, &c.; (3) Ferrous sulphate in the treatment of silver ores containing a little iron pyrites.

Selection of Fluxes.—In the choice of fluxes, when the gangue is siliceous, at least two bases must be added in order to form a fusible silicate. When the gangue is argillaceous, a single base is sufficient to form a double silicate. When the gangue is basic, that is, containing lime, magnesia, alumina, or iron, a siliceous flux must be added. Quartz alone is sufficient if the gangue already contains two or more bases, but, if there is but one base, clay or some other silicate must be added with the quartz. Siliceous slags may be advantageously used for the purpose.

Slags.—The silicates formed in metallurgical processes by the combination of silica with the earths and metallic oxides are termed *slags*. As a rule, slags are smelters' refuse. In the refining of metals, however, slags are frequently formed by the oxidation of the metallic impurities. Such slags consist largely of metallic oxides, and are smelted again in order to recover the large proportion of metals they contain. These slags may be distinguished as cinder or scoria. The quantities of these slags obtained are not very great, and they may therefore be more conveniently regarded as ores.

The bases that occur in silicate-slags, mostly combined with the silica, are—lime, alumina, magnesia, rarely ferric and manganic oxides, ferrous oxide, manganous oxide, zinc oxide, more rarely baryta, and alkalies in slags of all blast-furnaces using charcoal as fuel, and, in addition to these, small amounts of the metals that are being smelted are invariably present, partly in chemical combination with the silica, and partly in other combinations mechanically mixed with the slag.

Some oxides and earths, such as zinc oxide and alumina, not only interfere with the fluidity of the slag, but also cause a scum to form which is difficult to separate from the slag. In many slags, calcium fluoride is found. This is frequently the case in the slag from cupola furnaces, as fluorspar is often used as a flux in re-melting pig-iron. The calcium fluoride melts without decomposition, and is merely in a state of mechanical mixture

L

with the slag. This is also the case with the calcium sulphide frequently met with in blast-furnace slags.

The chemical composition of slags is variable. If a slag is distinctly crystallised, it may generally be assumed to have a definite chemical composition, and a formula may be calculated for it. If, however, it is not crystallised, nor even crystalline, it must be regarded either as a mixture of several silicates or as a solution of one silicate in another.

Silica consists of one atom of silicon and two atoms of oxygen, so that the various silicates have the compositions given below. $2RO + SiO_2$ is the monosilicate or neutral silicate of the metallurgist. It contains in acid and base equal amounts of oxygen, whilst the neutral silicate of the chemist, which has the formula $RO + SiO_2$, is termed a bisilicate by the metallurgist, because the acid contains twice as much oxygen as the base. Proceeding from the monosilicate, the following series of formulæ are obtained for silicates :—

$$4RO + SiO_2 = R_4SiO_6 \quad \text{Subsilicate}$$
$$2RO + SiO_2 = R_2SiO_4 \quad \text{Monosilicate}$$
$$RO + SiO_2 = RSiO_3 \quad \text{Bisilicate}$$
$$2RO + 3SiO_2 = R_2Si_3O_8 \quad \text{Trisilicate}$$
$$4RO + 3SiO_2 = R_4Si_3O_{10} \quad \text{Sesquisilicate}$$
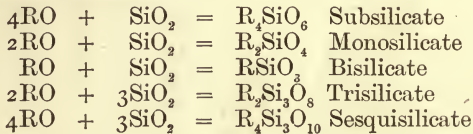
For bases having the composition R_2O_3 the formulæ are—

$$4R_2O_3 + 3SiO_2 = R_8Si_3O_{18} \quad \text{Subsilicate}$$
$$2R_2O_3 + 3SiO_2 = R_4Si_3O_{12} \quad \text{Monosilicate}$$
$$R_2O_3 + 3SiO_2 = R_2Si_3O_9 \quad \text{Bisilicate}$$
$$2R_2O_3 + 9SiO_2 = R_4Si_9O_{24} \quad \text{Trisilicate}$$
$$4R_2O_3 + 9SiO_2 = R_8Si_9O_{30} \quad \text{Sesquisilicate}$$
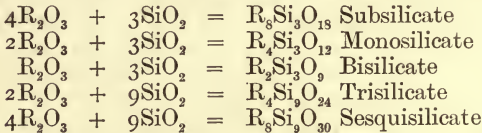
The quantities of oxygen in the bases bear the following proportions to those in the acids in the various silicates :—

		O in base : O in acid.
Subsilicate	. . . . .	2 : 1
Monosilicate	. . . . .	1 : 1
Bisilicate	. . . . .	1 : 2
Trisilicate	. . . . .	1 : 3
Sesquisilicate	. . . . .	2 : 3

Every sesquisilicate may be resolved into a monosilicate and a bisilicate; thus $R_4Si_3O_{10}$ is equal to $R_2SiO_4 + 2(RSiO_3)$ and $R_8Si_9O_{30}$ is equal to $R_4Si_3O_{12} + 2(R_2Si_3O_9)$. If a silicate contains but one base, it is termed a monobasic or simple silicate, but if two or more bases are present, it is termed a double silicate or a

multibasic silicate, and in the formula the silicates of the various bases are united by a plus sign.

A classification of the silicates as ortho- and meta-silicates, based upon their analogies to phosphates, was suggested by Odling ;* but it has not come into use amongst metallurgists.

The fusibility of slags is dependent on the amounts of silica and bases they contain. The subsilicates are very fusible, forming a limpid liquid ; they consolidate very rapidly and split up in so doing. They have usually a dark colour and, on account of the large proportion of bases they contain, a high specific gravity. The monosilicates are less fusible, and do not form so limpid a liquid. The bisilicates are less fusible still ; they form a viscous mass which may be drawn out into threads. They are usually glassy and consolidate slowly. The trisilicates also flow very slowly, consolidate slowly, and require a very high temperature for their formation.

The most fusible silicates are those of the alkalies, then follow those of lead, iron, manganese, and copper, and finally, the earthy silicates. The simple silicates are always less fusible than the double silicates.

Economic Application of Slags.—The slags obtained in smelting metals other than iron are largely used as fluxes in various metallurgical processes for taking up either the silica or the bases, or, when they are ferruginous, for precipitating purposes. Occasionally the slags are moulded into bricks, and used for walls or other constructions in which no great weight has to be sustained.

The slags obtained in iron smelting are used, if not too glassy, for macadamising roads. For the ballast of railway lines, glassy slags may advantageously be used, as the mass is very permeable and keeps the sleepers dry. In the form of large blocks, they may be used for road making. They may be moulded into bricks, the best results being obtained when the moulded bricks are kept at a white heat for several hours in a tightly closed space, whereby they are devitrified and become considerably harder if they are allowed to cool slowly under a cover of coal dust and ashes. Good bricks may be made of granulated slag mixed with lime, the proportions being usually 10 parts of slag-sand to 1 part of lime. Blast furnace slag, if not too acid, may be burnt in a state of powder with lime, and gives an hydraulic cement almost equal to Portland cement.

The manufacture of slag cement has of recent years acquired

* *Phil. Mag.*, vol. xviii. (1859), p. 368.

so considerable a development that it may safely be said that an advantageous method of utilising blast-furnace slag has at length been found. The following are analyses of slags actually used for this purpose :—

	Middles-brough.	Bilbao. Spain.	Saulines. France.	Choindez. Switzer-land.	Harz-burg. Germany.	Belgium.
Lime	32.75	47.30	47.20	45.11	48.59	44.75
Silica	30.00	32.90	31.65	26.88	30.72	32.51
Alumina . . .	28.00	13.25	17.00	24.12	16.40	13.91
Ferrous oxide . .	0.75	0.46	0.65	0.44	0.43	0.48
Magnesia . . .	5.25	1.37	1.36	1.09	1.28	2.20
Calcium sulphide .	1.90	3.42	—	1.86	2.16	4.90
Manganese oxide .	0.60	1.13	0.85	0.50	traces	0.60
Residue . . .	0.75	0.17	1.29	—	0.42	0.65
Totals . .	100.00	100.00	100.00	100.00	100.00	100.00

The slag is run into water so as to render it easy to obtain slag-sand. This is ground under edge-runners, and the pasty mass is spread on drying plates. The dried slag is then ground under millstones to a fine powder and sifted to exclude coarse particles. Freshly burnt lime is slaked, and then carefully screened, and 25 per cent. of this slaked lime is thoroughly mixed with 75 per cent. of slag-sand. Grosclaude * estimates the entire cost of works and plant for an annual output of 6000 tons at £6000.

The specific gravity of this cement is very low as compared with Portland cement, whilst the time occupied in setting is comparatively long. For purposes of storage it compares well with Portland cement. By exposure to the air it absorbs carbonic anhydride more rapidly than does Portland cement, but it does not deteriorate greatly by long exposure. Owing to the closeness of the particles, this cement appears to be well adapted for works under water, such as docks or breakwaters.

Blast furnace slag is also largely used for the production of slag wool, or silicate cotton, which is obtained by causing steam to impinge on to a jet of molten slag in such a way that the steam jet encounters only a half of the slag jet. Slag wool is extremely light and fire proof. It is a good non-conductor of heat and of sound, and it is so porous that it will absorb large quantities of water. It is used for covering steam and hot-air pipes. In Silesia and other localities, where ironworks and

* *Annales Industrielles*, 1889, p. 90.

collieries are in close proximity, blast-furnace slag is largely used for filling the excavations from which the coal has been removed. Finely pulverised blast-furnace slag has been found in Sweden to be an excellent manure for moorland which is deficient in lime, as well as for clay and sandy soils.

The slag obtained in the basic Bessemer process, on account of its high percentage of phosphorus, forms a valuable manure. Many thousands of tons of slag are annually employed for this purpose, it having been found that the phosphorus it contains is in a form that is very readily assimilated by the soil. The utilisation of basic Bessemer slag is referred to in a subsequent chapter.*

Calculation of Furnace Charges.—In order to obtain the greatest possible yield of metal with the least consumption of fuel, care must be taken to have a proper mixture of ore and flux. Ores reducible with difficulty should be mixed with fluxes that render the charge pasty, so that the slag-forming constituents do not melt before the metals are reduced from their combinations. When raw coal or coke is used as fuel, the quantity and composition of the ash must be taken into consideration, as this always contains silica. With charcoal as fuel, this may be neglected, as the percentage of ash is always low, and the ash itself, which is strongly alkaline, is a useful flux.

As an example of the calculations necessary, a charge of iron ore may be selected which is to be smelted with coke to grey pig iron, and for which the necessary amount of lime as flux is required to be determined. Experience has shown that in coke blast-furnaces, monosilicate slags should be produced, whilst in charcoal furnaces sesquisilicates to bisilicates are found most advantageous. For this example the author is much indebted to Professor C. A. M. Balling, Director of the School of Mines at Przibram in Bohemia, who has permitted him to borrow it from his valuable treatise on metallurgical chemistry.†

Let it be assumed that there are to be smelted four varieties of ore having the following compositions :—

	Fe.		Al_2O_3.		CaO.		MgO.		SiO_2.		S.
A.	54	...	7	...	2	...	—	...	12	...	—
B.	47	...	8	...	1	...	1	...	15	...	—
C.	38	...	10	...	2	...	1	...	24	...	1
D.	40	...	9	...	2	...	1	...	20	...	—

In order to simplify the calculations whole numbers are taken,

* Methods of utilising slag are fully described by G. Redgrave, *Journ. Soc. Arts*, vol. xxxviii. (1890), p. 221.
† *Compendium der metallurgischen Chemie*, Bonn, 1882.

and the percentages of water and carbonic anhydride are disregarded. The ore to be used as flux (I.) and the 10 per cent. of ash (II.) in the coke have the following percentage compositions :—

	Fe.		Al₂O₃.		CaO.		MgO.		SiO₂.		S.
I.	25	...	4	...	25	...	4	...	6	...	—
II.	12	...	35	...	1	...	1	...	44	...	0.5

For the production of 100 parts by weight of iron 190 parts by weight of coke are necessary.

In view of the large proportion of silica in the ores C and D, high percentages of these ores are inadmissible in the charge. The ore A, on the other hand, is the best, and must therefore form the greater portion of the charge, which is to be mixed so as to contain on an average 45 per cent. of iron. Taking into account the important constituents of the ores, the following weights would be selected for the charge :—

Ore B.		Ore C.		Ore D.		Flux.		Total.
25	...	10	...	15	...	15	...	65

It must now be calculated how much iron and slag-giving constituents this mixture contains, in order to determine the quantity of ore A that must be added to give an average of 45 per cent. of iron. In this way, by proportion the following amounts of the various constituents are calculated to be present :—

	Fe.	Al₂O₃.	CaO.	MgO.	SiO₂.	S.
25 parts of B contain . .	11.75	2.00	0.25	0.25	3.75	
10 ,, C ,, . .	3.80	1.00	0.20	0.10	2.40	0.10
15 ,, D ,, . .	6.00	1.35	0.30	0.15	3.00	
15 ,, flux ,, . .	3.75	0.60	3.75	0.60	0.90	
65 Totals . .	25.30	4.95	4.50	1.10	10.05	0.10

Regarding this ore-mixture as a single ore the percentage composition will be as follows :—

Fe.		Al₂O₃.		CaO.		MgO.		SiO₂.		S.
38.92	...	7.61	...	6.92	...	1.69	...	15.46	...	0.15

With this ore, or rather mixture containing 38.92 per cent. of iron, it is required to mix the ore A so as to bring the charge to 45 per cent. of iron. If the ore mixture is represented by x, we have the following equation :—

$$x + A = 100$$
$$38.92\,x + 54\,A = 100 \times 45$$

On solving this equation, A is found to be 40.5, and $x = 100 - A = 59.5$ parts by weight. The equation thus requires that 40.5 parts of the ore A should be mixed with 59.5 parts of the ore-mixture chosen, and consequently the 65 parts must be reduced by proportion to 59.5, giving the following percentages as the definite composition of the charge:—

Ore A.	Ore B.	Ore C.	Ore D.	Flux.	Total.
40 ...	23 ...	10 ...	13 ...	14 ...	100

In this charge the percentages of the various constituents are found by proportion to be as follows:—

	Fe.	Al$_2$O$_3$.	CaO.	MgO.	SiO$_2$.	S.
In 40 parts of A . . .	21.60	2.80	0.80	—	4.80	
23 ,, B . . .	10.80	1.84	0.23	0.23	3.45	
10 ,, C . . .	3.80	1.00	0.20	0.10	2.40	
13 ,, D . . .	5.20	1.17	0.26	0.13	2.60	
14 ,, flux . . .	3.50	0.56	3.50	0.56	0.84	0.10
100 Totals . .	44.90	7.37	4.99	1.02	14.09	0.10

For the production of 100 parts of iron,
$$100 : 45 = x : 100$$
$x = 222.2$ parts of this charge are required, and in this are contained the following weights of iron and slag-giving constituents:—

Fe.	Al$_2$O$_3$.	CaO.	MgO.	SiO$_2$.	S.
99.77 ...	16.40 ...	11.09 ...	2.26 ...	31.30 ...	0.22

For its production, 190 parts of coke are required, the ash of which, according to the analysis, contains:—

Fe.	Al$_2$O$_3$.	CaO.	MgO.	SiO$_2$.	S.
2.28 ...	6.65 ...	0.19 ...	0.19 ...	8.36 ...	0.95

It is therefore necessary to remove as slag: Al$_2$O$_3$ 23.05; CaO 11.28; MgO 2.45; SiO$_2$ 39.66; S 1.17.

For the formula: Al$_4$Si$_3$O$_{12}$ + Ca$_2$SiO$_4$ + Mg$_2$SiO$_4$, representing a monosilicate, the amount of silica slagged by the bases may be found by proportion with the aid of the atomic weights, thus:—

$$2Al_2O_3 : 3SiO_2 = 205.6 : 180 = 23.05 : x ; \quad x = 20.18$$
$$2CaO : SiO_2 = 112 : 60 = 11.28 : y ; \quad y = 6.04$$
$$2MgO : SiO_2 = 80 : 60 = 2.45 : z ; \quad z = 1.83$$

giving a total $(x + y + z)$ of 28.05 parts by weight of silica, so that $39.66 - 28.05 = 11.61$ parts of silica remain to be converted into slag. According to the same proportion—

$$SiO_2 : 2CaO = 60 : 112 = 11.61 : a$$

From which a is found to be 21.7 parts by weight of lime base, which, as calcium carbonate contains but 56 per cent. of CaO, is contained in 38.7 parts of calcium carbonate.

Similarly for removal as calcium sulphide, the sulphur requires, according to the proportion $S : CaO = 32 : 56 = 1.17 : \beta$, $\beta = 2.05$ parts of lime, which amount is contained in 3.65 parts of calcium carbonate. Consequently, altogether there is required $38.7 + 3.65 = 42.35$ parts of calcium carbonate. But as this is added in the form of impure limestone containing only some 95 per cent. of calcium carbonate, the quantity to be added will be 44.58 parts. As this amount, however, is required for 222 parts of charge, 100 parts will require 20.1 parts of limestone as flux. In this example, the small quantity of limestone required is explained by the fact that 14 parts of fluxing ore, containing 25 per cent. of lime, have already been added.

All these tedious calculations may be reduced to a few multiplications and additions by employing the accompanying table that has been computed by Professor Balling :—

TABLE A. For ascertaining the necessary amounts of Bases to convert given amounts of Silica into slag.		TABLE B. For ascertaining the necessary amounts of Silica to convert given amounts of Bases into slag.	
One part by Weight of Silica requires—	Parts by Weight of Bases.	One part by Weight of Base requires—	Parts by Weight of Silica.
For Monosilicates—		For Monosilicates—	
Lime.	1.86	Lime.	0.535
Magnesia .	1.33	Magnesia .	0.750
Alumina .	1.14	Alumina .	0.873
Ferrous oxide .	2.40	Ferrous oxide .	0.416
Manganous oxide .	2.36	Manganous oxide .	0.422
For Bisilicates—		For Bisilicates—	
Lime.	0.93	Lime.	1.070
Magnesia .	0.66	Magnesia .	1.500
Alumina .	0.57	Alumina .	1.747
Ferrous oxide .	1.20	Ferrous oxide .	0.833
Manganous oxide .	1.18	Manganous oxide .	0.845
For Sesquisilicates—		For Sesquisilicates—	
Lime.	1.24	Lime.	0.803
Magnesia .	0.88	Magnesia .	1.125
Alumina .	0.76	Alumina .	1.310
Ferrous oxide .	1.60	Ferrous oxide .	0.625
Manganous oxide .	1.57	Manganous oxide .	0.633

In order to show the simplicity of the use of this table, the same problem may be solved with its aid. For ascertaining the amount of silica converted into slag by the bases in the charge, Table B. is used. In the section for monosilicates, the corresponding figures are found for the bases present, and these figures multiplied together give the following products:—

$$
\begin{array}{lllllll}
Al_2O_3 & . & . & . & . & 23.05 & \times & 0.873 & = & 20.12 \\
CaO & . & . & . & . & 11.28 & \times & 0.535 & = & 6.04 \\
MgO & . & . & . & . & 2.45 & \times & 0.750 & = & 1.84 \\
\end{array}
$$

Total . . . . . $=$ 28.00

Thus 28.00 parts of silica (28.05 in the previous calculation) are converted into slag, and of the total amount, 39.66 parts of silica present, there remain 39.66—28.00 = 11.66 parts to be converted into slag by the addition of lime. On referring to Table A., it will be seen that the corresponding amount of lime is 1.86, the product being 11.66 × 1.86 = 21.69. Lastly, for the formation of calcium sulphide, 1 part of sulphur requires $\frac{56}{32}$ = 1.75 of lime, and there is 1.17 part of sulphur to be passed into the slag. This requires 1.17 × 1.75 = 2.047 parts of lime. Thus, altogether 21.69 + 2.047 = 23.737 parts of lime are required. One part of lime is contained in $\frac{100}{56}$ = 1.785 of calcium carbonate, the required addition of limestone as flux is therefore 23.737 × 1.785 = 42.37 parts (as compared with 42.35 in the previous solution).

In order to entirely obviate the necessity for any calculation whatever, Professor Balling has devised a method of solving the problem graphically. The method is based on the similarity of triangles. From any point a (Fig. 53), two lines are drawn at right angles, and these form two sides of a right-angled triangle. The co-ordinate lines are divided into equal parts. If as many parts of one line are taken as there are equivalents of acid in the slag to be formed, and, similarly, as many parts of the other line as there are equivalents of base, and if the end points of the two sides of the triangle are joined by the hypothenuse, then it is merely necessary to draw from any given point in one side a line parallel to the hypothenuse in order to find on the two sides the equivalent amounts of base and acid in the given silicate.

Fig. 53 is a reduced sketch of the triangles for the monosilicates of the earths that are usually required. For practical purposes, the best unit of length to adopt is the centimetre, so that tenths (millimetres) and half-tenths may be read. As, however, the triangles on this scale would be too large, and as only lower

figures are used, the triangles may be drawn on a reduced scale, for which the following scheme will be found to answer under all conditions :—

The lime monosilicate requires for base $2CaO = 2 \times 56 = 112$ units of length, and for perpendicular $1SiO_2 = 60$. The magnesia monosilicate requires for base $2MgO = 2 \times 40 = 80$, and for perpendicular $1SiO_2 = 60$. Lastly, the alumina monosilicate requires for base $2Al_2O_3 = 2 \times 102.8 = 205.6$, and for perpendicular $3SiO_2 = 3 \times 60 =$
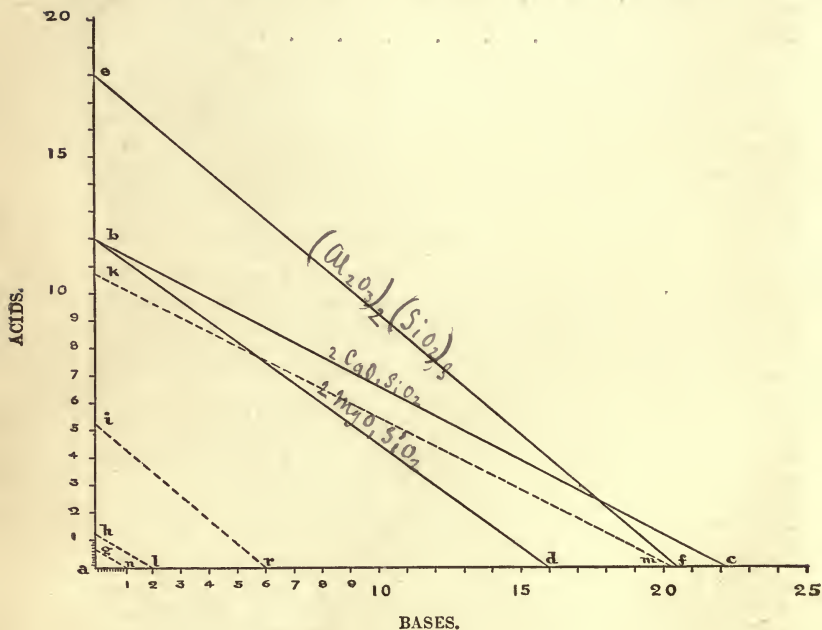
FIG. 53.

180. These lengths are reduced in the triangles for monosilicates of lime and magnesia by one-fifth, and in the triangle for the monosilicate of alumina by one-tenth. Thus the triangle, $a\,b\,c$, is that of the lime silicate, $a\,b$ containing $\dfrac{60}{5} = 12$ units of length for silica, and $a\,c\,\dfrac{112}{5} = 22.4$ units for lime. Similarly, in the

triangle, $a\,b\,d$ representing the magnesia silicate, $a\,b$ contains 12 units for silica, and $a\,d\,\dfrac{80}{5}=16$ units for magnesia. Lastly, in the triangle, $a\,e\,f$, representing the alumina silicate, $a\,e$ contains $\dfrac{180}{10}=18$ units for silica, and $a\,f\,\dfrac{205.6}{10}=20.56$ units for alumina.

As an illustration of the application of the graphic method, let it be assumed that in a coke blast-furnace, a charge has to be smelted in which the constituents to be converted into slag average—

CaO.		MgO.		Al_2O_3.		SiO_2.
2	...	1	...	6	...	18

The amount of lime to be added is determined in the following manner :—In order to determine the amount of silica converted into slag by the bases already present, from the point l, representing the units of base (in this case 2 parts), a line is drawn parallel to the hypothenuse $b\,c$ of the lime triangle. This cuts the perpendicular, representing the silica units, at the point h, and the length $a\,h$ represents the units of weight of silica which slag off the lime already present in the charge. Similarly, the line $g\,n$ drawn parallel to $b\,d$, shows the amount of silica required by one part of magnesia, and the line $i\,r$, drawn parallel to $e\,f$, that required by 6 parts of alumina. On measuring these lengths with the dividers on a decimal scale they are found to be : $a\,h = 1.17$; $a\,g = 0.75$; $a\,i = 5.23$; giving a total of 7.15 units as the amount of silica slagged by the bases present in the charge, and there consequently remains $18 - 7.15 = 10.85$ parts of silica to be converted into slag by the addition of lime. If, then, from the point $k = 10.85$ parts of silica, a line is drawn parallel to the hypothenuse of the lime silicate, it cuts the base line at the point m, which represents 20.15 parts of lime, an amount contained in $20.15 \times 1.785 = 35.9$ parts of calcium carbonate.

This method is extremely rapid, and, with careful graduation, gives results of great accuracy. In order to apply the method to bisilicates, the amount of silica must be doubled, or those of the bases must be halved.

Classification of Metallurgical Processes.—Metals may be extracted from their ores by the following methods :—

1. By *liquation*—that is, a separation of the easily fusible metals or metallic compounds from the infusible ones, or the gangue, at a low temperature, by taking advantage of the different melting points. In this way, bismuth and sulphide of anti-

mony are obtained, and argentiferous lead is separated from copper.

2. By *distillation* and *sublimation*—that is, heating the ore, until the metal is driven off in the form of vapour, and condensed in a liquid or solid state. Mercury is extracted from its ore by distillation, and arsenic is obtained by sublimation.

3. By reduction of metallic oxides at a high temperature. In the case of metals possessing a slight affinity for oxygen, the reduction may be effected by merely heating the oxide, whereby it splits up into metal and oxygen. The reduction is usually effected by heating the oxides with carbon or other substances possessing a greater affinity for oxygen than is possessed by the metal.. In addition to solid carbon the substances used are carbonic oxide, marsh-gas, and hydrogen, as well as sulphur in the reverberatory-furnace processes for extracting copper and lead. The reactions are shown by the following equations:—

$$ZnO + C = Zn + CO.$$
$$2PbO + C = 2Pb + CO_2$$
$$FeO + C = Fe + CO$$
$$FeO + CO = Fe + CO_2$$
$$3FeO + CH_4 = 3Fe + CO + 2H_2O$$
$$FeO + H_2 = Fe + H_2O$$
$$PbS + PbSO_4 = 2Pb + 2SO_2$$
$$Cu_2S + CuSO_4 = 3Cu + 2SO_2$$
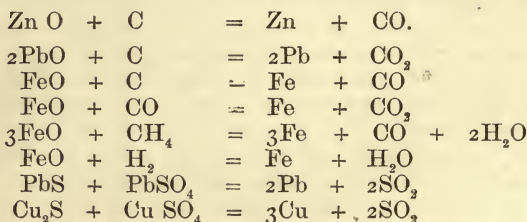
4. By decomposing metallic sulphides by means of iron at a high temperature. Lead and antimony are extracted from their ores in this way, the equation in the case of lead being—

$$PbS + Fe = Pb + FeS$$
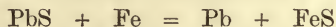
5. By extraction by means of molten lead. The precious metals are extracted in this manner.

$$(Ag + Cu) + Pb = (Pb + Ag) + Cu.$$
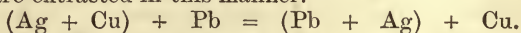
6. By extraction by means of molten zinc, as in the extraction of silver and gold from lead by the Parkes process.

7. By extraction by means of mercury in the cold. This process is known as *amalgamation*. It is used for extracting silver and gold from their ores, the mercury being subsequently driven off by heat.

8. By extraction in the wet way and subsequent precipitation, as metal or as oxide or sulphide. In some cases the compound is dissolved in acids, as in the separation of silver from gold, and in the extraction of copper and nickel. In other cases,

the metal is first converted into a chloride, which is dissolved in a solution of salt or of sodium hyposulphite, as in the extraction of silver by Augustin's process, or the metal is converted into a sulphate, which is dissolved in water, as in Ziervogel's process. The extraction may also be effected by treating oxides with salts, as in the Hunt and Douglas method of extracting copper.

$$3CuO + 2FeCl_2 = Fe_2O_3 + CuCl_2 + Cu_2Cl_2$$
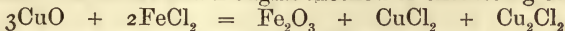
9. By electrolysis, as in the deposition of copper.

10. By the action of highly oxidisable substances on metallic salts, as in the precipitation of gold from its solution as chloride by ferrous sulphate, or of aluminium from its chlorides by sodium.

11. By crystallisation, as in Pattinson's method of extracting silver.

Roasting and Calcination.—These terms are frequently used indiscriminately to indicate the operations of expelling water, carbonic anhydride, or sulphur from the ore, by heating the substance to a temperature below its melting point. The term calcination should be confined to the application of heat in the expulsion of carbonic anhydride or volatile matters, whilst the term roasting should be used in all cases where a chemical change is involved, resulting in the addition of an element.

Roasting is one of the most important of metallurgical processes. In the treatment of almost all ores it is required as a preliminary process to render them more porous and more suitable for the subsequent smelting, the success of which is dependent on the manner in which the roasting has been effected.

There are several kinds of roasting. An *oxidising* roasting is one in which the metalliferous substance is oxidised by heating it in contact with air. A *reducing* roasting consists in heating the substance in a reducing atmosphere. When it is required to obtain chlorides instead of oxides, the material is roasted with salt. This operation is termed a *chloridising* roasting. It is especially important in the treatment of silver ores. Under the action of a high temperature the salt acts on the sulphates present, and forms chlorides. Its action may also be due to the formation of chlorine by the action of silica and sulphuric anhydride on the salt, or to the evolution of hydrochloric acid, due to the presence of moisture in the atmosphere in which the material is being roasted. In some cases, as a preliminary operation for hydrometallurgical processes, it is necessary to conduct the roasting in such a manner that sulphates are formed. It necessitates a low

temperature and a limited supply of air. This operation is termed *sulphating* roasting.

Oxidising Agents.—Atmospheric air is the simplest source of oxygen. The carbonic anhydride it contains may be neglected. Attention, however, must be paid to the aqueous vapour. Air, at the ordinary temperature, contains an amount of moisture equal to o.oo62 of the weight of dry air, or since water contains $\frac{8}{9}$ths of its weight of oxygen, while dry air contains less than a quarter, it follows that the moister the air is the more oxidising it will be. The cooling action of water-vapour, however, counteracts the advantage derived from its excess of oxygen. Moist air is consequently useful only when the hydrogen it contains is set at liberty during the reactions and is free to combine with sulphur or certain other metalloids. Air is employed at the ordinary pressure or at the pressure of several atmospheres, for the temperature of combustion increases with the pressure.

Water is an active oxidising agent in the case of certain metals which have a strong affinity for oxygen ; but in other cases its oxidising action is sensible only at a high temperature. The decomposition of water absorbs much heat, and aqueous vapour can therefore be employed only as an oxidising agent when its cooling effect is desirable, as in the refining of iron. Aqueous vapour is also used for separating zinc from lead. In passing steam over sulphides of oxidisable metals at a red heat the sulphur is eliminated as sulphuretted hydrogen, while the metal is oxidised. This reaction is employed in the roasting of sulphides of iron, and in the treatment of sulphides, arseno-sulphides and antimonio-sulphides of copper and silver.

Metallic oxides are frequently used as oxidising agents. Oxides of manganese, iron and lead are those most generally employed. Oxide of copper is used more rarely. Manganese peroxide is occasionally useful in the oxidation of impurities in metals. Ferrous oxide, or ferrous silicate, acts as a carrier of atmospheric oxygen. When ferrous silicate, containing less than 30 per cent. of silica, is exposed in a molten state to the action of air, the iron in excess gradually becomes oxidised, and crystals of magnetic oxide are formed. These render the silicate less fusible, and fall by their superior density to the bottom of the mass. Sometimes, as when such a slag covers a bath of impure metal, the magnetic oxide thus formed gives up its excess of oxygen to the elements in the metal to be refined, and again becomes ferrous oxide, and thus acts as a carrier of atmospheric oxygen to the carbon which has to be oxidised. An illustration of this is afforded by a stage

of the puddling of iron, a process which is conducted in the presence of a layer of ferruginous cinder.

Lead oxide is an energetic oxidising agent on account of its being readily reducible to the metallic state. It is, however, expensive, and yields but 7 per cent. of oxygen. Lead oxide and lead sulphide, when heated together, give metallic lead—

$$2PbO + PbS = 3Pb + SO_2$$
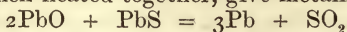
Oxides of copper and antimony serve as oxidisers in the treatment of these metals. In heating together the sulphide and oxide of copper, copper is obtained. Potassium and sodium nitrates are employed in refining silver and antimony, and in the "Heaton" process sodium nitrate is employed to convert phosphorus and vanadium in certain varieties of pig-iron into sodium phosphate and vanadate.

Metallic sulphates are often used as oxidising agents, the sulphate oxidising the sulphide and reducing the metal. In the case of iron in the blast furnace, carbonic anhydride, as is shown in the following chapter, also acts as an oxidiser.

Reducing Agents.—When a metal is separated from a state of chemical combination, it is said to be reduced, and the process of separation is termed *reduction*. The agents employed for this purpose are mainly carbon and hydrogen, or their compounds. Occasionally, however, the metallurgist makes use of iron, manganese, lead, or of sulphides and arsenides. The efficacy of a reducing agent depends on the absence of oxidised or inert elements. Thus, on account of the water and oxidised compounds they contain, wood, peat, and lignite are less energetic as reducing agents than coal. Similarly, coals rich in carbon are more valuable as reducing agents than coals rich in oxygen.

Carbon can take up $1\frac{1}{3}$rd or $2\frac{2}{3}$rds of its weight of oxygen according to the oxide in whose presence it is used, to the temperature at which the reduction is effected, and to the relative proportion between the oxygen to be removed and the carbon employed. In the first case carbonic oxide is formed, and in the second carbonic anhydride. The reduction of metals, of which the oxides are easily reduced, such as lead and copper, is complete even if carbonic anhydride alone is formed. In the case of iron, however, total reduction is not possible unless carbonic oxide is present in excess, on account of the oxidising action of carbonic anhydride. Indeed, a mixture of equal volumes of carbonic oxide and carbonic anhydride will not reduce iron oxides below ferrous oxide. This is also true of manganese oxides.

Reduction by solid carbon is slow, and is effected merely by

cementation, that is, by a gradual transmitting action, if carbonic oxide is not formed. This gas is the most important reducing agent. It penetrates to the centre of the oxidised substance, absorbs its oxygen, and is converted into carbonic anhydride. In this way 1 part by weight of carbonic oxide gives 1.57 parts of carbonic anhydride. Besides this, Gruner * and Sir Lowthian Bell † have shown that, even at low temperatures, carbon, in the presence of iron, separates out from carbonic oxide,

$$2CO = CO_2 + C,$$
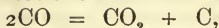
and has a powerful reducing action. It continuously converts carbonic anhydride into the lower oxide. Reference is made to this subject in the description of the blast furnace given in the following chapter.

In addition to the above-mentioned reducing agents, metals and metalloids are sometimes used to remove oxygen. Thus, iron deoxidises the salts and oxides of copper, of lead, and of mercury, and sodium liberates the metals magnesium and aluminium, from their haloid salts. Sulphides and arsenides are also employed. Thus, sulphides of iron and zinc separate copper from certain slags. Silicates of iron and zinc are formed, while sulphur retains the copper in the regulus.

Chemical Agents.—Certain sulphurising agents are employed in metallurgical processes. These are specially useful in the treatment of silver and copper. The agents are iron or copper pyrites, barium or calcium sulphates, and, less frequently, metallic sulphides. Nickel and cobalt behave with regard to arsenic as silver and copper do in the case of sulphur. These metals may be protected, by means of their affinity for arsenic, from the scorifying action of silicates.

Chlorine is largely used in the treatment of gold and silver ores. It is employed in the gaseous state or in the form of alkaline hypochlorites. The perchlorides of iron, copper, and mercury act as chloridising agents by being converted into lower chlorides. They are obtained usually by the direct action of hydrochloric acid on peroxides. Iodine is used in the metallurgy of silver, and bromine in that of gold.

The agents employed for effecting the solution of metallic substances are very varied. The most important solvent is water, which is used for dissolving sulphates of iron, copper, and zinc. Other salts are dissolved by salt solutions; thus, chloride of silver is dissolved by an aqueous solution of sodium chloride.

* *Ann. de Phys. et de Chim.*, 1872; *Traité de Métallurgie*, vol. i. (1875), p. 172.
† *Chemical Phenomena of Iron Smelting.*

Calcium chloride, sodium hyposulphite, and ammonium carbonate are also used. Compounds of sulphur, oxygen, and calcium are now largely used in the metallurgy of silver. Metallic oxides are dissolved by acids, gold and platinum are dissolved by aqua regia, and in the amalgamation of gold and silver, mercury is the solvent employed.

In metallurgical processes there are scarcely any limits to the use of ordinary chemical reagents beyond those imposed by the price of the material.

CHAPTER VII.

FURNACES.

Materials used in the Construction of Furnaces. — In addition to the ordinary building materials used for the exterior portions of furnaces, refractory bricks and materials are required for the interior where a high temperature and the scouring action of metallic oxides have to be resisted. These materials may be used either in the natural state or as bricks. Of the natural materials, sandstones are most largely employed, the best varieties being those in which the quartz grains are cemented by a siliceous material. In the form of quartz, silica is able to resist all temperatures except that of the oxy-hydrogen blowpipe. Coarse-grained sandstones, such as millstone-grit, are frequently advantageously used. The Dinas rock found in the Vale of Neath, South Wales, is an example of this type. It usually contains 98 per cent. of silica. The pulverised rock is mixed with a little lime or clay to make it cohere, and is pressed into bricks. These resist a very high temperature, and are especially useful for the arches of reverberatory furnaces, as they expand with heat. Their composition, however, does not enable them to resist the action of metallic oxides. In steel-melting furnaces, where Dinas bricks are used, the tie-rods must be slackened as the heat increases, and tightened when the furnace subsequently cools. Silica bricks should be set as hot as possible, and the temperature of the furnace gradually raised. Ganister is a siliceous material, somewhat similar to the Dinas stone, found in the lower coal-measures of Yorkshire.

There are three classes of refractory materials :—

1. *Acid*, such as Dinas stone and ganister.
2. *Neutral*, such as graphite, chrome-iron ore, and fire-clay.
3. *Basic*, such as bauxite, dolomite, and magnesite.

Basic materials are now largely used. Bauxite is used for resisting metallic oxides, and for that reason it is used for lining Siemens furnaces. It is first calcined with 3 per cent. of

argillaceous clay containing 6 per cent. of graphite. It is essentially a hydrated ferric aluminate, and has the following composition :—

Al_2O_3.		Fe_2O_3.		SiO_2.		H_2O.
50 to 60	...	24 to 25	...	3 to 5	...	10 to 15

The use of basic refractory materials has been rendered necessary by the extension of the basic Bessemer process. Formerly the Bessemer converter, capable of holding 5 tons of metal, was invariably lined with ganister or Dinas stone. With such a lining, however, it was impossible to get rid of the phosphorus in the iron, whilst with a basic lining this is easily accomplished. Lime is one of the most refractory substances known, but it cannot be used on account of its readiness to become hydrated, and consequently to disintegrate. Magnesia, too, does not appear to answer well; but magnesite gives excellent bricks. Its great cost, however, precludes its general adoption. The mixtures of lime and magnesia, obtained by heating dolomite, give the most satisfactory results. Coated with tar, they are easily protected from moisture, and the proportion of silica they contain is considered advantageous. A refractory material of this kind containing

$MgCO_3$.		$CaCO_3$.		SiO_2.		Fe_2O_3,Al_2O_3.
88	...	7	...	4	...	1

is largely used. The slag obtained from basic refractory materials in the Bessemer converter is being largely used as a fertiliser for agricultural purposes on account of the phosphorus it contains. Some 400,000 tons of it are annually used in Germany.

Fire-bricks are mostly made of fire-clay, mixed with quartz, burnt clay, or pulverised refractory materials that have previously been used. The admixture of graphite is not so usual for fire-bricks as for the refractory crucibles in which metals and alloys are melted.

Fire-clays consist essentially of hydrated aluminium silicates, having the following composition :—

SiO_2.		Al_2O_3.		H_2O.
50 to 55	...	30 to 35	...	10 to 15

When lime, magnesia, potash, or soda are present in quantities exceeding 1 per cent. the clay becomes fusible. In aluminous clays less than 0.7 per cent. of these oxides does not depreciate their refractory value. As a rule, a small amount of these oxides or of ferrous oxide is sufficient to condemn a clay. Thus ordinary shale fuses at a comparatively low temperature, on account of its large percentage of alkaline oxides and ferrous oxide.

The plasticity of clays depends upon the fineness of the particles

and the amount of water present. When calcined, clays cease to be plastic when moistened, on account of the molecular alteration brought about by the calcination. Fire-clays contract when heated, even after all their combined water has been driven off. Heating, however, up to 100° does not affect plasticity; it merely drives off the hygroscopic water. The quality of the clay is largely dependent upon the free silica it contains. Windsor fire-bricks, which may advantageously be used when the temperatures are not high, are made of a mixture of sand and fire-clay in equal proportions.

The mortar employed for setting fire-bricks is prepared from the same materials as the bricks themselves, or from good clay. Lime mortar must not be employed for work that has to support high temperatures.[*]

Crucibles.—For special metallurgical purposes, in the furnaces are placed crucibles (manufacture of cast steel, zinc, smalts, antimony), or tubes or muffles (Belgian and Silesian methods of smelting zinc), or retorts (arsenic smelting), or lastly, pear-shaped vessels, open at both ends, termed aludels (mercury smelting). As most of these vessels must be made of refractory materials, they may be conveniently discussed here.

Crucibles are required to resist (1) high temperatures; (2) alternating temperatures; and (3) the corroding action of metallic oxides. They must also not be brittle or "tender" when hot. They may be made of clay, graphite, gas-carbon, and many other materials, according to requirements. When made of clay, two-thirds are raw clay and one-third is burnt clay, or pulverised material obtained from old but cleaned pots. By this addition, contraction on drying is avoided.

In order to test fire-clay, a piece is fashioned with sharp angles, dried, and exposed to a white heat in a muffle; it is then examined to see if the edges have fused. A similar test should be made in a reducing atmosphere, the test-piece being placed in a crucible packed with charcoal. In order to test the resistance of a crucible to corrosion, it may be half filled with copper, which is then melted, and a little borax inserted so as to just form a ring round the edge of the molten metal and yet leave the centre free for oxidation. The borax will absorb the oxide and rapidly corrode the crucible unless it be of excellent quality. The behaviour of the crucible under the weight of the copper melted indicates the other qualities of the crucible. In selecting clay for crucibles, special care must be taken that neither iron pyrites nor more than a

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[*] Snelus, *Journ. Iron and Steel Inst.*, 1875, p. 513.

minute percentage of potash or soda is present. A small quantity of lime is of no importance.

The so-called plumbago crucibles are made of clay and graphite, in the proportion of 51 of the former to 49 of the latter. Only certain varieties of graphite can be used for crucible-making, the texture being of great importance. This can only be determined by experiment. Ceylon graphite contains 79·4 per cent. of carbon, 15.5 per cent. of ash, the remainder being volatile matter. The ash may contain as much as 12 per cent. of ferric oxide, which must be removed by treatment with sulphuric acid. The graphite is picked, ground, sifted, and mixed with the fire-clay, and left for some time to " mellow" after it has been kneaded damp. The crucibles are moulded, dried, and then burnt in kilns. Obviously, an oxidising atmosphere must always be avoided. In order to prevent absorption of moisture and salts, as in cases of shipment, and to enable rapid alterations of temperature to be better withstood, the finished crucibles are dipped in milk of clay, dried, glazed, and then dipped in tar. Crucibles made in this way by the Patent Plumbago Crucible Company, of Battersea, will stand 40 meltings of gold without sensible deterioration.

The pots used in the chlorination process for parting gold and silver are soaked in borax solution, dried and heated. The borax then melts and clogs the pores, and prevents the escape of the silver chloride, which is very fluid.

Classification of Furnaces.—The words *hearth, forge*, and *furnace* are applied to structures in which ores or metals are submitted to high temperatures. A furnace is composed of an interior part, of fire-resisting materials, and an exterior part built for the purpose of consolidating the interior structure. Furnaces may be divided into two classes—(1) those in which the charge and fuel are in intimate contact, there being no independent hearth or fireplace, and (2) those in which the fuel and ore are kept separate, the fuel being burnt in an independent hearth. The first class of furnaces may be sub-divided, according to their height and construction, into *hearths* and *blast-furnaces;* the former are imperfect appliances that usually do not work continuously, whilst in the blast-furnace the action is continuous. The second class is sub-divided into (*a*) *reverberatory-furnaces;* a group in which gas-furnaces may be included, and (*b*) *retort-furnaces.* In the former, the charge only comes in contact with the flame of the fuel, whilst in the retort-furnaces it does not come into contact with the combustible gases of the fuel at all, but is separated from them by walls that merely

transmit the heat. These walls usually form part of separate closed vessels, crucibles, muffles, or retorts, but occasionally they are part of the furnace itself. In this classification, the Bessemer converter is omitted. It cannot be classed as either a hearth or blast-furnace, but it may be described as a vessel usually pear-shaped, in which the impurities contained in the metal treated constitute the fuel which is burnt by a forced current of air. Furnaces may be further divided into those worked by means of a natural current of air, and those worked by a forced current of air. The classification of furnaces may then be summarised thus :—

I.—HEARTHS.

(*a*) Worked by means of a natural current of air. 1. Roasting hearth (piles, stalls, pits, kilns); 2. Liquation-hearth (hearth for liquating argentiferous copper).

(*b*) Worked by means of a forced draught (the smith's forge, iron refinery).

II.—SHAFT-FURNACES.

(*a*) Draught-furnaces (iron ore calciners).

(*b*) Blast-furnaces (iron blast-furnace, Raschette-furnace, Pilz-furnace, cupola-furnace).

III.—REVERBERATORY-FURNACES.

(*a*) Worked by means of natural draught (puddling-furnace).

(*b*) Worked by means of a forced draught (cupellation-furnace).

IV.—CLOSED-VESSEL FURNACES.

May be divided, according to the form of the vessel employed, into—

(*a*) Crucible-furnace (Deville blast-furnace).

(*b*) retort-furnace (for zinc, mercury).

(*c*) tube-furnace (for bismuth),

(*d*) muffle-furnace (for arsenic),

or, according to the process carried out in it, into—

(*a*) smelting-furnace (ordinary assay-furnace).

(*b*) roasting-furnace (arsenic).

(*c*) liquation-furnace (bismuth).

(*d*) distillation-furnace (zinc, mercury).

(*e*) sublimation-furnace (arsenious acid).

(*f*) cementation-furnace (cement steel).

Whether the furnace is worked by natural or forced draught, the general principles involved in the combustion of fuel apply.

The fuel employed in either case may be the same, but the products of its combustion may be widely different. The form and dimensions of the furnace will obviously give rise to a very varied series of results; since on them depends the amount of fuel that can be burnt in a given time, and the degree of perfection of combustion that can be attained, the temperature actually engendered being dependent on the calorific power of the fuel. There may, in fact, be any variations in heat-units between 2473 and 8080 *calories*, the calorific powers of carbon when burnt to carbonic oxide and to carbonic anhydride respectively. In a furnace without an independent hearth, the most important part is that in which the work is principally done. This may be conveniently localised as the zone of combustion. Thus, as Gruner expresses it, for a given fuel burnt in a certain way, the heat developed will simply be proportional to the weight of fuel burnt, whilst the temperature depends on the rapidity of combustion—that is, on the ratio between the volume of the zone of combustion and the weight of coal or coke burnt in an hour. The smaller this ratio, the higher the temperature will be.

In order to show how varied the conditions may be, the following two cases may be cited :—(1) A vat-shaped furnace, such as is used in the Cleveland district for calcining ironstone with a natural draught of air. One hundred and fifteen tons of iron carbonate are calcined in twenty-four hours with a consumption of 4 tons 12 cwt. of coal. The height of the furnace is 33 feet, and its total internal capacity is 8000 cubic feet; but the work of the furnace—namely, that of driving off carbonic anhydride and moisture from an iron ore, is not confined to a limited zone; indeed, the volume of this zone of combustion may be taken to be 1400 cubic feet. Compare this with (2) a modern blast-furnace, such as that used at the Ormsby Ironworks, Middlesborough, a furnace to which reference will again be made in dealing with the blast-furnace. The height of the furnace is 76 feet, and its out-turn is 2453 tons per month, or about 80 tons of pig-iron in twenty-four hours. In this case heated air is driven in, a course which is necessary in order to overcome the resistance of the superincumbent and partially fused mass of ore, fuel, and flux, and the result is that the combustion of the fuel is more or less limited to an intensely hot zone of combustion, the capacity of which does not exceed 200 cubic feet.

Furnaces with independent hearths are usually reverberatory-furnaces, although there are cases in which vat-shaped furnaces are supplemented by fire-grates, which are usually symmetrically arranged round the base. The object of isolating the fuel from

the ore is in order to prevent chemical action of a kind that is not wanted, and generally to enable the nature of the products of combustion admitted into the furnace to be controlled. It would be useless, for instance, to admit torrents of carbonic oxide into a furnace where an oxidising action was wanted, and conversely the predominance of an atmosphere of carbonic anhydride would be fatal to a reducing action.

In France it is usual to consider a reverberatory-furnace as consisting of a grate to hold the fuel, and the "laboratory" portion in which a given operation is conducted. The nature of the operation may be infinitely varied, and the temperature of the laboratory may vary from the dull red heat required for roasting pyritic ores to the intense heat required for melting steel. Obviously, the dimensions of the grate in relation to those of the laboratory will vary considerably, and Gruner has given valuable data for determining what these ratios should be. He shows, for instance, that in conducting certain typical operations, it is necessary to burn in an hour the following amounts of fuel, in lbs. for every square foot of grate area :—

Furnace.	Lbs. per sq. ft.
Furnace for roasting sulphides	3 to 8
Fires for stationary boilers	8 to 20
Furnaces used in smelting lead ores	12 to 16
Furnaces for copper smelting	15 to 30
Pudding furnaces	20 to 30
Steel melting furnaces	41 to 81
Locomotive fires	81 to 102

Lastly, Gruner has given the relation between the volume of the laboratory portion of the furnace and the amount of coal or coke burnt in an hour on the grate, distinguishing between furnaces in which the heating has to be slow or rapid. In the former case, the volume of the laboratory part for every cwt. of coal burnt in air is—

	Cubic feet.
In brick-making	1794
roasting copper ores	538
reducing zinc	101

whilst in furnaces with rapid heating, it is—

	Cubic feet.
In fusion of copper regulus at Swansea	50
ordinary puddling	17½ to 20
steel melting on the bed of a reverberatory-furnace	2½ to 3½

1. **Hearths.**—A hearth is a low furnace in which the material to be treated is exposed to the direct action of solid fuel. Heaps,

stalls, and kilns for roasting ore, are also included in this category, as the action of the fuel is the same. Consequently, hearths are not necessarily enclosed furnaces, but may exist without the aid of any brickwork at all. The pyramidal heaps, in which the roasting of copper ores is effected, are free or unwalled, about 30 feet square at the base, and built upon level ground. A bed of wood, about 1 foot in thickness, is formed, and on this alternated layers of ore and charcoal are piled to the vertical height of 10 feet. Some ironstone from the coal-measures may be roasted in heaps without the addition of fuel. The proportion of bitumen in the copper shale of Mansfeld is almost sufficient for its calcination. With sulphuretted ores, a bed of fuel is used, the burning sulphur keeping up the roasting temperature. Coke-ovens may also be classed as hearths, and so also may the primitive liquation-hearth formerly employed for separating easily fusible constituents out of metallic mixtures.

Hearths worked by means of a forced current of air may be employed for melting or for heating a substance to a very high temperature without altering its state of aggregation, as in welding and forging metals that are not readily fusible.

An example of this class of hearth is the refinery formerly largely used in the manufacture of malleable iron. It consists of a rectangular hearth, provided with inclined tuyeres, through which air is blown upon the surface of the molten iron, so that the silicon in the iron is oxidised, forming with a portion of the iron a fusible ferrous silicate. This process is now unimportant, being confined to forges in a few localities making special qualities of malleable iron.

Further examples are afforded by the shallow hearths used for lead-smelting. In the North of England, a furnace of this kind, known as the *ore-hearth*, is often used. It consists of a cubical chamber, about 22 inches side, lined with cast-iron. In the back wall is fixed a tuyere for the introduction of the blast. In front is the work-stone, which is placed at a slight inclination to the bottom of the hearth. The melted lead flows from the hearth down an oblique channel in the work-stone to a lead pot placed before the work-stone. The operation lasts about twelve hours, the production being 1 to $1\frac{1}{2}$ ton of lead. Peat was formerly used as fuel, but it has now been abandoned and coal is generally used.

In hearths and kilns of this class, the introduction of cold material renders the combustion of the fuel, whether gaseous or solid, more or less imperfect, so that the products of combustion contain an inordinate amount of unburnt gases, especially of carbonic oxide. As a rule, in a kiln the position of the zone

of combustion is fixed, but it occurred to Hoffmann,* a German architect, to devise a kiln in which the position of the zone
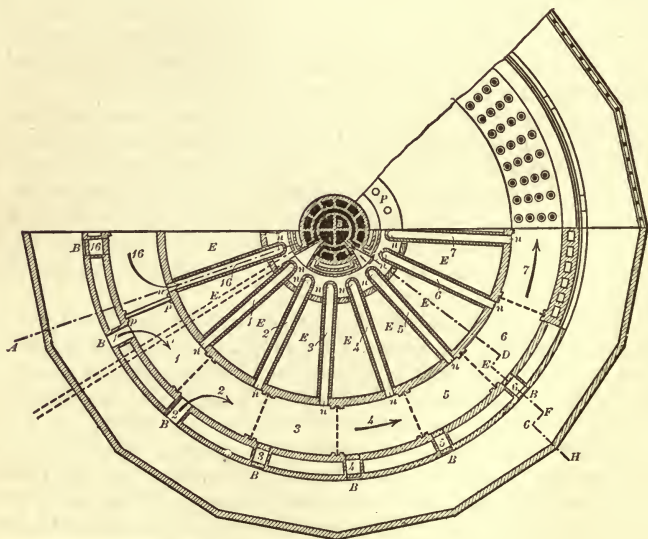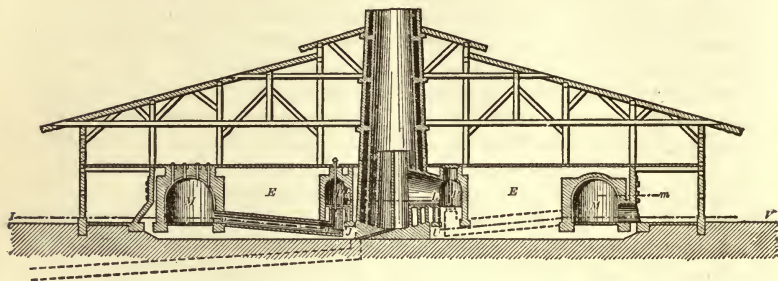
FIG. 54.

of combustion can be varied at will, and he thus succeeded in effecting a considerable economy of fuel. In an ordinary kiln

* *Annales des Mines*, vol. xx. (1871).

there is a continuous ascending column of gas, and a descending column of solid material. In the Hoffmann kiln, on the other hand, the solid material remains stationary, while the gaseous current alone moves. The kiln may be either circular or oval in section, the circular being the more usual form. This is shown in Fig. 54. It consists of a circular tunnel, MM, which can be divided into any number of compartments, twelve or sixteen being the usual number. These compartments are, however, in direct communication with each other, except at one point, where an iron plate, pp, placed across the tunnel, interrupts the continuity. This plate may be inserted through the roof of the tunnel down grooves, nn, provided for its reception, in the walls. Each space between two sets of grooves is provided with an internal flue, E_1E_2, which, by the removal of a damper, can be placed in communication with a central chimney, and each space has also a door, BB, in the outer wall. Only two of these doors are open at a time. The whole of the tunnel is kept full of material (ores to be calcined, or bricks to be burnt), except one compartment, which is always empty. The position of the empty compartment varies from day to day. Let the plate occupy the position, pp, shown in Fig. 54. The newest material has been charged in behind it into compartment 16. Air enters in front of it through the open door of the empty compartment No. 1, and through the door, also open, of the next compartment, which contains finished material that has been longer in the furnace than the rest, and has but little heat to give up to the in-coming current of air. This current is drawn by natural draught round the entire tunnel, and can only enter the chimney through one or more of the flues that have been opened behind the plate. After an interval of twenty-four hours from the last charging, the position of the iron partition is shifted to the next groove to the right, the compartment No. 1 is filled, and the one, No. 2, in front of the plate is emptied. Thus, new material is continually kept behind the plate, and finished material in front of it. Air entering comes in contact with material which gradually increases in temperature, for it will be obvious that the position of the hottest part of the furnace must be continually travelling round the circle, and that in a number of days, corresponding with the number of compartments, the zone of combustion will have travelled completely round the circuit. The air and the material to be treated enter and leave the furnace in a cold condition, so that there can be no waste of heat, provided that the adjustment of the dampers in the flues through which the gases pass to the chimney, is carefully effected. In order to remedy local irregu-

larities of combustion, air may, if necessary, be admitted through suitable orifices in the roof.

The volume of each compartment may vary from 282 to 1765 cubic feet. In order to facilitate charging and to secure perfect uniformity of temperature, the height of the tunnel should not exceed 9 feet.
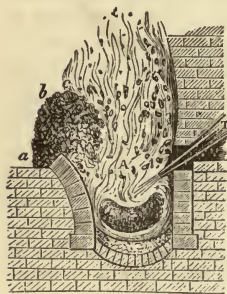
FIG. 55.

In Catalonia, a low hearth, the Catalan furnace (Fig. 55), is still occasionally to be met with. It is used for the production of malleable iron direct from the ore. It is made of blocks of cast-iron and has a sandstone bottom. The tuyere is made of sheet copper. The blast is supplied by a water-blowing machine, or *trompe*, which may be made from a hollow tree trunk, 15 feet high, at the top of which is a water-box with a plug. The water falls down the pipe into the windbox, carrying air with it, and causing a pressure of $1\frac{1}{2}$ to 2 lbs. per square inch in the hearth.

2. **Shaft-furnaces.**—In all the members of this group the fuel and ore are charged into a common receptacle, the axis of which is vertical. Certain of them, as the kilns in which limestone or ore is calcined, are worked by a natural current of air, the furnace itself forming a capacious chimney.

The form of these furnaces is very varied, according to the nature of the ore and of the fuel employed. Furnaces of this kind may be egg-shaped, cylindrical or conical. Small kilns with circular horizontal section effect the most uniform roasting, give rise to the least loss of heat by radiation, and wear well. They, however, necessitate the use of expensive bricks of special shape. The height is dependent on the size of the pieces and on the fusibility of the ore. The width is dependent on the quantity of ore to be roasted. In large kilns of circular section it is difficult to maintain a uniform temperature. Large kilns have consequently an elliptical or rectangular section. In the latter case the corners are rounded off.

The best examples of this type of furnace are afforded by the kilns employed for calcining iron ores. One of the best forms is that of Gjers (Fig. 56), which is extensively used in the Cleveland district. The drawing, to the scale of 10 feet to the inch, shows this kiln partly in elevation and partly in section. The body is of fire-brick cased with malleable iron plates. The bottom of the brickwork rests on a cast-iron ring, *a*, and the whole is

supported by cast-iron pillars, *b*, leaving a clear space between the bottom of the kiln and the floor. The latter is covered by iron plates, *c*, on the centre of which is fixed a cast-iron cone, *d*, 8 feet in height and 8 feet in diameter at the base. This causes the descending roasted ore to pass outwards. Fresh ore and coal
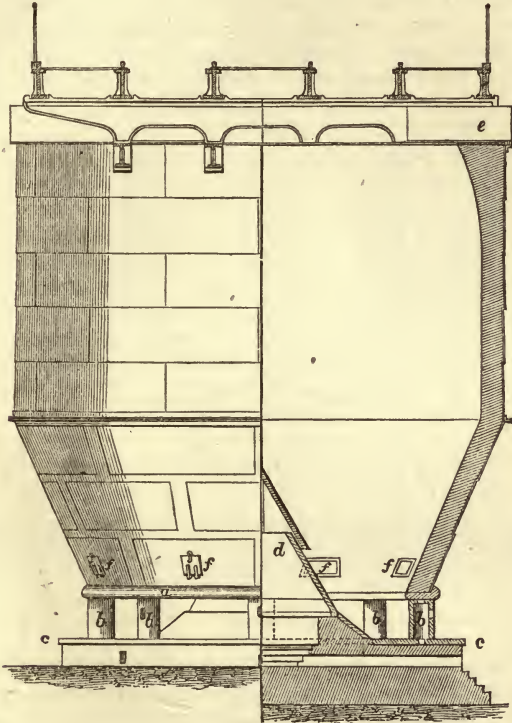
FIG. 56.

are constantly being added from the filling gallery, *e*. Around the lower tier of plates are openings, *f*, which are usually closed by doors, but which serve for the admission of air or tools in case of the ore becoming clotted. These kilns are usually 33 feet in height, 24 feet in diameter at the widest part, and have a capacity of

8000 cubic feet.   They calcine 800 tons of iron ore per week, the consumption of coal amounting to 1 ton for 25 tons of ore.

In Styria, kilns are used provided with step-grates.   A kiln of this kind is shown in Fig. 57, in vertical section drawn to the same scale as the preceding figure.   The masonry, *a*, is of rubble-work, the lining, *b*, of the kiln is of fire-brick, the grate, *c*, and the bottom, *d*, are of cast-iron.

In all blast-furnaces carbonic oxide is the main reducing agent, but in certain forms, such as those employed in the smelting of lead ores where only moderate temperatures are required, care is taken that the atmosphere is not too reducing, or intractable
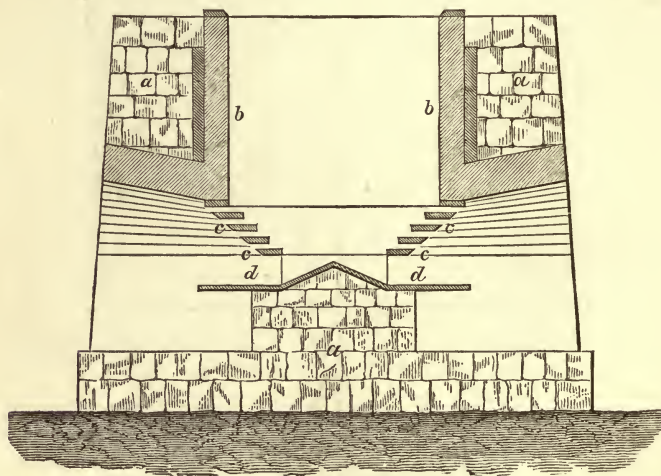
FIG. 57.

masses of iron will be produced which will impede the action of the furnace.   The generation of carbonic oxide in front of tuyeres supplies the heat to melt the slag and metal, whilst the gas itself is the reducing agent throughout the process.   Usually by far the most important point to consider is the temperature actually attained in the zone of combustion—that is to say, the portion of the furnace near the tuyeres where the fuel is actually burnt. The temperature will depend on the relation between the volume of the zone of combustion and the weight of fuel burnt in a an hour.   The smaller this ratio is, the higher the temperature will be.
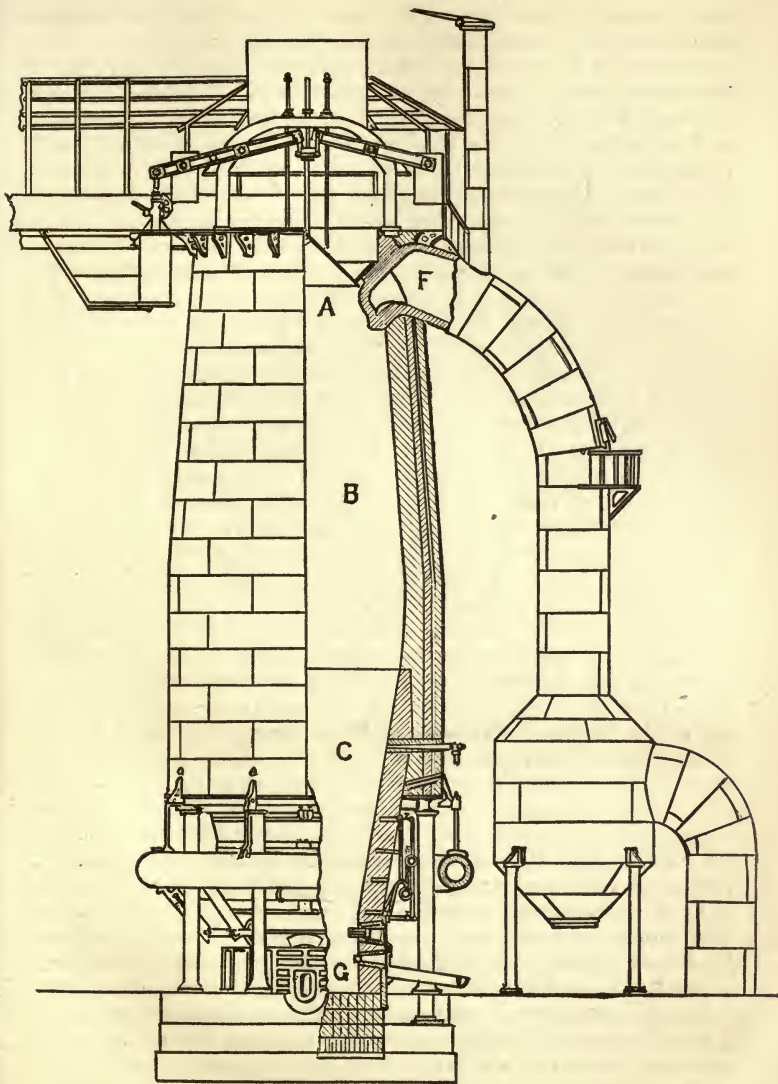
FIG. 58.

The most important member of the group of furnaces without separate hearth is the blast-furnace. As its name implies, it is worked by a forced current of air supplied by a bellows or by blowing-engines. The blast-furnace in which pig-iron is made is shown in Fig. 58. In former times charcoal was exclusively the fuel employed, whilst at the present time coke is mostly used. Raw fuel (coal or anthracite) is only adopted in special cases. The modern blast-furnace, in which coke is used as fuel, is 70 to 80 feet in height, some of the larger examples attaining to 100 feet. Charcoal blast-furnaces are considerably smaller. Formerly, the blast-furnace was a heavy conical mass of masonry some 30 feet in height. It is now a much lighter structure, formed of a wrought-iron casing lined with brickwork. In order to distinguish it from the older forms, it is termed a cupola blast-furnace. In the upper opening, or throat, fuel or ore are charged, being allowed to fall into the furnace, usually through some form of appliance for distributing the charge. In the lower narrow portion of the furnace, highly compressed air is forced through a number (usually five to eight) of horizontal nozzles or tuyeres arranged in a circle. When the blast is previously heated, the water-tuyere is always employed. It consists of a hollow truncated cone, through which a current of water circulates. In the space in front of the tuyeres, the consumption of the fuel is effected, which is already highly heated in its descent through the furnace, and a temperature of more than 2000° is obtained. The plane in the blast-furnace where the greatest diameter is reached is termed the *boshes*, and the cylindrical portion at the base is the *hearth*, G, in which the molten material collects. The top of the furnace is surrounded by a charging gallery, and is usually covered in by an iron cup and cone, A, the latter of which may be lowered by a counterpoise and winch or by an hydraulic cylinder, when material is to be charged in, the waste gases passing through a side tube, F, whence they are led to the stoves for heating the blast, or are burnt under boilers. The stack is carried on an iron ring resting upon iron columns, the object being to have all the working parts of the furnace readily accessible so that they can be repaired from time to time. In front of the hearth an opening extends from the hearth-bottom to a little above the level of the tuyeres. The arch above this opening is called the *tymp arch*. The sides of the opening are prolonged outwards into a rectangular cavity, the *fore hearth*, which is bounded in front by a firebrick wall called the *dam*, carried up to the tuyere level and supported by a cast-iron *dam plate*, a semicircular notch, the *cinder notch*, in the top edge serving as a

passage for the slag. The *tap-hole* for withdrawing the molten iron is a narrow vertical opening in the bottom of the dam. The iron is run into sand moulds, forming *pigs* about 3 feet long.

A large modern blast-furnace produces 75 to 100 tons of pig-iron in twenty-four hours, whilst small charcoal blast-furnaces yield only 5 tons in the same time. Sometimes a furnace charge is obstructed in its descent. When the lower portion is melted, the obstructed unreduced portion, or *scaffold*, is apt to give way suddenly and fall into the hearth.

Notwithstanding that iron-smelting dates from a very early period, the chemical changes that occur were very imperfectly understood in this country, until the subject was investigated by Sir Lowthian Bell * and Dr. C. R. Alder Wright.† The ores employed are usually subjected to a preliminary calcining, so as to convert ferrous carbonate into ferric oxide, to expel water, and to open out the texture of the ore. In some cases, however, the ore exists naturally as ferric oxide. The general composition of the ores chiefly used is :—

Red hæmatite :—Ferric oxide, with little or no earthy matter.
Magnetic ore :—Ferric and ferrous oxides, with earthy matter.
Spathic ore :—Ferrous carbonate and manganese carbonate, crystalline.
Clay ironstone :—Ferrous carbonate and much earthy matter.
Brown hæmatite :—Hydrated ferric oxide and earthy matter.

When the carbonate is not calcined before use, it soon loses its carbonic anhydride, leaving behind an oxide of iron. This occurs in the top portion of the furnace, so that virtually the ores used may be regarded as consisting essentially of some form of iron oxide with a varying amount of earthy matter. The fuel used is usually coke or charcoal. When raw coal is employed it is completely coked in the top portion of the furnace, so that the fuel burnt at the tuyeres is invariably carbon. This carbon is either burnt directly to carbonic oxide, or if burnt first to carbonic anhydride, it is immediately converted into carbonic oxide by the incandescent carbon. Most of the nitrogen of the blast remains unchanged, and any moisture in the blast is converted into a mixture of carbonic oxide and hydrogen. The amount of the latter necessarily varies with the hygrometric state of the atmosphere. The influence of the small quantity of hydrogen in blast-furnace gases is insignificant, since the gases issuing from the top of the furnace contain as much free hydrogen as that brought in by the

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* *Chemical Phenomena of Iron Smelting*, London, 1872.
† *Proc. Roy. Inst. of Great Britain*, vol. vii. (1874), p. 248.

blast. Indeed, the liberation of hydrogen is injurious to the action rather than advantageous, for experience shows that the more moisture enters the furnace the more fuel is required to do the work. Virtually, therefore, the air passing into the blast-furnace becomes converted into a mixture of about two volumes of nitrogen and one volume of carbonic oxide. This ascends through the furnace and produces a number of complex chemical changes as it comes in contact with the ore. These changes are indicated by Dr. Alder Wright by the following equations :—

[A] Reduction of higher oxide to lower oxide and metal by gaseous carbonic oxide.

$$(1) \quad Fe_xO_y \quad + \quad CO \quad = \quad Fe_xO_{y-1} \quad + \quad CO_2$$
$$(2) \quad Fe_xO_y \quad + \quad yCO \quad = \quad xFe \quad + \quad yCO_2$$
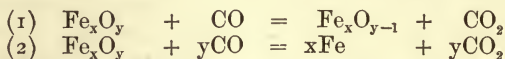
[B] Oxidation of metal and lower oxide to higher oxide by carbonic anhydride.

$$(3) \quad xFe \quad + \quad yCO_2 \quad = \quad Fe_xO_y \quad + \quad yCO$$
$$(4) \quad Fe_xO_{y-1} \quad + \quad CO_2 \quad = \quad Fe_xO_y \quad + \quad CO$$
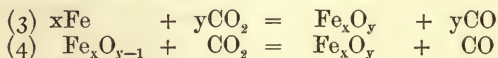
[C] Reduction of carbonic oxide to carbon.

$$(5) \quad xFe \quad + \quad yCO \quad = \quad Fe_xO_y \quad + \quad yC$$
$$(6) \quad Fe_xO_{y-1} \quad + \quad CO \quad = \quad Fe_xO_y \quad + \quad C$$
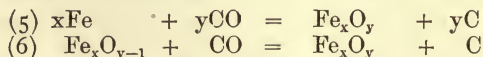
[D] Reaction of reduced carbon on iron oxide forming carbonic anhydride.

$$(7) \quad 2Fe_xO_y \quad + \quad C \quad = \quad CO_2 \quad + \quad 2Fe_xO_{y-1}$$
$$(8) \quad 2Fe_xO_y \quad + \quad yC \quad = \quad yCO_2 \quad + \quad 2xFe$$
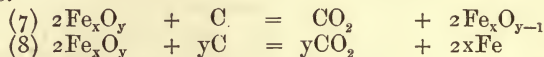
[E] Reaction of carbonic anhydride on reduced carbon.

$$(9) \quad CO_2 \quad + \quad C \quad = \quad 2CO$$
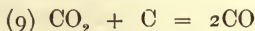
Although carbonic oxide exerts no action on ferric oxide at ordinary temperatures, yet its influence is appreciable at 150°, whilst in the converse changes [B] the oxidising effect of carbonic anhydride is scarcely appreciable at a temperature of 300°, but is noticeable at 400° and is very considerable at 600°. As regards equation (2) it may be remarked that it is impracticable to reduce the whole of the ferric oxide by means of carbonic oxide at any temperature short of a white heat. In fact, iron decomposes carbonic oxide at temperatures below this in virtue of equation (5).

At any given point in the blast-furnace, all the chemical tendencies thus indicated are at work simultaneously, with more or less vigour according to circumstances. The action actually taking place at this point is, therefore, that due to the single resultant of the various forces involved—namely, the iron-reducing ten-

dencies [A] and [D], the iron-oxidising [B] and [C], the carbon-reducing [C], and the carbon-oxidising [D] and [E] tendencies. Knowledge of the relative magnitude of these forces has been gained from the careful experiments of Sir Lowthian Bell and Dr. Alder-Wright. In tracing out the general chemical changes undergone by the oxide of iron, the furnace may be conveniently divided into three regions. In the uppermost region, tendencies [A] and [D] jointly are stronger than [B] and [C] jointly, and consequently rapid reduction of ferric oxide takes place. In this region, too, tendency [C] is more powerful than tendencies [D] and [E], and consequently carbon deposition takes place to a large extent. Here, too, the limestone flux is for the most part calcined into quicklime, raw coal, if used, is coked, and if iron carbonate is used, instead of oxide, it becomes converted into oxide, the reducing and carbon-depositing reactions going on simultaneously with the formation of the oxide.

In the middle region, the iron-reducing tendencies are almost balanced by the iron-oxidising ones, whilst the carbon-depositing tendencies are equalled by the carbon-oxidising ones. Here reduction takes place, but only languidly, the chief effect produced in passing through this region being an increase of temperature.

In the lowest region, the reduction of the residual iron oxide is completed chiefly through the agency of cyanides formed in the vicinity of the tuyeres; the reduced iron melts dissolving a certain amount of the finely divided carbon in contact with it, together with small quantities of silicon, phosphorus, and sulphur reduced by subsidiary reactions. The non-metallic constituents of the ore and the lime of the limestone also fuse, forming slag.

The nitrogen brought into the furnace acts solely as a diluent, except in the lower portions of the furnace. It has long been known that when nascent potassium or sodium vapour finds itself simultaneously in contact with carbon and nitrogen, the three elements combine, forming a metallic cyanide. The cyanide thus formed acts on the last portions of unreduced oxide of iron, converting it into metal and becoming itself changed to cyanate. This is probably decomposed with the formation of an alkaline carbonate and the elimination of nitrogen. The alkaline salts condensed in the upper portions of the furnace are again brought down to the level of the tuyeres as the materials sink. Consequently each particle of alkali metal does duty over and over again, the alkalies introduced in small quantities in the fuel accumulating in the furnace to a very large extent. As much as 4 cwt. of alkali metals and 2 cwt. of cyanogen per ton of iron made have been repeatedly found in the gases near the level of

the tuyeres. This concentration of alkali explains the fact that furnaces reduce more readily after they have been some time in blast.

In order to effect the smelting of iron, a definite amount of heat is required to perform the general work of the furnace, the various items in the appropriation of heat in an 80-foot blast-furnace, during the production of 20 cwt. of pig-iron from Cleveland ore being as follows :—

Constant requirements of furnace—

	Cwt. Heat-units.	
Reduction of iron from ferric oxide . .	33,108	
Impregnation with carbon	1,440	
Reduction of phosphorus, sulphur, and silicon	4,174	
Fusion of pig-iron	6,600	
Radiation from walls of furnace . . .	3,658	
Cooling tuyeres by water	1,818	
Other sources of loss	3,202	
		54,000
Variable sources of loss of heat—		
Fusion of slag	16,720	
Expulsion of carbonic anhydride from limestone	5,054	
Decomposition of carbonic anhydride . .	5,248	
Decomposition of water in blast . . .	2,720	
Evaporation of water in coke . . .	313	
		30,055
Carried out by escaping gases		8,860
Total		92,915
Brought in by hot blast		11,919
Heat produced by combustion of coke		80,996

In order to produce this heat with a minimum expenditure of fuel, it is necessary that the whole of the carbon used as fuel should be oxidised to carbonic anhydride, an ideal that can only be realised in the reduction of lead oxide. The relative strengths of the forces involved in the nine reactions described are, in the case of iron ores, such that it is not possible to convert more than 35 or 40 per cent. of the carbon burnt into carbonic anhydride, the rest necessarily escaping as carbonic oxide. Consequently more fuel must be used to do the work of the furnace.

The most economical results are obtained when the ratio $\dfrac{CO_2}{CO}$ is greatest. This ratio, however, itself is modified by the temperature, the velocity, and the distribution of the gaseous current. Care must be taken to lessen, as far as possible, the amount of

the carbon burnt by the carbonic anhydride. The solid carbon is divided into two portions—one burnt in the zone of fusion, and the other in the zone of reduction. In the second case the reduction is effected with consumption of solid carbon, whilst in the former case, it is effected solely by the gases. The ideal case would be that in which carbon descends to the level of the tuyeres, and is there converted into carbonic oxide.

A convenient classification of blast-furnaces is that based on the ratio of the maximum diameter to the height. In this manner the following three classes may be distinguished :—

1. Squat furnaces, in which the height is less than, or equal to, three times the diameter, $\frac{H}{D} < 3$.

2. Ordinary furnaces, in which the ratio $\frac{H}{D}$ varies between 3 and 4, but is usually about 3.5.

3. Elongated furnaces, in which the ratio $\frac{H}{D}$ is greater than 4.

The following table gives comparative data of the dimensions and workings of ten typical blast-furnaces used for the smelting of iron :—

	Cubic Capacity.	Total Height.		Diameter at Hearth.		Diameter at Boshes.		Diameter at Throat.		Daily Out-turn.	Time in Fur-nace.	Fuel per Ton of Metal.
	cub. ft.	ft.	ins.	ft.	ins.	ft.	ins.	ft.	ins.	tons.	hours.	lbs.
1	30,000	85	0	8	0	28	0	19	0	70	150	2308
2	18,000	80	0	11	0	22	0	16	0	270	21	1863
3	15,000	75	0	11	0	20	0	15	4	175	24	2116
4	14,000	75	0	8	0	21	0	14	0	107	36	2130
5	8,824	73	8	9	6	15	6	11	9	142	20	1943
6	6,676	72	4	8	6	15	0	9	6	114	19	1697
7	2,000	50	0	5	6	10	0	5	6	48	8	1870
8	1,872	49	8	4	6	10	4	3	4½	24	10	1365
9	1,235	37	3½	5	8	8	4½	3	1½	24	4	1653
10	1,000	37	6	5	6	7	0	3	0	20	7	1585

In the first six furnaces coke is the fuel employed, whilst charcoal is used in the last four. The names and situations of the furnaces are : 1. Newport, England ; 2. Edgar Thomson "F," Pittsburgh, United States ; 3. North Chicago, No. 6, Chicago, United States ; 4. North Lonsdale, No. 3, Lancashire ; 5, Union, No. 3 and No. 4 ; 6. Union, No. 2, Chicago ; 7. Midland, Craw-ford County, Missouri, United States ; 8. Treibach, Austria ; 9.

Ferdinand, Hieflau, Austria; 10. Wrbna, Eisenerz, Austria. The first four of these furnaces belong to the second class, in which $\frac{H}{D}$ is less than 4, whilst the last six are elongated furnaces in which the ratio $\frac{H}{D}$ is greater than 4. The following are examples of the first class, in which $\frac{H}{D}$ is less than 3.

	Name.	Cubic Capacity.	Height.	Diameter at Throat.	Diameter at Boshes.	Daily Out-turn.
		cub. ft.	ft.	ft. ins.	ft. ins.	tons.
11	Longwy, France .	14,656	65	13 6	23 0	40
12	Clarence (old type)	6,003	50	7 10	16 6	30
13	Thornaby „ .	12,784	60	14 9	20 0	
14	Ormesby . .	40,984	90	15 9	30 0	

In furnaces of this type, the working is irregular on account of the contraction at the throat, which renders it difficult to apply any mechanical method of distributing the charge uniformly.

Mr. E. Walsh [*] shows that by placing the boshes, or widest diameter of the furnace, entirely within the zone of complete fusion a constant supply of fuel at the level of the tuyeres would be secured. He also concludes that, within practical limits, the narrower the furnace-shaft is constructed the more energetic the actions of reduction and carbon-impregnation will be. This view is supported by the outlines of the ten furnaces shown in Fig. 59. It may be noted that the Union No. 2 (6 in table) and the Treibach No. 3 (8 in table) do not owe their low fuel consumption to great capacity, to the employment of high temperature of blast, nor to the great length of time the materials are allowed to remain in the furnace.

It was formerly the practice to allow the waste gases to burn at the throat of the furnace. Since the introduction of the hot blast, however, it has become usual to apply some arrangement for closing the throat of the furnace and for collecting the waste gas. The *cup and cone*, invented by Parry, is the arrangement generally used. The throat is closed by an iron cup-shaped casting, the diameter of which at the lower end is about one-half of that of the throat of the furnace. Beneath this cup, a cast-iron cone is suspended from its apex, and when the charge has descended

* *Engineering*, vol. xlii. (1886), p. 513; *Trans. Amer. Inst. M.E.*, 1886.
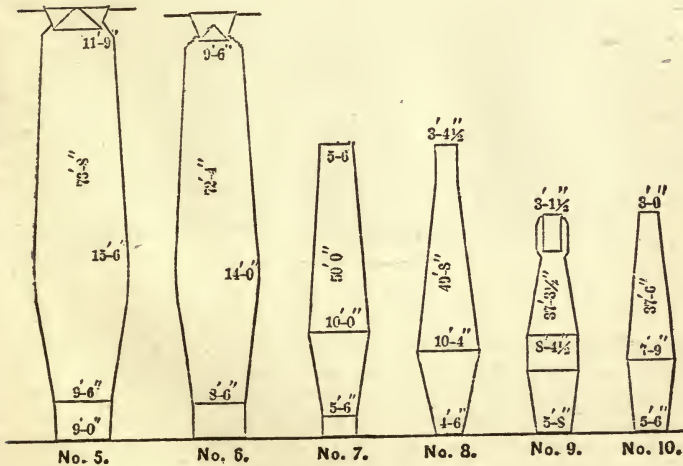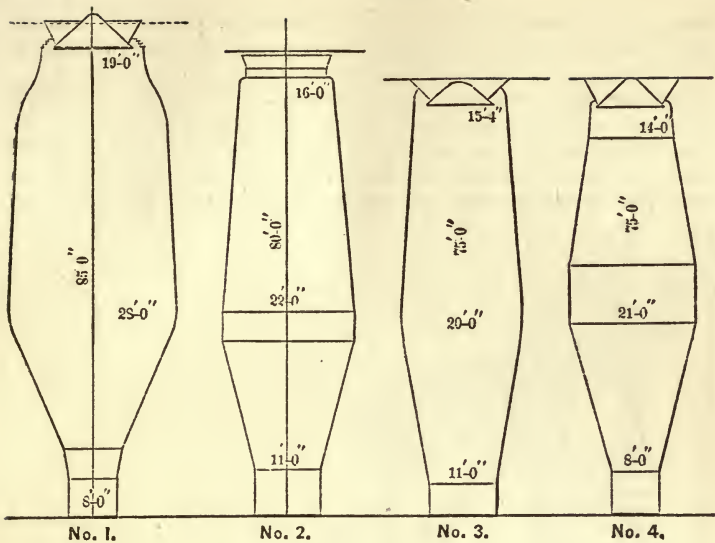
FIG. 59.

from the cup which forms a hopper, the cone is raised so as to completely close the throat, and the gases pass out through a lateral pipe. A method of closing the top is shown in Fig. 60.

In Germany, arrangements are largely used by means of which the gases are withdrawn from the centre of the throat instead of from the sides. The apparatus of Langen and of Von Hoff afford good examples. In the former, the bell-shaped tube which closes the throat is raised, whilst in the latter it is lowered, in

FIG. 60.
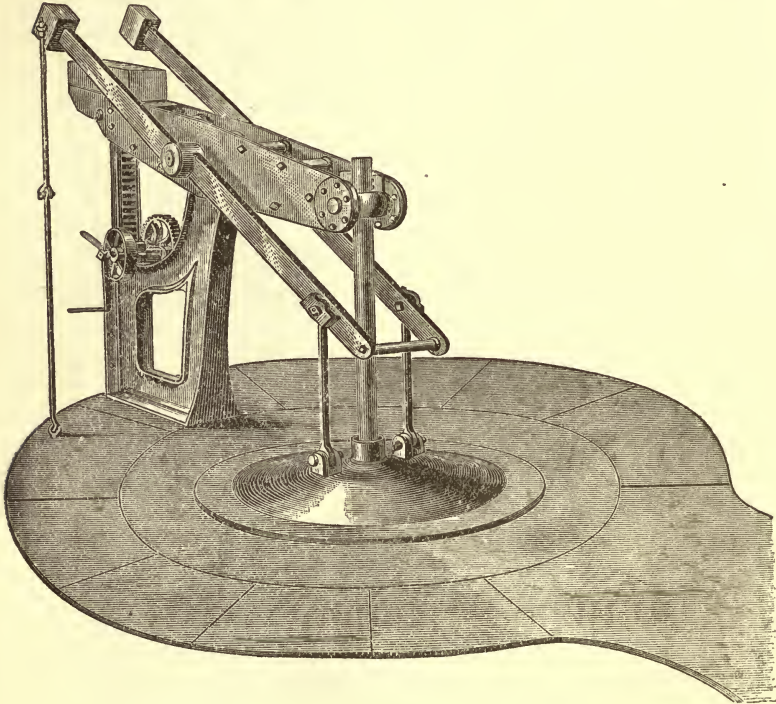
order to allow the charge to fall into the furnace. In both cases, gas-tight joints are obtained by the aid of water troughs.

Numerous attempts have been made to ascertain the changes in the materials during their descent in a blast-furnace, with reference to the arrangement of the constituents. A valuable series of experiments have been made by Profs. R. H. Richards and R. W.

Lodge * with a view to elucidate this subject. They constructed a model consisting of a vertical section of a furnace at the Edgar Thomson works, 40 inches in height, and made to the scale of half an inch to the foot. The horizontal section of the space through which the charge falling at any point in the descent is $1\frac{1}{2}$ inch multiplied by the diameter of the furnace at that place. The back and sides of the model were of wood, and the front of glass, the intermediate space measuring $1\frac{1}{2}$ inch. Below was a small hopper into which the charge fell, and from which it was shovelled back to the cup and cone. Every shovelful withdrawn settled the contents of the stack sufficiently to receive a new charge above, and in this way a great variety of feeds were tried, and the arrangement caused by them observed through the glass. The material used for the charges was composed of pebbles and clean quartz sand, the different sizes being mixed in the following proportions per cent. :—

	Lot 1.	Lot 2.	Lot 3.	Lot 4.
Through $\frac{1}{2}$ in. sieve on $\frac{1}{4}$ in. sieve .	38.74	51.66	64.0	76.08
,, $\frac{1}{4}$ in. ,, $\frac{1}{8}$ in. ,, .	2.56	1.81	2.0	2.43
,, $\frac{1}{8}$ in. ,, $\frac{1}{16}$ in. ,, .	13.67	11.17	9.0	6.39
,, $\frac{1}{16}$ in. ,, $\frac{1}{30}$ in. ,, .	4.56	3.32	2.3	1.40
,, $\frac{1}{30}$ in. sieve . . .	40.46	32.02	22.7	13.69

Each lot of materials so mixed was used for a series of tests, and in every case, as soon as the model had got into normal working, a photograph of the condition of the charge was taken. These photographs are in series, with two variables, namely, the kind of cone or distributor, and the proportion of coarse and fine in the material used. A similar model may be seen in the author's lecture-room, where it has been found very useful.

An examination of the photographs shows :—1. That a cone which is large in reference to the stock line, always gives the charge in three columns, the two outer being fine and the one inner being coarse. 2. That a cone which is small in reference to the stock line and which is kept full fed, always yields the charge in five columns ; the centre is coarse, then a ring of fine, and then margins of coarse again. 3. That a furnace fed without a cone, and whose top is smaller than the stock line, will give a fairly even mixture, the coarse material being slightly concen-

* *Transactions of the American Institute of Mining Engineers*, vol. xvi. (1888).

trated in the margin. 4. That a furnace fed with a central funnel gives three columns, one fine in the centre and two coarse columns on the sides. 5. That if the stock line be varied from high to low, with a small cone, the arrangement of material resulting will vary from five to three columns. 6. Columns of coarse material appear to settle more rapidly, and those of fine material less rapidly.

With a view to produce a better distribution of heat, Truran proposed, in 1857, to increase the sectional area of the blast-furnace from the hearth to the throat. This plan was adopted by Raschette in 1862. His furnace in section is a narrow rectangle with six or eight tuyeres on each side, placed so as not to be directly opposite. Under the hearth, there is a chamber containing a grate, communicating with channels traversing the masonry of the stack. The masonry may by this means be dried, and the construction of the furnace is not dependent on the season of the year. As the blast is distributed over a large section in the zone of fusion, the combustion in this furnace is perfect, and a large out-turn is possible. The Raschette furnace is used in the Ural for smelting iron ores, but it has not been found to answer for this purpose in other parts of Europe. It is, however, largely used for smelting lead and copper ores. The Raschette furnace used for smelting lead ores in the Upper Hartz is 20 feet high, 7 feet 6 inches long, 4 feet 10 inches wide at top, and 3 feet at bottom. There are five tuyeres at each side, and, in the more recent furnace, one at each end.

Rectangular furnaces of the Raschette type are largely used in Colorado for lead-smelting. The furnaces used at Leadville are described in great detail by Mr. S. F. Emmons.* The furnace is formed of two independent parts, the masonry stack, *a*, (Figs. 61, 62) supported on a main cast-iron plate, *b*, resting on cast-iron pillars, *c*, and the crucible upon which rest the water jackets. These constitute one of the greatest improvements ever introduced in the construction of blast-furnaces. They are hollow boxes, made of cast-iron, malleable iron, or steel boiler-plate, in which water circulates freely, so that the temperature of this portion of the furnace wall, where the most intense heat prevails in the interior, never exceeds 70°. The water-jacket arrangement is always sectional, so as to afford every facility for the removal of the jackets when the furnaces need important repairs. This arrangement must be highly commended, as it

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* *Geology and Mining Industry of Leadville, Colorado,* Washington, 1886, p. 659.
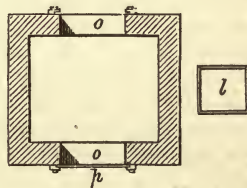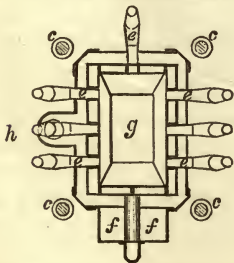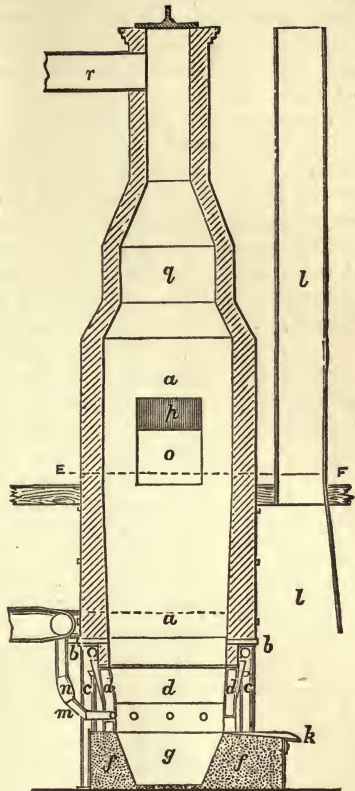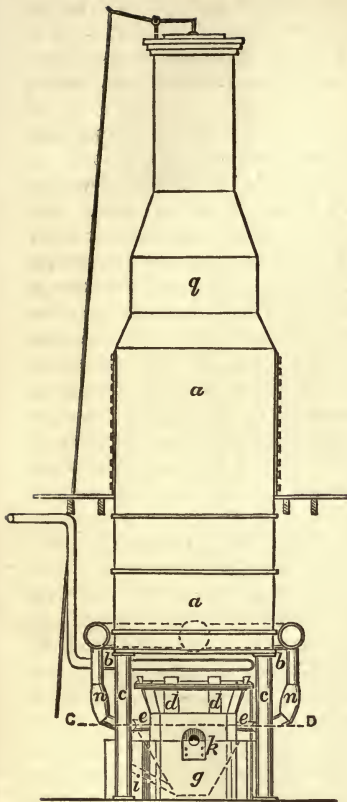
FIG. 61.   FIG. 62.

admits of the expansion and contraction of this portion of the furnace without altering the relative positions of the parts. The importance of this arrangement will be appreciated when it is stated that smelting campaigns of thirteen months are known at Leadville.

The Leadville rectangular furnace is shown in the accompanying figures, 61 and 62, which are drawn to a scale of 9 feet to the inch. The dimensions of the furnaces vary at the different works, as the daily smelting capacity varies from 15 to 40 tons. The water-jackets, d, are, in the furnace represented, twelve in number, bolted together and provided with openings for the tuyeres, e. A cold-water pipe runs round the furnace, and supplies water to the water-jackets. The lower ends of the latter rest on the hearth, f, which consists of cast-iron plates lined with fire-bricks

or brasque. The usual form of the bottom is shown at g. The hearth-plates enclose the lead-well, h, and the channel, i, through which the molten lead rises to the level that it occupies in the furnace, and can be ladled into moulds without interrupting the work. At the side of the furnace, an opening is left in the water-jacket for tapping off the slag, which runs down the gutter, k, when the clay stopping the aperture is pierced. A hood, l, is placed so as to carry off any fumes evolved during tapping. When cold blast is employed, the tuyeres are connected to the blast-pipes by flexible canvas hose, n, and a slide, m, at the elbow of the nozzle, admits of looking into the interior of the furnace.
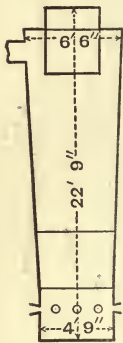
FIG. 63.

The feed openings, o, are closed by counterpoised doors, p, and the furnace terminates in a short chimney, q, communicating by a flue, r, with dust-chambers.

Blast-furnaces of the Pilz type are also used in Colorado; but the rectangular furnace of the Raschette type is generally preferred, as it is less expensive in construction. In Europe, on the other hand, the former has almost entirely superseded the latter. The Pilz furnace, which is generally employed for smelting mixed ores of lead and copper, is circular in section. Its internal profile, which is shown in Fig. 63, differs from any of the types given in Fig. 59. In this case $\dfrac{H}{D}$ is more than three, but the widest part is at the top, the contraction being gradual to the "crucible" portion of the furnace in which the tuyeres are placed. The
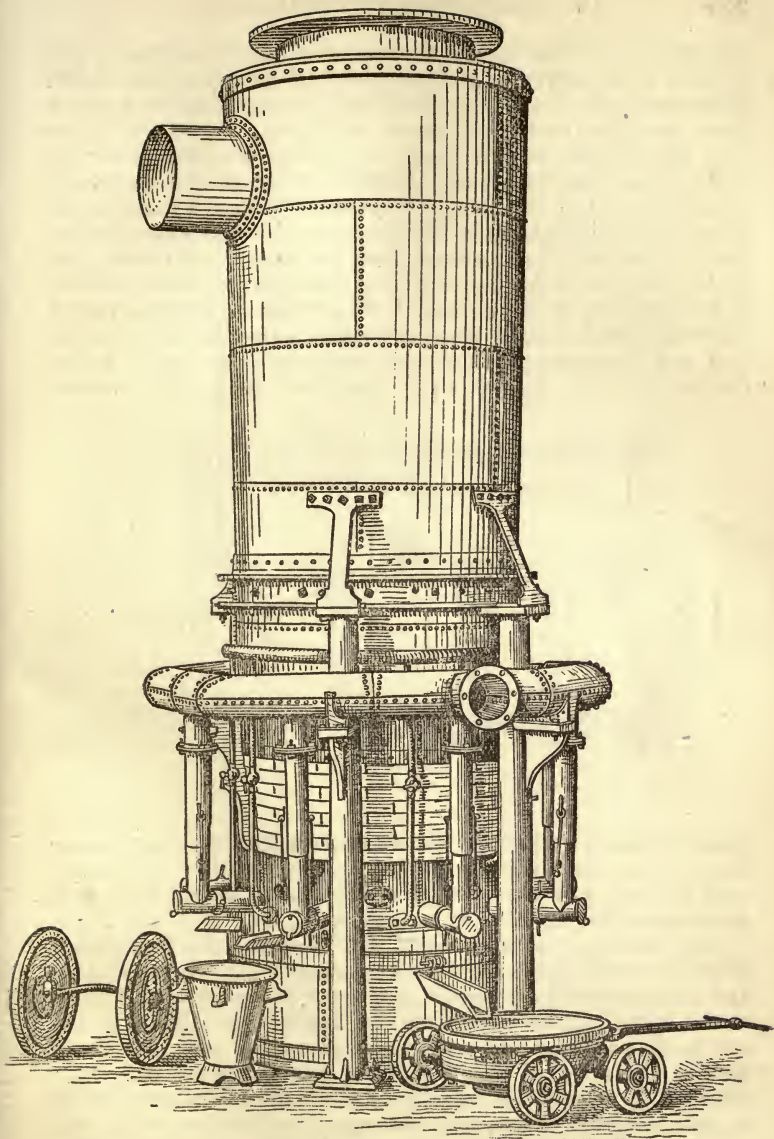
FIG. 64.

actual area at the throat is, however, much restricted by a
cylinder of wrought iron through which the charge is introduced.
The appearance of the exterior of the furnace, in its most recent
form as used at Freiberg, is shown in Fig. 64.

3. **Reverberatory Furnaces.**—These are constructed of very
varied forms and dimensions, but their construction is guided by
principles common to them all.   Reference to Figs. 65 and 66 will
show that the reverberatory furnace consists of two main portions,
the fire-place (either an ordinary grate or a producer), and the labo-
ratory part, the fuel being separated from the ore, or the material
to be heated, by means of a *fire-bridge*, which is simply a wall of
refractory brick, usually furnished with an air-channel to keep it
cool, and sometimes provided with orifices which admit air into
the furnace.   As the flames pass over this bridge and *reverberate*
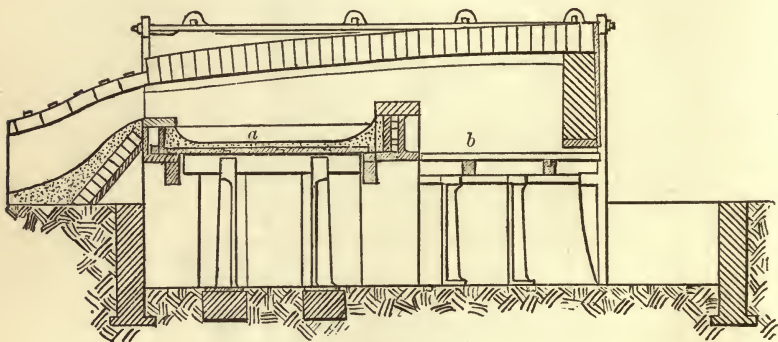
FIG. 65.

into the laboratory part, it will be evident that its height in re-
lation to the position of the roof has to be regulated with much
care, for on it will depend whether the flames act directly or by
radiation on the material to be heated.

The laboratory part is connected, by means of a flue, with a
chimney, which serves for the withdrawal of the consumed gases,
and in many cases also for the production of draught.   A damper
at the base of the chimney or in the flue enables the current of
air to be regulated; and, taken in connection with the thick-
ness of the layer of fuel burnt on the fire-place, the atmo-
sphere may be rendered oxidising, neutral or reducing at will.   It
is now necessary to consider the way in which the details and
dimensions of the furnace may be varied.   Figs. 65, 66, exhibiting

two extreme cases, show how much the dimensions of the laboratory part in relation to the fire-place may vary. In Fig. 66 a more or less pulverulent material has to be kept compara-
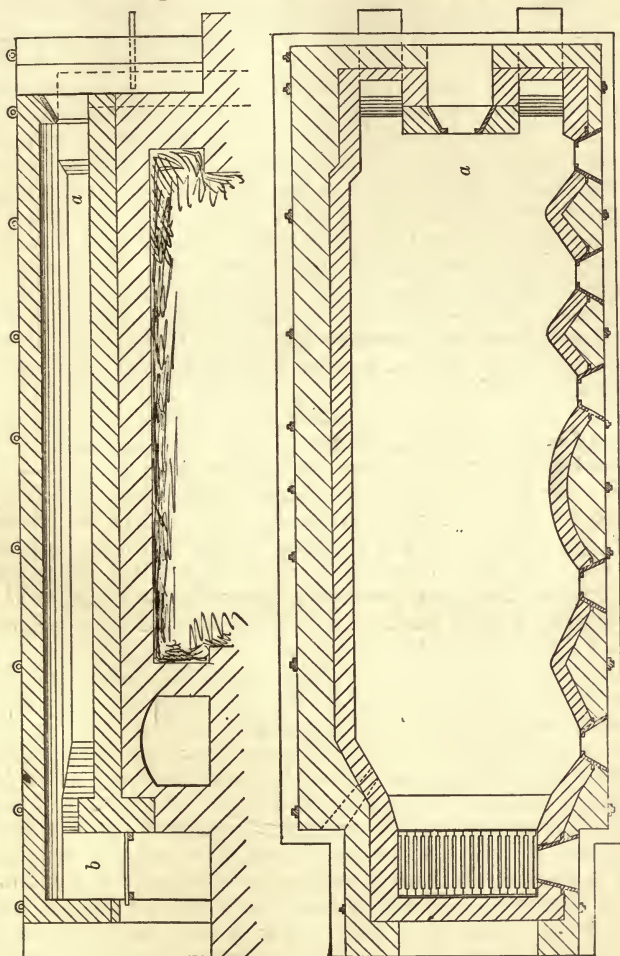
FIG. 66.

tively cool at the end of the furnace furthest from the fire-place, b, and to be gradually advanced to the hottest part, which is, of course, in close proximity to the fire-place. On the other hand,

in Fig. 65, a puddling furnace, the material, although energeti-
cally stirred, retains its original position on the bed, *a*, and has to
be actually melted.   In the former case the bed of the furnace is
a plane, which may slope, but which is usually horizontal.   In
cases similar to the latter, in which the charge has to be wholly
or partially melted, the bed is concave.   The nature of the
material of which the furnace-bed is composed is very varied.
In cases where the temperature is not high, as in the calcination
of lead ore, fire-bricks, which need not be very refractory, are
used.   In copper-smelting furnaces some 2 feet of siliceous sand
is rammed tight.   Brickwork is unsuitable for this purpose, as
the regulus, or copper, resting on it works down through the
joints.   In Swansea the furnace bottoms are made of a mode-
rately refractory sand containing 88 per cent. of silica.   In
certain lead-smelting furnaces the working bottom of the fur-
nace is made of the grey slag supplied by the furnace itself.
The bed of the puddling furnace introduced by Cort was made
of sand.   In 1818 the iron bottom was substituted with great
advantage.

In order to show the way in which the dimensions of furnaces
employed for different purposes are related, it will be well to give
the following examples based on data furnished by Gruner :—

1. In a reverberatory furnace used at Swansea for the refining
of copper, in which anthracite is burnt, the volume of the labora-
tory is 158 cubic feet, the sectional area of the fire-place is
19 square feet, the consumption of anthracite is 2.30 lbs. per
square foot of fire-place per hour, the cubic contents of the
laboratory is 8.3 cubic feet for every square foot of the fire-place,
and the weight of the material treated is 10 tons.   The tempera-
ture attained is high, as copper has to be melted ; but it falls far
short of that required in the puddling furnace where wrought
iron has to be kept near its melting point.

2. In a puddling furnace it will be seen that the volume of the
laboratory in relation to the sectional area of the fire-place is rela-
tively much smaller.   Thus, in a puddling furnace in operation
in South Wales, the volume of the laboratory is 35 cubic feet,
the sectional area of the fire-place is 9 square feet, the consump-
tion of coal is 3.6 lbs. per square foot of fire-place per hour, the
cubic contents of the laboratory is 3.9 cubic feet for every square
foot of the fire-place, and the weight of the material treated
only 4 cwt.

EXAMPLES OF REVERBERATORY FURNACES.

	1. German Long-bedded Calciner. (ft. in.)	2. Caldera (Chili) Copper-furnaces (*Howe*). (ft. in.)	3. Cwm Avon (S. Wales) Copper-furnaces (*Leey*). (ft. in.)	4. Butte Copper-furnace (*Peters*). (ft. in.)	5. Flowing Lead-furnace. (ft. in.)	6. Flintshire Lead-furnace. (ft. in.)	7. South Staffordshire Puddling Furnace (Model in the School of Mines). (ft. in.)	8. English Cupellation Furnace. (ft. in.)
Length of hearth	39 0	16 6	16 0	14 6	11 6	11 0	5 3	1 9
Width of hearth at middle	9 0	11 6	12 0	11 6	7 0	9 6	4 9	4 0
Length of fire-place	6 6	5 8	4 0	4 6	2 6	2 6	3 9	2 0
Width of fire-place	1 6	5 3	4 0	4 0	2 6	4 3	3 9	2 10
Depth of fire-place below top of bridge	—	1 5	3 6	2 4	2 6	1 9	1 6	1 9
Height of bridge above hearth	—	1 2	—	1 4	1 0	0 9	0 6	1 9
Height of chimney	—	—	—	50 0	—	—	30–50 ft.	—

In the table on the preceding page the dimensions of typical
reverberatory furnaces are given.   No. 1 is a German furnace for
roasting galena, a long-bedded calciner (*Fortschaufelungsofen*).
There are four working doors; 15 cwt. of raw ore are charged in
every six hours at the flue end of the furnace.   The furnace is
thus able to calcine 3 tons of ore in twenty-four hours.   No. 2 is
a reverberatory furnace for smelting copper, used in Chili.   The
same dimensions apply to the furnaces used for ore-smelting, for
smelting for "blue metal," and for roasting-smelting for Chili
bars.   In the ore-smelting furnace, the length of the operation is
seven and a half hours, the charge 3.52 tons, and the consump-
tion of fuel 0.52 ton of bituminous coal.

No. 3 is the South Wales copper-furnace, the same dimensions
applying to the furnaces for ore-smelting, for the smelting of the
different kinds of regulus known as " blue metal," for white metal
and for blister copper.   No. 4 is an American furnace used for
ore-smelting.   The charge is 3.3 tons, and the duration of the
operation five hours, the consumption of fuel amounting to 10 cwt.
of bituminous coal.   No. 5 is the so-called flowing furnace used
for lead-smelting by the Cornish method.   There are two doors
on each side.   The charge is 2 tons of calcined ore, which is
spread over the sloping bed.   It melts in about three hours.   The
charge is then mixed with lime and anthracite and 2 cwt. of
scrap iron are placed in the furnace at the tap-hole.   The charge
is then re-melted, and the furnace tapped by means of an iron
bar.   The reduced lead flows into a pot outside the furnace, and
is followed by regulus formed in the reduction of lead sulphide
by iron in the second fusion.   Finally, the slag begins to flow
and runs along a gutter into a pit outside.   The whole operation
occupies eight hours, the consumption of coal being 9 cwt. per ton
of ore.   No. 6 is the Flintshire furnace used for lead-smelting.
There are three doors on each side, the front ones being used for
stirring the charge, and the back ones for tapping the slag.   The
roof is low and inclines towards the flue end.   In the middle
there is a hopper for charging.   The bed slopes from all sides to-
wards a well, in front of the tap-hole, where reduced lead collects.
The usual charge is 21 cwt. of ore, the consumption of coal being
12 to 16 cwt.   No. 7 (Fig. 65) is a South Staffordshire puddling
furnace, which may be taken as typical of this class.   There is a
model of it at the School of Mines, London.   The roof is a low, flat
arch with a slight slope towards the flue end.   The working door,
placed at one side of the furnace, is about 10 inches above the
furnace bottom.   It is closed by a fire-brick slab, suspended from
a lever.   Below the door is the tap-hole, which is closed with sand

during the working of the furnace. No. 8 is the English cupellation-furnace, in which lead is separated from silver by the joint action of air and heat. The bed of this furnace is movable and is made of bone-ash, a material that resists the corroding action of the litharge (lead oxide) formed during the process. The movable bed, or *test*, consists of an oval wrought-iron frame lined with bone-ash. One end of the test is perforated with a number of holes through which the litharge, as it forms, flows into a receptacle below. A large portion of the litharge is, however, absorbed by the bed. Air is supplied by means of a tuyere. In the German cupellation-furnace, which is also of the reverberatory type, the roof is movable and the bed fixed. The latter is concave and circular, 8 to 10 feet in diameter; it is made of marl. The roof consists of a movable iron cover lined with clay. A pair of inclined tuyeres at one side of the bed supply the necessary air, and the litharge flows off through an opening on the opposite side.

The most important reverberatory furnace in which gaseous fuel is employed is the regenerative open-hearth steel-melting furnace of Sir W. Siemens. Steel is produced in this furnace by three methods: (1) by the fusion of a mixture of pig iron and scrap iron; (2) by the fusion of pig iron with rich oxides of iron; and (3) by a combination of these two processes (the Siemens-Martin process).

The regenerative furnace of Siemens is composed of a multiple series of passages in refractory bricks piled one over the other. These passages are traversed alternately by the burnt gases which give up their heat, and by the air or gas which enters to perform the work required in the metallurgical operation. By giving the conduit sufficient length and the hot gases a slight velocity they may be made to issue almost cold, whilst the air which it is proposed to heat gradually reaches hotter and hotter regions. The heating appliances vary in character according to whether the gas and air are at high or low tension. When the tension is low, chambers or conduits in refractory brick will be sufficient; but when the tension is high, the entire system of heating appliance must be enveloped in a case of sheet-iron, in which air may be compressed.

The usual form of regenerative furnace resembles an ordinary reverberatory furnace symmetrically arranged at its two ends instead of having the grate at one end and the flue at the other. Chambers beneath are filled with brick so piled that air or gas can freely circulate. The combustible gas enters by a tunnel into one of these chambers, and the air to effect the combustion enters

by another tunnel into another chamber. The gas and air are both led to the hearth, where they meet, and the air burning the gas, the flame produced plays freely on the material on the hearth. The burnt gases then pass into two other chambers, and in slowly passing through them give up their heat to the bricks and finally reach the chimney. In the direct passage which the gases traverse there are two valves, by means of which the direction of the current may readily be reversed. When the bricks have acquired a temperature but little lower than that of the burnt gas, the valves are turned through an angle of 90°. The combustible gases then enter one of the chambers just heated, and the air enters the other, and in slowly ascending through the chambers they become heated at the expense of the bricks; they meet at the hearth as before, and in burning develop a degree of heat, the intensity of which depends on the extent to which they have been heated. The products of combustion, after having done their work on the hearth of the furnace, pass through the chambers first mentioned to the chimney. When these chambers become heated, the direction of the current is again reversed, and so on.

By this alternate play of the valves the air and the combustible gas are heated; the temperature of combustion is thus increased, and a very high temperature may be obtained. At the same time, even if the temperature that would be obtained without this preliminary heating were sufficient for the required operation, it is obvious that by heating the air and combustible gas, a great economy in fuel can be effected.

In order to ensure that the gas shall not escape into the chimney at a temperature higher than 100° to 150°, it is necessary for there to be 14 or 15 sq. ft. of brick surface for every 2 lbs. of coal burnt between two reversals. The arrangement of the bricks in the chambers is not a matter of indifference. They should be so disposed as to leave as much space free as full. At the base, however, the passage should be restricted in order to force the gas to pass in a more uniform manner through the mass. The drying, the lighting, and the reversal of the valves must be effected with precaution. It is necessary to avoid explosive mixtures of air and gas. This is easily effected by diminishing the supply of air.

The great advantage of the regenerative furnace is that an oxidising, neutral, or reducing atmosphere may be obtained at will by regulating the supply of air.

The gas, it will be noted, does not come from any fire-place in the furnace itself, but is generated in a separate appliance. This

gas-producer consists essentially of a fire-grate on which a thick layer of fuel is maintained. The combustible part of the coal, usually small coal, is converted into carbonic oxide, hydrogen, and hydrocarbons, which are carried forward through flues to the furnaces in which they are burnt.

The gases on leaving the producer have an initial temperature of about 350°. By a curious syphon-like arrangement, they are made to rush forward with increased velocity. They are cooled in the vertical part of a tube, and then, as their density is thus increased, they rush down the tube with increased velocity.

Mr. F. Siemens has modified the original open-hearth furnace by substituting a domed roof for the flattened one previously used. The ports in this furnace are horizontal, and consequently the gas burns in an enlarged chamber above the bed out of contact with the roof or the charge. The work is thus done by radiation, by which means the durability of the furnace has been much increased.

In a new form of Siemens furnace, described by Mr. J. Head * and Mr. P. Pouff, the gases leaving the furnace-chamber are directed, partly through an air regenerator and partly under the grate of the producer, there to be reconverted into combustible gases, and to do the work of distilling hydrocarbons from the coal. In fact, the gas-producer in this case utilises the heat formerly deposited in the gas-regenerators, and in doing so transforms spent gases into combustible gases. For the propulsion of the gases through the converter-producer, a steam jet is employed. The steam is superheated by the waste gases from the furnace, and mixing with them forms a very hot blast under the grate. This form of furnace may be constructed in various ways, the one shown in Fig. 67 having been successfully used in heating and welding iron. It is a radiation-furnace, heated by means of a horse-shoe flame. This form of flame offers advantages, but its adoption is not obligatory, as the flame may be made to traverse the heating chamber from end to end in the usual manner. A, A′, are reversible regenerators for air, on the top of which is built the gas-producer or converter B, of which F, F′, are the charging hoppers and N, N′, the grates. The heating-chamber E, adjoins the producer resting on the ground, or in some cases a pit may be provided below it. C, C′, are the flues leading the combustible gas to the furnace chamber E, the passage of the gas in these flues being controlled by the valves D, D′, at the two ends of a rocking-beam, so that the outlets are opened and shut

* Journ. Iron and Steel Inst., 1889, No. ii. p. 256.
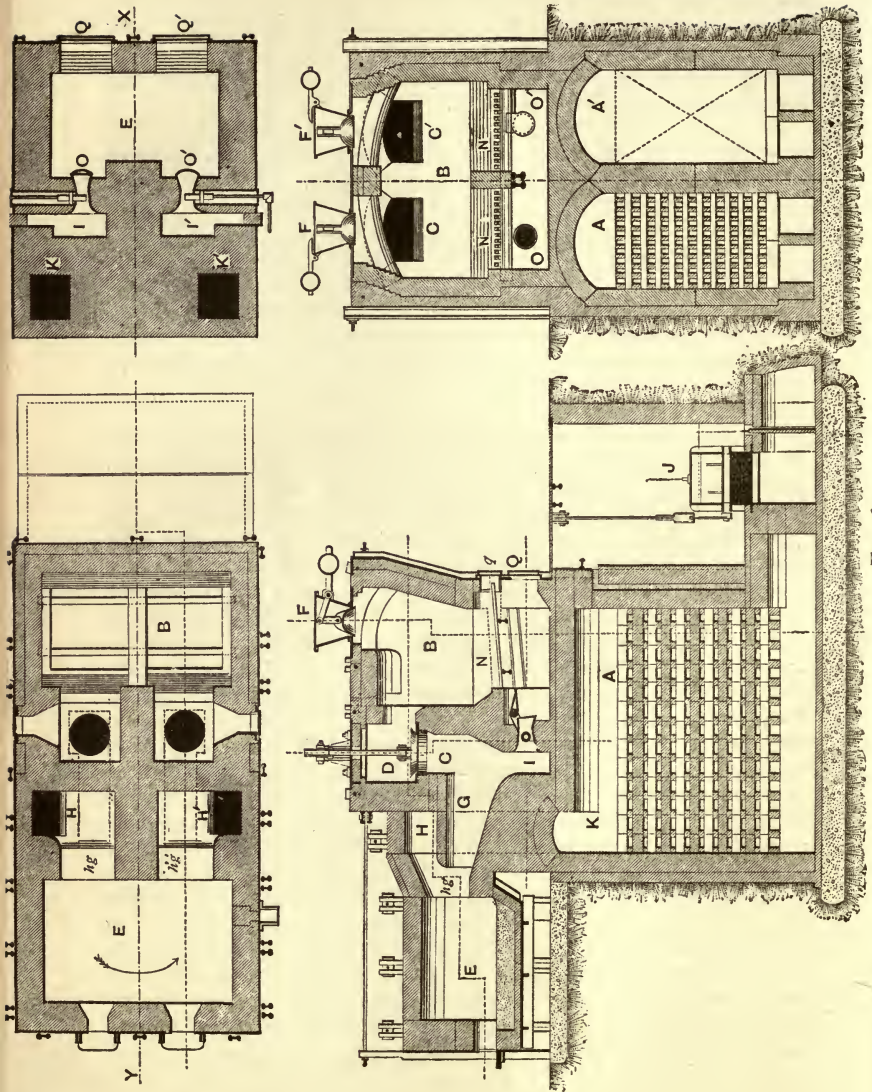
FIG. 67.

alternately to convey the gas to one or other of two ports (one shown) G, of the heating-chamber E. H, H′, are the air-ports of the heating-chamber, communicating through the flues K, K′, with the regenerators A, A′. I, I′, are steam-jets, placed in the return flues, for directing a portion of the waste products of combustion to the grates of the converter. J is the valve for reversing the direction of the air flowing into the furnace, and of the products of combustion through the regenerators to the chimney-flue. O, O′, are hinged caps for alternately admitting and shutting off the products of combustion from the heating-chamber to the converter. These caps are worked automatically by means of the connections O, O′, attached to the rocking-beam, the same movement which closes D opening O′, and that which closes D′ opening O. Q, q, are doors for giving access to the grates of the converter for clearing them.

The mode of working the furnace is as follows:—Gas from the converter B passes through the flue C′ and the valve D′ to the gas-port G′, and into the combustion-chamber h′ g′. Air for combustion passes through the regenerator A′, the air-flue K′, and the air-port H′ into the combustion-chamber, where it meets the gas from the converter, and combustion ensues. The horse-shoe flame sweeps round the heating-chamber E, the products of combustion passing away by the second combustion-chamber h g, go partly through the regenerator A, and reversing valve J into the chimney-flue, and partly down the flue G, whence they are drawn by means of the steam jet I through the capped inlet O under the grates of the producer B, there to be con-verted into combustible gases. From time to time the direction of the flame in the furnace is reversed by manipulating the rocking-beam, carrying the valves D, D′, and the reversing valve J in the usual manner of working regenerative gas-furnaces. An auxiliary steam-jet is provided for supplying air to start the producer when the furnace is first heated up.

Besides the advantages in the saving of fuel, labour, and metal, the simplicity of design of the new furnace renders its cost of construction not much greater than that of a solid-fuel furnace, while its cost of maintenance is very much less. The cost of construction of the new furnace is found to be about two-fifths of that of the old form of regenerative gas-furnace, of the same productive capacity, with separate gas-producers and gas-regenerators, and the space occupied below ground is also considerably reduced.

In order to ecomonise labour, various modifications of the re-verberatory furnace have been invented. The laboratory has been

considerably increased in height, and the material allowed to fall
as a shower of dust through a shaft that is traversed from
bottom to top by the flame from a lateral fire-place. In some
cases the dust falls freely ; in others there are obstacles in the
way. The most successful furnace of the former class is that
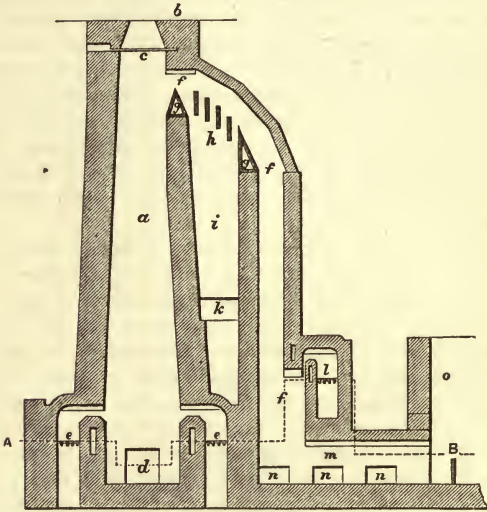
FIG. 68.
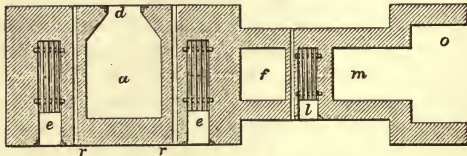
FIG. 69.

of Stetefeldt for roasting argentiferous ores. The furnaces of
Gerstenhöfer and Hasenclever may be taken as types of the
latter class.

In the Stetefeldt furnace, the pulverised ore, mixed with salt,
is charged in at the top of the shaft a (Figs. 68 and 69) by the

aid of a mechanical feeder arranged at b on the top of the shaft. The ore falls in a slow stream down the shaft and encounters the flames proceeding from the fire-places, e, e. For the ore which is carried along the flue, f, through which the gases escape, a third fire-place, l, is provided. This assists the action of the main shaft, and causes the ore to reach the flue m in a completely roasted and chloridised state, if it has not already been discharged through the door d upon the cooling floor. At h there are cast-iron plates, which form the bottom of the flue, and which allow any dust settling to fall into the chamber i, whence it is removed through the door k. The flue bridges, g, g, are of cast-iron. The fire-places and arches are of fire-brick; the remainder of the furnace is of common brick.

The vertical shaft is usually 30 to 35 feet in height, and 4 to 5 feet square at the base. These furnaces roast about 40 tons of ore in twenty-four hours. In Utah as much as 64 tons are treated daily. In the Stetefeldt furnace the chloridising roasting action is very rapid and complete, whilst the expenditure of labour and of fuel is small.*

4. **Closed-vessel Furnaces.**—In furnaces of this class the material to be heated is separated from the fuel by an envelope, in the form of a closed vessel. The vessel is heated by being in contact with the fuel, or by the flame developed from a fire on a grate, or lastly by the gases from a producer. The form of the vessel is determined by the process that is to be undertaken. Thus, for simple heating, the muffle is employed, whilst for fusion crucibles are used. Retorts and similar vessels are used exclusively for distillation and sublimation.

The ordinary assay furnace may be taken as typical of the wind-furnaces used by the brass-founder. These furnaces vary according to the size and number of crucibles inserted in them. The crucible gas-furnace used for melting steel consists of a long hearth on which the crucibles are placed in pairs. This hearth has a movable roof through which the crucibles may be withdrawn, and on the long sides are the flues from the regenerators, the construction of which is similar to that of other regenerative furnaces.

The best example of a retort-furnace is afforded by the furnace used in Belgium for smelting zinc ores. In this furnace the ores are reduced in a number of fire-clay retorts with a bellied fire-clay nozzle in which the zinc condenses, and a sheet-iron tube in which

* Küstel, "Roasting of Gold and Silver Ores." 1871; "The Stetefeldt Furnace, San Francisco, 1878"; *Engineering*, 1885, Sept. 25.

the zinc oxide is collected. The retorts are placed in rows in a vertical arched chamber, with a fire-place at the base. In recent furnaces of this kind the fire-place is arranged for gaseous firing.

The furnaces are usually built in pairs, back to back. At Angleur* they contain 160 retorts on either side. The charge for each retort is 25 lbs. of a mixture of equal weights of powdered roasted blende and non-caking coal.
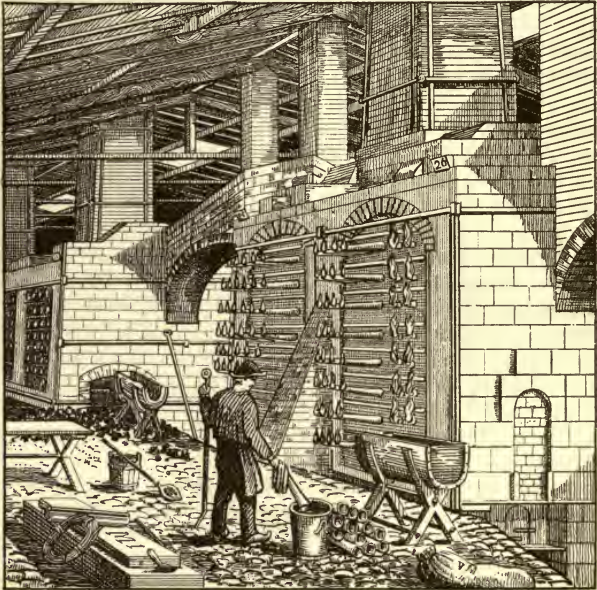
FIG. 70.

An external view of the Belgian zinc furnace is shown in Fig. 70.

Retort-furnaces are also used for smelting mercury ores, the condensers sometimes consisting of earthen pipes, or *aludels* (Fig. 71), thrust one into another. The ore is roasted in a circular kiln with a system of openings connecting with a series of ranges of aludels resting on the doubly inclined surface of a

* See article Zinc, by de Lalande, in Wurtz, *Dict. de Chem.*

terrace. In the recent furnaces at Almadén there are sixteen of these ranges.*

FIG. 71.

The tube-furnace is occasionally employed in the extraction of bismuth from its ores by liquation. Native bismuth melts at 264°, and advantage was taken of this fact to separate it from the more or less infusible materials accompanying it. This process has, however, been almost entirely supplanted by ordinary smelting and wet methods. The liquation-furnace, used at Schneeberg, in Saxony, contains a series of cast-iron tubes, oval in section, and inclining towards the front, where the ore is placed. The liquated metal is received in iron vessels heated by a separate fire.

A furnace of the closed-vessel type is used in the manufacture of steel by the addition of carbon to malleable iron, a process termed *cementation*. The furnace (Fig. 72) consists of a rectangular chamber supplied with chimneys, c c, and divided into two parts by a fire-place, a, on either side of which is a rectangular fire-brick vessel, or *converting-pot*, b, varying from 8 to 15 feet in length and 3 feet in width and depth. These pots are thoroughly heated by the flames, and the products of combustion reach the conical hood, e, some 40 feet in height, which serves to prevent loss of heat by radiation as well as to carry off the smoke. At d there is a man-hole, built up during the working of the furnace, but opened for cooling down and for the withdrawal of the charge.

The Bessemer Converter.—This furnace has the shape of a pear, the form originally given it by Bessemer. Unlike all other smelting furnaces, the converter is usually not fixed but supported on standards by trunnions. To one of these a pinion is keyed, by means of which the vessel can be moved through an angle of 170°, so that the molten metal may be poured from its mouth. The other trunnion is hollow and admits the blast to the vessel. A pipe from this trunnion passes to the tuyere-box, forming the bottom of the converter, which is perforated by ten to nineteen circular holes, into each of which is placed a conical fire-clay tuyere, perforated with twelve holes each $\frac{3}{8}$ inch in diameter.

The Bessemer process was first patented on October 17, 1855, and was described in a paper read before the British Association, in which the inventor claimed a method of making wrought-iron without using fuel, but it must be remembered that the combustion of the carbon, silicon, and other elements in the pig-iron during their elimination provides the heat necessary for maintaining even molten wrought-iron in a fluid state. The process consists essentially in blowing large quantities of compressed air through numerous small jets into a molten mass of pig-iron, thereby effecting the rapid combustion of the carbon, silicon and manganese present in the metal. The excitement caused by the invention in all iron-making countries was immense, as it was thought that the wrought-iron industry was doomed, since the quantity of pig-iron (about 3 tons) that a puddling furnace could treat in twenty-four hours, could be dealt with in the Bessemer converter in twenty minutes. It was, however, soon found that the expectations were not completely fulfilled; good steel could not be obtained from all kinds of pig-iron, as all the impurities could not be removed. Phosphorus, of which 1 to 2 thousandths suffice to render steel brittle and cold-short, remained completely unattacked. It was, therefore, necessary to employ pure pig-iron containing but a low proportion of phosphorus. Previous to 1855, the annual production of steel in Great Britain was 51,000 tons, at a price of about £50 per ton. At the present time, in Sheffield alone, 830,000

FIG. 72.

tons are produced annually, and throughout Europe 3,000,000 tons, at a price of £7 to £10 per ton.

Bessemer's original rotating converter was spherical,* so as to reduce the loss of heat by radiation as far as possible. Some of his early experiments were made in an upright fixed cylindrical vessel, very similar to the Bessemer converters recently introduced for treating small charges.

The charge of pig-iron is either melted in a cupola or run directly from the blast-furnace into the converter. The blast is turned on, and combustion goes on in two stages :—

1. *Scorification*, during which stage the graphitic carbon passes into the combined state, silicon becomes oxidised, and silicates of iron and manganese are formed. This stage lasts from four to six minutes.

2. *Ebullition*, during which stage the carbon is rapidly oxidised by the blast, carbonic oxide being evolved in large quantities. This stage lasts six to eight minutes.

The first stage is accompanied by a reddish-yellow flame, the second by a more brilliant display of flame and sparks, and numerous small detonations. The first stage yields but little flame, as the products are solid—oxides of silicon and manganese. The products of the second stage, however, being gaseous—oxides of carbon—that stage is accompanied by a greater evolution of flame. As soon as the carbon has gone, the flame drops. A trained eye notices this immediately, and the operation must be stopped, or iron will be oxidised. It is usual to eliminate all the carbon, and then to add the required amount in the form of spiegeleisen. The manganese in the spiegeleisen is also useful— indeed, essential. It probably acts on dissolved oxides in the metal, and "masks" the action of the sulphur. When manganese only is required, ferro-manganese is added. This contains considerably more manganese than spiegeleisen does in proportion to its carbon.

The duration of a "blow" varies with the variety of pig-iron, its quantity, and the pressure of blast used. When the iron contains little silicon and manganese, the duration may be fifteen to twenty minutes; when the iron contains much of these elements, thirty minutes may be required. The loss of iron rarely exceeds 9 to 12 per cent. when the pig-iron is run direct, but it may reach 15 per cent. when the metal is remelted in a cupola. With a pair of converters working in conjunction, ten to fifteen blows per

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* Sir H. Bessemer gives sixteen drawings of early forms of converters, *Journ. Iron and Steel Inst.*, 1886, p. 638.

twenty-four hours may be obtained, and when movable bottoms are applied to the converters, as many as twenty can be obtained in that time.

The details of the construction of the Bessemer converter may be seen from Fig. 73, which is from a drawing specially prepared for this work by Mr. P. C. Gilchrist. It represents the best form of converter for the basic Bessemer process.

The phosphorus is not eliminated in the " acid process," because the converter lining consists almost exclusively of silica and the oxides of phosphorus have a weaker acid reaction than the silica has. A basic slag is absolutely indispensable for the removal of the phosphorus, and even if the slag was not rich in silica derived from the silicon in the pig-iron, it could never acquire a basic character, since silica would be obtained from the lining. In 1835 Berthier showed that in the puddling process, the phosphorus was removed by the aid of basic slag (tap cinder), and attempts were made by von Tunner and by Gruner to replace the acid lining of the Bessemer converter by a basic one, so as to eliminate the phosphorus, but difficulties of various kinds presented themselves, until three School of Mines men, Snelus, Thomas, and Gilchrist, directed their attention to the problem. Dolomite, a mixture of calcium and magnesium carbonates, is calcined at a high temperature, then powdered, and mixed with heated anhydrous tar, and moulded into bricks under a pressure amounting to 200 atmospheres. The bottom of the converter is rammed out of the same material, and heated to incipient redness, whereby the greater portion of the tar is expelled. In a converter lined with this material, if lime be added to the charge, a basic slag may be produced, which combines with the phosphorus burnt to phosphoric anhydride.

If a pig-iron is selected for the basic Bessemer process containing as much silicon as that employed in the acid process, a large addition of lime is necessary, and so much slag is produced as to render the process almost impracticable. It is therefore found advisable to employ a white pig-iron containing a small percentage of silicon. In this case, although cold at first, the blow is very hot at the end, owing to the oxidation of the phosphorus. In this process it is necessary to melt the pig-iron in a cupola at a high temperature, to add hot lime, and to have large tuyeres and considerable pressure of blast.

The most suitable pig-iron for the basic Bessemer process contains—

Silicon.	Sulphur.	Phosphorus.	Manganese.	Carbon.
0.5 to 1.8 ...	under 0.3 ...	0.8 to 3.0 ...	under 2.5 ...	about 3.0
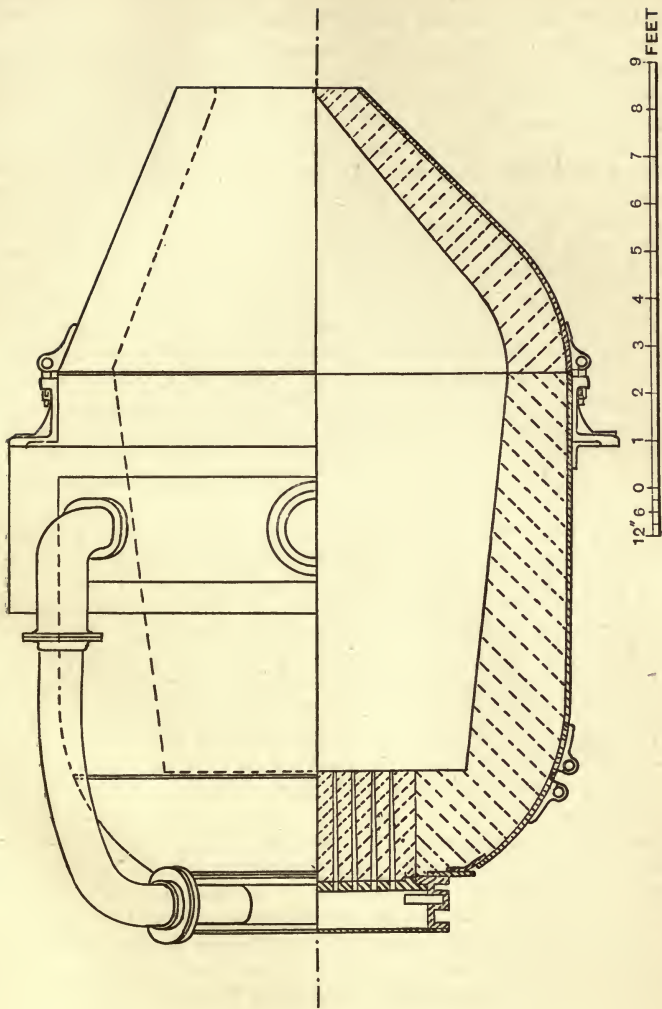
FIG. 73.

As the amount of sulphur is not sensibly reduced, 0.3 per cent. is the limit which may be present in the pig-iron.

One important feature of the basic process is the value of the slag incidentally produced. It consists chiefly of lime and phosphoric anhydride. Of the latter there is as much as 13 to 20 per cent. Both these materials are used as fertilisers by the agriculturist, and basic slag, as might have been expected, has been found to be a valuable manure. According to Gilchrist,* in 1889 as much as 600,000 tons of this slag were made, containing 17 per cent. of phosphoric anhydride and 60 per cent. of lime. It is, of course, not a suitable fertiliser for all soils, calcareous ones for instance, but for sour, peaty, and clay soils it is of great value, as is shown by the fact that all the 600,000 tons were sold at from 20s. to 30s. per ton at the works. It is interesting to note that the phosphoric anhydride is combined with the lime in an unusual manner. Instead of being an insoluble tribasic phosphate, it is a readily soluble tetra-basic phosphate, and, if it be finely ground, the phosphorus it contains is readily assimilated by plants. At first attempts were made to treat it by various chemical methods, but it has been found best to simply grind it and use it in fine powder.

Of late years an attempt has been made to revert to a type of converter employed by Sir Henry Bessemer in his earlier experiments. It is of small size and has horizontal tuyeres. In the case of the Clapp-Griffiths converter † these are symmetrically arranged in the walls of the converter near the base. There is a very low pressure of blast, 5 to 6 lbs. per square inch, and the valves are adjusted automatically. The converters are adapted to charges varying from 1 to 3 tons. The Robert converter ‡ is small, and is adapted to charges of 1 ton or more, the charges in no case exceeding 3 tons. By the action of the blast through a range of tuyeres inclined at different angles, a rotary motion is gradually imparted to the fluid metal. These tuyeres are placed high up in the converter, and by tilting it and by manipulating the blast-valve, the operator can change the volume and pressure of the blast. The converters are mounted on trunnions in the usual way, and are revolved by means of hand-gearing. The main point about these little appliances is that they bring the production of soft steel within the reach of small manufacturers. In Clapp-Griffiths' practice it has been found that by

* *Journ. Iron and Steel Inst.*, 1887, No. i. p. 212, where there is also a bibliography of the subject.
† *Ibid.*, 1883, No. ii. p. 705.
‡ F. L. Garrison, *Ibid.*, 1889, No. ii. p. 266.

keeping the carbon low, a certain amount of phosphorus may be allowed to remain in the steel without injury to the properties of the metal.

The Bessemer converter has been modified and employed for smelting copper regulus. The early experiments were not successful. In 1880, however, Pierre Manhès, the proprietor of the Vedènes copper works, Department of Vaucluse, France, obtained patents for its use in copper smelting, and smelting works were erected at Eguilles, near Avignon.[*]

The saving in fuel effected by the use of the converter is very considerable, and it is claimed that the Manhès process renders copper smelting possible in countries where, owing to the high price of fuel, the Welsh process is out of the question. As will subsequently be shown, the Welsh process consists of six to eight successive roastings and fusions in order to obtain coarse copper from the ore, all the operations being effected in large reverberatory furnaces. In the Manhès process from one to three of these operations are effected by blowing air through copper regulus in a converter which differs considerably from that employed for iron-smelting

Its later form is a horizontal cylinder, holding about 1 ton of regulus, and turning on axial trunnions, through one of which the blast passes to a row of tuyeres, parallel to the axis. The level of the tuyeres can be altered as the " blow " progresses, and the copper as it is reduced sinks to the bottom of the converter, which is gradually turned so as to permit the blast to pass into the regulus above the level of the copper, which thus escapes chilling. The blow lasts 15 to 20 minutes, and at one operation " blister copper " may be obtained from the " white metal " of the Welsh smelter. For poorer regulus of 50 to 60 per cent. of copper (blue metal), it is well to blow twice in separate converters. The regulus may be run into the converter direct from the smelting furnace.

[*] *Annales des Mines*, 8th series vol. iii. p. 429.

CHAPTER VIII.

MEANS OF SUPPLYING AIR TO FURNACES.

Methods of Producing Draught. — In every furnace it is necessary to conduct away the gaseous products of combustion to enable fresh air to enter and to give up its oxygen to the fuel. This passage of the fire gases from the furnace and of the air to the furnace may be effected in two ways :—First, by exhausting the products of combustion ; and, second, by forcing in air for combustion. In the former method, a space containing rarefied air is formed in the furnace, and atmospheric air flows in from outside so as to preserve the equilibrium, whilst in the latter method the pressure in the furnace is greater than that of the air outside, and consequently the air and the fire gases are forced out. Although the current is usually the same in both cases, the influence on the combustion may be different when the movement is effected by the compression or rarefaction of the air.

The exhaustion of the air is usually effected by means of chimneys. The chimney or stack may be regarded as a vertical pipe containing heated and expanded gaseous products of combustion. The column of gas within the chimney is, in consequence of the expansion due to heat, considerably lighter than a column of air of the same height at the ordinary temperature. The consequence is, that owing to the difference of weight, there is an excess of pressure of air under the grate, and movement ensues. This difference in the weight of the hot and cold columns is equal to the weight of the increase in volume that would be produced by heating the cold column of air to the temperature of the chimney. If the elongation thus produced be represented by h, the velocity of the movement $v = \sqrt{2gh}$; but h is dependent both on the height of the cold column of air and on the difference of temperature within and outside the chimney, whence it follows that theoretically the velocity of a current of gas within a chimney increases proportionately with the square root of the height and the square root of the difference of the external and internal temperatures, and that consequently the action of equal increments of height

and temperature becomes continually smaller.   But the action of a chimney does not depend so much on the velocity produced as on the weight of air supplied in a given period of time.   The higher the products of combustion are heated, when they pass into the chimney, the greater is their volume, and with equal velocity the less weight of gas would actually pass through the same chimney.   The velocities, it has been shown, increase with the difference of the external and internal temperatures, but only in proportion to the square roots, whilst the relative weight of the gases decrease in direct proportion to the temperature by $\frac{1}{273}$ of the original volume for every degree Centigrade.   There must therefore be a limit where the action of the chimney reaches its maximum, and it has been calculated that this maximum is attained when the difference of temperature amounts to 273°, or, in other words, when the external air is at the mean temperature, and the chimney gases have a temperature of 300°.   Similarly it has been calculated that the quantities of air supplied to the chimney between 200° and 400° differ but slightly, so that for the chimney-draught these temperatures appear to be the most suitable, whilst for the utilisation of heat in the furnace the lower chimney temperature is obviously to be preferred, and even when the temperature of the chimney gases is only 100°, the quantity of air drawn in is to that drawn in by a chimney having a temperature of 300° as 7 : 8.

The amount of gas passing out of the chimney could be determined from the height and temperature of the shaft and the specific gravity of the gases, if only the resistance given by friction to the gases in motion and the so-called " free section " were known. The term " free section " is applied to the sum of the areas of the interstices between the lumps of fuel on the grate.   The smaller this free section is, the quicker is the motion of the air in it, and the more perfect the combustion, provided that the reduction in section is due to a diminution of the area of the grate and not to undue clogging of the layers of fuel which, by increasing the friction, at once diminishes the action of the shaft as the volume of air supplied is necessarily lessened.   For this reason small grates give rapid combustion and large grates slow combustion, with the same chimney.   It has, however, previously been shown that a rapid motion of the air, in this case equivalent to rapid combustion, facilitates the production of carbonic anhydride, whilst a slow motion facilitates the production of carbonic oxide. As a rule, therefore, for the production of heat and for high temperature, rapid combustion on a small grate is to be preferred to slow combustion on a large grate.

The height of the stack must increase with (1) the rapidity of the combustion; (2) the height of the layer of fuel on the grate; and (3) the resistance to which the current is exposed in passing from the grate to the foot of the stack. On the other hand, the height of the stack must increase in inverse ratio to the temperature of the evolved gas.

For furnaces in which the combustion is not rapid, and in which there is but slight frictional resistance, as in furnaces from which the gases pass directly to the shaft, the height of the stack need not exceed 33 feet. Welding, puddling and other furnaces, in which the combustion is rapid, require a shaft at least 50 feet in height, if the gases pass into it at a high temperature; but if they are cooled on their way, and have great frictional resistance to overcome by being utilised, before they reach the shaft, for other purposes, as for heating steam-boilers, it is advisable to make the shaft 65 to 80 feet, or even 100 feet if the length of the flues is considerable, and if they are narrow and crooked.

A chimney is frequently arranged so as to be common to several furnaces, and in this the gases from all the furnaces unite. Its section is calculated on the assumption that the minimum velocity of the gases in the chimney (6½ feet per second) is not exceeded, even if only one of the furnaces be working and the others are cold. At the same time, in order to prevent an unduly decreased velocity when all the furnaces are at work, the common shaft must be made of considerable height, usually 130 to 165 feet. To ensure the successful working of chimneys of this kind, it is important that the up-currents should pass into the shaft in parallel directions, so as to prevent suction being arrested by the impact on each other by converging streams of gases. In order that cold air shall not be drawn into the shaft from a furnace that is not being worked, every flue passing from the furnaces to the shaft must be furnished with a damper.

The vertical projection of the interior of the shaft may be either of the same width above or below, or there may be a slight narrowing at the top. The tapering shape increases the stability of the shafts, especially when they are exposed to the action of storms. It has been proved theoretically that a slight divergence towards the top gives a better draught. The angle at which the sides are inclined to the perpendicular should be 0.5 to 1.5 degree.

Any cooling of the gases interferes with the draught. For this reason brick shafts are preferable to iron ones, and the interior should be made as smooth as may be, so as to lessen friction.

The first researches on chimney gases are due to Péclet, who published some analyses in 1828; but his results and those of different experimenters who followed him, were open to the objection that the samples taken for analysis were only small fractions of the total gases in the flues, and, as they were not taken with sufficient frequency, they could not represent the mean composition. This grave defect was, however, remedied by Scheurer-Kestner in an elaborate research on the composition of the flue gases of boiler furnaces, which will always form the basis of future experiments in this direction.

A series of experiments conducted by this distinguished chemist and Meunier, in 1868, on the combustion of fuel in boiler furnaces, showed the difficulty of burning fuel completely on the grate of a furnace; and the analyses of the gases made by them led to the conclusion that the products of combustion always contain unburned constituents, even in the case of a thin layer of fuel and an excess of air of more than 50 per cent.; that is to say, with volumes of 240 cubic feet of air for every lb. of coal burnt, instead of 128 to 160 cubic feet. They also showed that the mean proportion of unburned hydrogen reached 20 per cent. of the total amount present. This points to the fact that hydrogen is more difficult to burn, even under favourable conditions, than carbonic oxide, and that with a thin layer of incandescent fuel, the unburned carbon in the gas exists more often in the form of a hydrocarbon than in that of carbonic oxide.

In securing a representative sample of gas, the position of the flue from which the gases are withdrawn, is by no means a matter of indifference. With a view to collect soot, it should, of course, be as near to the incandescent fuel as possible; but Cailletet has shown that the gaseous products from furnaces must not be collected immediately after being liberated from the fuel, for a current of gases from a mass of incandescent fuel may contain notably more carbonic oxide than the same gases do when cold—that is, during the cooling, combination of carbonic oxide and oxygen takes place.

In a series of tests made by the author[*] in connection with an exhibition opened with a view to abate the nuisance arising from smoke, 85 cases showed that the relation by weight between the carbon completely burnt to carbonic anhydride, and that present in the form of hydrocarbons or carbonic oxide, varies between the limits of 1000 : 4 and 1000 : 375. There were, how-

[*] *Report of Smoke Abatement Committee*, London, 1882, in which volume there are references to the literature of the subject.

ever, only 9 cases in which a ratio of 1000 : 200 was exceeded, and but 3 in which the ratio was less than 1000 : 10.

In 17 cases given by Scheurer-Kestner, this relation varied from 1000 : 10 to 1000 : 211, the result being mainly dependent on the amount of air introduced to effect the combustion. With reference to the hydrogen, it is to be observed that in these experiments, the proportion of carbon completely burnt to carbonic anhydride to the hydrogen present either in the free state or as hydrocarbons, varies from 1000 : 3 to 1000 : 16. The loss of carbon in the form of soot never exceeds 1 per cent. of the fuel burnt, while the mean loss is probably between 0.5 and 0.75 per cent.*

Blowing Engines.—The mechanical appliances employed for the production of a stream of compressed air are so varied in their details that it is impossible to do more than allude to them, the construction and the principles involved falling more in the province of the mechanical engineer than in that of the metallurgist.

In early times the blast was obtained solely from leathern bellows, which were at first single-acting and subsequently double-acting, but as leather soon becomes inflexible and brittle, it was found advisable to employ wooden bellows. In this way was evolved the box-blower, with single-acting movement of a piston. In the course of time cast-iron was substituted for wood, and the iron blast-cylinder, one of the forms of blowing engines still in general use, was obtained. In addition to this, for low pressures and large volumes of blast, fans and blowers are largely used.

A blowing cylinder consists of a cast-iron cylinder fitted with a piston receiving a reciprocating motion from the crank-shaft of the engine. At every stroke air is drawn into the cylinder on one side, and on the other compressed air is forced into a reservoir or into the blast-main. The interior of the cylinder is connected with the atmosphere on the one hand, and with the blast-main or reservoir on the other, by means of flap- or disc-valves fitted in the cylinder-covers. The piston is actuated by engines of the vertical direct-acting, or of the beam-engine type, the former being now generally preferred. On the Continent the blowing engines are frequently of the horizontal, direct-acting, condensing or compound class. The amount of blast required to be delivered is often very considerable, as is shown by the following examples :—

* For fuller information on this subject the student is referred to Gruner's *Traité de Métallurgie*, and Ledebur, *Die Oefen*.

The celebrated blowing engine at Dowlais, in South Wales, has a blowing cylinder 144 inches in diameter, and a stroke of 144 inches. The areas of the admission and discharge valves are 56 square feet and 16 square feet respectively, the former being equal to half the area of the piston. The steam-cylinder is of 55 inches diameter, and its piston has a stroke of 13 feet. The volume of blast delivered is 51,000 cubic feet per minute, at a pressure of $3\frac{1}{2}$ lbs.

At Newport, near Middlesborough,[*] there are four direct-acting blowing engines, with steam cylinders of 32 inches, and blowing cylinders of 66 inches, and 4 feet stroke. These are supplied with steam at a pressure of 55 lbs. per square inch by eight Cornish boilers, fired by waste gas, 35 feet long and $5\frac{1}{2}$ feet in diameter, with an internal flue of $2\frac{3}{4}$ feet in diameter. The engines make twenty-four revolutions per minute, and deliver 8000 cubic feet of blast per minute to each furnace, at a pressure of $4\frac{1}{2}$ lbs.

At the Lucy furnace in Pittsburgh, where the greatest out-turn of iron for one day was 340 tons, for one week 1946 tons, and for one month 7919 tons, the diameter of the blowing cylinder is 84 inches, that of the steam cylinder 42 inches, the length of stroke 60 inches, and diameter of fly-wheel 24 feet.[†]

For foundry purposes the blast is usually supplied by centrifugal fans or by blowers. The fan, although possessing the advantage of great simplicity, has but limited application, since it is useless when pressures exceeding about 6 inches of water-column are required to be produced. In such cases, the Root's blower, or a machine of similar type, may be advantageously employed. It consists of an iron casing, in which are placed a pair of revolving cast-iron wafters driven by belts off pulleys, and making about 400 revolutions per minute, the smallest possible clearance being left between the two curved surfaces as they revolve.

The blast is conveyed in air-tight rivetted sheet-iron or steel pipes or *mains* of ample cross-section, to the hot-blast stoves.

Hot-blast Stoves.—The temperature of combustion increases with the temperature of the air consumed up to the limits which are fixed by dissociation. Hot air economises, in the blast-furnace, a sum of *calories* equal to that which it brings, but if this heat has to be initially imparted to the air by the combustion of a fuel of equal value to that consumed in the furnace, it is

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* *Journ. Iron and Steel Inst.*, 1887, p. 92.
† *Ibid.*, 1888, No. i. p. 311.

evident that the economy will be at best but doubtful. In all
cases the advantage of hot blast will be in direct proportion to
the cheapness of the fuel that is burnt in heating the blast.
There is a great advantage when the waste heat of the furnace
can be utilised in this way. By employing a fuel identical with
that burnt in the blast-furnace, it would appear, however, that
there is still a distinct advantage due to the more perfect com-
bustion of the carbon that is attained in the furnace, there being
produced a greater proportion of
carbonic anhydride as compared
with that of carbonic oxide.

The apparatus in which the blast
is heated before passing to the fur-
nace is heated by solid fuel or by
the waste gases from the furnace.

Two substances are employed to
transfer the heat. These are iron
and fire-brick. The first appliances
for heating the blast date from
1828, when they were introduced
by Neilson at Glasgow. This dis-
covery, that 100 lbs. of coal burnt
in heating the blast was able to
save 300 or 400 lbs. of fuel burnt
in the furnace, was received with
disbelief, and ironmasters were
very slow in availing themselves
of one of the most important in-
ventions which had been made in
connection with the metallurgy of
iron.

FIG. 74.

The cast-iron hot-blast stoves
now used in metallurgical works
may be referred to two types, both
introduced at the same date. In
1833 Faber du Faur invented a
hot-blast stove, consisting of six-
teen cast-iron pipes united by semi-
circular bends, forming one long serpentine pipe enclosed in a
chamber heated by the waste gases from the blast-furnace. It
was placed directly above the throat of the furnace. The second
type of iron hot-blast stove differs from the former in that the
blast-current is split in its passage through the stove. It con-
sists of an oblong fire-brick chamber, containing a series of
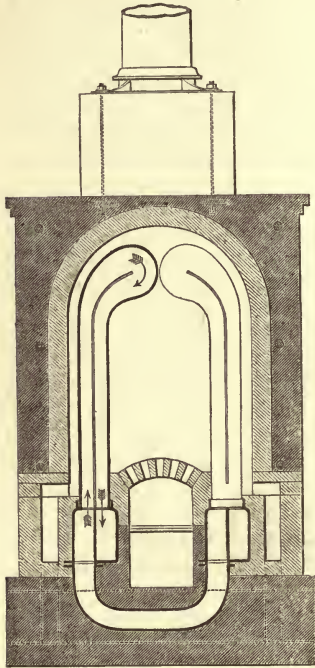
Λ-shaped cast-iron pipes, that connect two parallel horizontal main pipes, embedded in the masonry on either side of the rectangular fire-place that extends throughout the stove.

A modification of this second type is the so-called pistol-pipe stove (Fig. 74). In this case the arch is replaced by a single pipe divided longitudinally, the division reaching nearly to the top, which is enlarged in the form of the stock of a pistol.

Two types of regenerative hot-blast stoves are employed. These are based on the principle of the intermittent absorption of heat by masses of fire-brick and the transference of the heat to the blast. The first stove of this type was constructed by Cowper in 1860; it is similar in arrangement to a Siemens regenerator. It is enclosed, however, in an iron case so as to withstand the pressure of the blast. The first stove of the second type was constructed by Whitwell in 1865 for the Thornaby works at Stockton. It is essentially a serpentine pipe-stove constructed of fire-brick.

The Cowper stove, which is represented in sectional elevation and plan in Figs. 75 and 76, consists of a sheet-iron tower I, of circular horizontal section, closed with a dome-shaped roof B, and lined internally with fire-brick. A circular flame-flue F, extends from the base to the dome, whilst the remainder of the stove is filled with fire-brick chequer-work, and forms the regenerator R. The waste gases from the blast-furnace pass in by the valve G, and are burnt at N, the necessary air for combustion entering by the valve A. The flame descends through the chequer-work and passes out by the chimney-valve V. In this way the brickwork becomes heated. The valves G, A, and V are closed, and cold blast, admitted through the valve C, is passed through in the reverse direction. It absorbs heat from the chequer-work and is delivered as hot-blast by the valve H. The chequer-work is constructed of Cowper's honeycomb bricks. Two stoves are worked in conjunction, one being heated while the blast passes through the other. It is advisable to have a third in reserve. These stoves are 40 to 65 feet high and 26 to 28 feet in diameter. Compared with pipe-stoves the saving of fuel is about 20 per cent. and the increased make is also 20 per cent. An exact average of over 100 stoves shows the saving in fuel to amount to a little over 5 cwt. of coke per ton of iron.* In 1883 there were 360 of these stoves at work in Europe and America.

The Whitwell stove is shown in Fig. 77. It is merely a brickwork serpentine pipe formed by vertical walls, and enclosed in a cylindrical case. The waste gases from the furnace enter

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* E. A. Cowper, *Journ Iron and Steel Inst.*, 1883, p. 576.

at A and are burnt by air admitted through the passages a, a.
The flame passes up and down the passages formed by the dividing
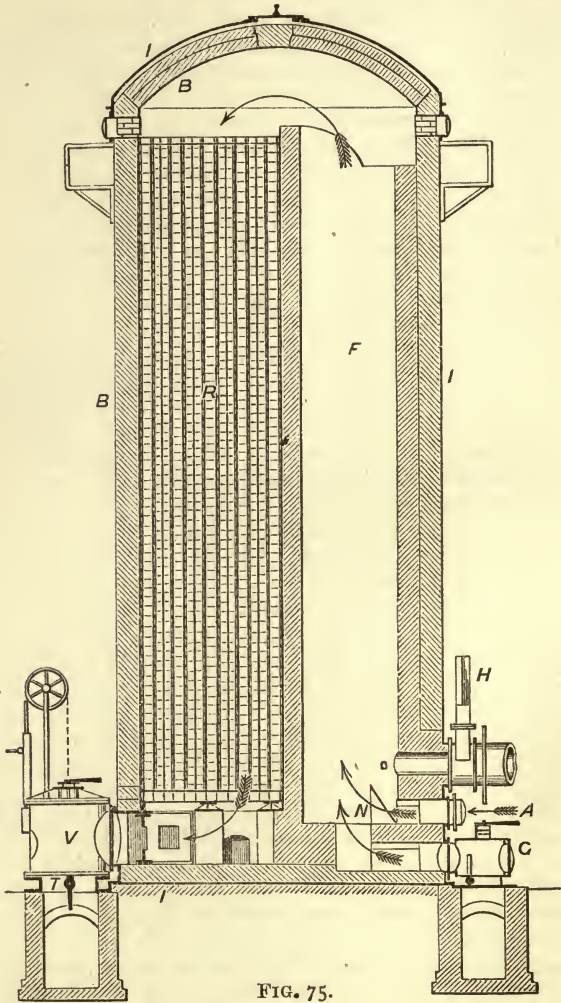
FIG. 75.

walls, and escapes to the chimney by the passage C. When
the stove is heated, the gas and chimney valves are closed, and

cold blast is admitted at D, and passes out heated at B. The walls forming the regenerator consist of 5-inch brickwork. The
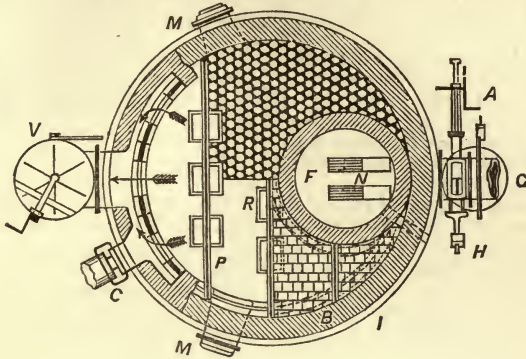
FIG. 76.
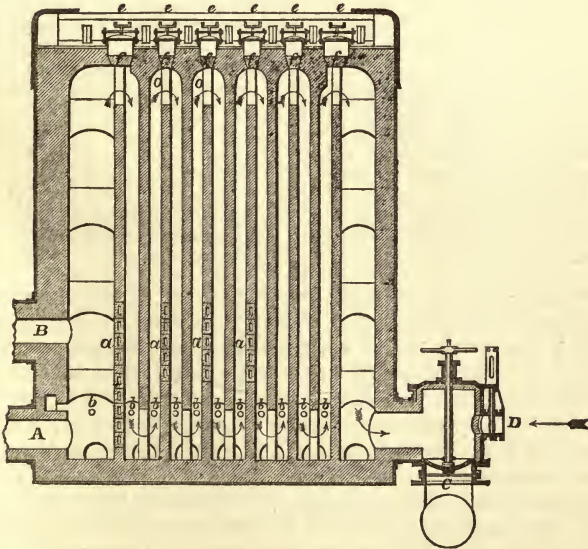
FIG. 77.

older forms of Whitwell stove were 25 feet in height. Recently the height has been greatly increased, the largest size adopted

being about 70 feet high and 25 feet in diameter. A domed top is now used.

The relative merits of fire-brick and iron hot-blast stoves may be seen from the following comparison drawn by Lürmann :*—

Fire-brick stoves may be heated to very high temperatures without interfering with their working, if the dust contained in the blast-furnace gases contains no basic constituent which has a detrimental action on the fire-brick.

Iron stoves can only be heated to the temperature at which the cast-iron, of which they are made, softens.

The heating surface of fire-brick stoves must be considerable if the temperature of the blast is not to be altered too rapidly, and if the working is not to be interrupted too often. The cost of erection of these stoves is consequently high. The cost of maintenance, on the other hand, is very low.

Iron stoves, with sufficient heating surface for the amount of blast to be heated, necessitate a smaller expenditure of capital than the older forms of fire-brick stoves, and give uniform temperatures. They, however, present the danger of the working being interfered with on account of pipes having to be replaced, and consequently the cost of maintenance is high. On the other hand, the value of the worn-out material of the iron stoves is higher than that of the fire-brick ones.

The older forms of fire-brick stoves are not easily cleaned. By rendering cleaning possible, the construction becomes more complicated, and the cost is consequently increased.

Iron stoves are easily cleaned.

Fire-brick stoves require a skilled attendant, as the working is intermittent.

Iron stoves may be entrusted to the ordinary workmen, and demand no special skill.

Fire-brick stoves, as compared with those of iron, possess the advantage of effecting a saving in heat by lowering the temperature at which the products of combustion enter the chimney. The quantity of coke consumed when fire-brick stoves are employed being less than when iron stoves are used, the weight of furnace gases is correspondingly affected. Sir Lowthian Bell † assumes that for 20 units of iron made there are 122 units of gas in the former against 129 units in the latter. Allowing 10 per cent. of free atmospheric air in the burnt gases as they leave the stoves, their weight may be taken at 212 and 240 units respectively per 20 units of iron produced. The two accounts may be stated as follows :—

* *Stahl und Eisen*, 1882, p. 361.
† *Journ. Iron and Steel Inst.*, 1883, p. 119.

FIRE-BRICK STOVES.

Heat from combustion of furnace gases . .		83,700 *calories*
Less loss of sensible heat in products of combustion—212 wt. × 189° temp.		
× 0.24 sp. ht.	= 9,616	
Allow loss of 10 per cent. for radiation	= 8,370	
		17,986
Leaving available	.	65,714
Contained in blast	.	16,018
Leaving for other purposes . . .	.	49,696

IRON-PIPE STOVES.

Heat from combustion of furnace gases . .		88,500 *calories*
Less loss of sensible heat in products of combustion—240 wt. × 624° temp.		
× 0.24 sp. ht.	= 35,942	
Allow loss of 10 per cent. for radiation	= 8,850	
		44,792
Leaving available	.	43,708
Contained in blast	.	11,584
Leaving for other purposes . . .	.	32,124

Whether heated in brick or in iron stoves, the blast is conveyed to the furnace in mains lined with fire-brick.

CHAPTER IX.

TYPICAL METALLURGICAL PROCESSES.

Classification of Processes.—The methods that are adopted in extracting metals from their ores may conveniently be grouped in the following manner :—

A. Dry Processes.

I. *a. By Simple Fusion with Suitable Fluxes.*

(*a*) In blast or reverberatory furnaces.	1. Gold 2. Silver 3. Platinum 4. Copper	This process is only applicable to metals in an uncombined form.
(*b*) In tube furnace.	5. Bismuth	By liquation.

β. *By Simple Heating.*

(*a*) In kilns or reverberatories.	1. Mercury	From its sulphide, the presence of air being necessary.
(*b*) In retorts.	2. Arsenic	From sulphides of arsenic and iron, air excluded, always with appliances for condensing the volatilised metal.

II. *By Reduction of Oxide by Carbon.*

(*a*) In blast furnaces or, more rarely, in hearths or crucibles.	1. Copper 2. Lead 3. Antimony 4. Nickel	Usually after previous roasting of sulphide or arsenide ;
	5. Iron 6. Nickel 7. Manganese	Usually with simultaneous carburisation of the liberated metal.
(*b*) In reverberatory furnace.	8. Tin. 9. Bismuth.	
(*c*) In retort furnaces.	10. Zinc 11. Arsenic 12. Sodium.	Always after roasting the ore ; and with volatilisation of the liberated metal.
(*d*) In furnaces heated electrically.	13. Aluminium.	

'III. *By Concentration as Sulphide;*

usually followed by reaction between sulphide and oxide,
or between sulphide and sulphate.

(*a*) In reverberatory furnaces.	1. Copper 2. Lead .	Usually after partial roasting; sometimes, in the case of lead and antimony, the removal of the sulphur and precipitation of the metals is aided by a cheaper metal, iron.
(*b*) In liquation furnace.	3. Antimony	

IV. *By Concentration in Sulphide, or Arsenide,*
and subsequent smelting as in II. or III.

In reverberatory or blast furnaces.	1. Gold. 2. Silver. 3. Nickel. 4. Cobalt.

V. *By Concentration in Other Metals, by Fusion.*

Usually in blast furnaces; but often in reverberatory furnaces.	1. Gold. 2. Silver. 3. Platinum.	The metal is subsequently concentrated or extracted by (1) cupellation, (2) crystallisation (Pattinson process), (3) liquation, (4) recourse to wet methods, (5) superior affinity of a third metal (zinc in Parkes' process), (6) distillation (treatment of gold amalgam).

VI. *By Reduction of a Haloid Salt.*

In reverberatory furnaces or in crucibles.	1. Aluminium. 2. Magnesium.	The halogen is removed by sodium.

B. PROCESSES INVOLVING THE USE OF MERCURY.

(*a*) In cradles, flumes, stamp batteries, concentrators . (*b*) In pans and appliances of varied form .	1. Gold .	As part of the operation of dressing the ore.
(*a*) In heaps (*b*) In barrels (*c*) In copper-lined tubs (*d*) In cast-iron pans .	2. Silver	Patio process. Old Freiberg process. Cazo process. Modern pan-amalgamation.

C. WET PROCESSES.

a. Methods of Solution.

These processes are usually conducted in earthenware vessels,
or cast-iron pans, or wooden vats, usually lined.

I. *Solution in Acids.*

1. Gold . . In aqua regia.
2. Platinum . Ditto.
3. Silver . . In nitric or sulphuric acid.
4. Bismuth . In hydrochloric acid.
5. Nickel.
6. Cobalt.   The oxides, obtained by
7. Zinc .   roasting sulphides or arsenides,
8. Copper   are dissolved usually in hydro-
9. Lead .   chloric acid.

II. *Roasting to Sulphate, and extracting with Water.*

1. Silver . . (Ziervogel process.)
2. Copper . The metal is precipitated by iron.

III. *Roasting with Salt, Soluble Chloride being formed.*

1. Silver . . (Augustin and Von Patera processes.)
2. Copper . (Longmaid and other processes.)

IV. *Formation of Soluble Chloride by Gaseous Chlorine.*

1. Gold . . Plattner's process and its modifications. In some cases, chlorine is replaced by bromine, a soluble bromide being formed.
2. Silver . . Any silver chloride, formed in the treatment of gold, may be dissolved out by sodium hyposulphite or brine.

β. *Methods of Precipitation.*

1. Silver .   Replacement by a cheaper metal.
2. Copper .
1. Gold .   By a precipitating agent.
2. Platinum .   By a reducing gas.
1. Bismuth .
2. Nickel .   By precipitation, followed
3. Cobalt . by reduction in the dry
4. Zinc . way.
5. Lead .

D. ELECTROLYTIC METHODS.

At the present time, electrolysis is mainly employed in the refining of copper. Numerous electrolytic methods of extracting

metals from their ores have frequently been brought forward; few, however, have advanced beyond the experimental stage.

1. Copper	.	From blister-copper or regulus.
2. Lead .	.	Keith's process.
3. Gold .	.	By nascent chlorine produced electrolytically.
4. Aluminium		From aluminium in its fused haloid salt.
5. Antimony .		Borchers' process.*

It is impossible in a work of this description to deal fully with the methods that are adopted in extracting even the principal metals from their ores, nor is it desirable to attempt to do this, for the student has an abundant technical literature at his disposal. It is far more important that at the outset of his work he should make himself familiar with the nature of metallurgical operations generally, so that he may see in what points they differ from those conducted either in the laboratory or in purely chemical works. With this object in view, a few typical metallurgical processes have been chosen for somewhat full treatment, care having been taken to select those which present considerable complexity of detail, since a knowledge of such groups of processes as those adopted in industrial centres like Swansea, Denver, and Freiberg gives the student a clearer insight into metallurgy than desultory reading affords.

Welsh Method of Copper-smelting.—This method, in modified forms, conducted in reverberatory furnaces, is employed for a large proportion of the world's production of copper. In Germany a blast-furnace method is employed. The one broad distinction between this method and the Welsh method consists in the fact that in the latter copper sulphide is the reducing agent, whilst in the German process it is carbonic oxide. Both processes depend essentially on the affinity which copper has for sulphur, which enables it to form a regulus while the associated metals are eliminated in an oxidised form.

In the Welsh method (Fig. 78) comparatively poor ores, consisting of copper pyrites with a considerable proportion of iron pyrites, containing 5 to 15 per cent. of copper, richer ores of the same composition containing 15 to 25 per cent. of copper, and copper pyrites with oxidised ores, are mixed so as to contain 9 to 15 per cent. of copper. The smelting method varies with

* *Dingler's Polytechnisches Journal*, vol. cclxvi. (1888), p. 283. On electrolytic methods consult Balling, *Die Electro-Metallurgie.*

WELSH PROCESS OF COPPER SMELTING.
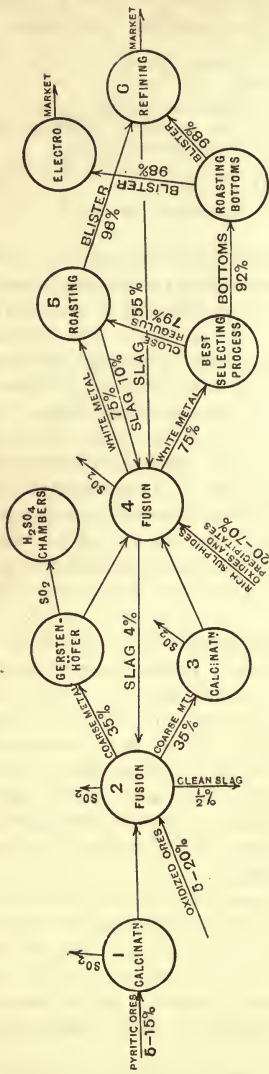
FIG. 78.

the nature of the ore, but it usually comprises six distinct processes :—

1. *Calcination of Mixed Ores.* —This consists in roasting the pyritic ores, whether rich or poor, containing iron pyrites, arsenic, and antimony. The roasting is always incomplete, and the extent to which it is carried depends on the proportion of sulphides available for the subsequent operations.

2. *Fusion of the Roasted Ores for Regulus.*—The ores are fused with slag rich in cuprous oxide, known as *metal-slag*, from the fourth operation. Fluorspar is useful as a flux, and is added with oxides and carbonates. The operation gives two products—a regulus, *coarse-metal*, in which it has been attempted to concentrate all the copper, and a slag, *ore-furnace slag* which seldom contains more than 0.5 per cent. of copper and is mostly thrown away. The regulus contains 30 to 34 per cent. of copper and 23 per cent. of sulphur. It also contains a notable quantity of arsenic, antimony, and tin.

3. *Calcination of Coarse-metal.* —This calcination is always incomplete, but its degree of perfection depends on the quantity of oxidised ores which it is possible to reserve for the subsequent operation.

4. *Fusion of Calcined Coarse-metal.*—In this operation roasted regulus and sulphuretted ore rich in copper, and containing

but little sulphide of iron, are employed. Oxidised ores of copper, free from arsenic, antimony, and tin, are also added. Two products are obtained, regulus, containing 65 to 80 per cent. of copper, and 18 to 22 per cent. of sulphur. The slag, *metal-slag*, is a ferrous silicate, containing a little oxide of copper and shots of metallic copper, the total amount of copper it contains being 2 to 3 per cent. This slag is melted in operation 2.

5. *Roasting the Regulus.*—This operation is very complex, and comprises a series of fusions and roastings in an oxidising atmosphere. Its object is to purify the regulus and to scorify the iron, and to bring as much as possible of the copper to the metallic state. To operations of this character the Welsh smelter applies the term roasting, as distinguished from calcining. Two products are obtained, *blister-copper*, containing about 98 per cent. of copper, and a slag, *roaster-slag*, which always contains oxide of copper, shots of metallic copper, and often a small proportion of arsenic, antimony, and tin. This slag is usually added to the charge in operation 4.

6. *Refining and Toughening.*—The object of this operation is to purify the copper by oxidising the foreign bodies that it contains. The refining should bring the metal to a malleable state, *marketable* copper. The slag obtained, *refinery-slag*, is very rich in copper, about 55 per cent., and is added to the charge in operation 4.

In the Welsh method of copper smelting, reverberatory furnaces are exclusively employed, the area of the grate being generally about one-fifth of that of the hearth. The furnaces used for calcination have very deep fireplaces, so as to give reducing gases; but they have an abundant supply of oxygen from the air, which is admitted through holes in the fire-bridge. The ore is charged-in through a flat hopper, in which it is allowed to dry for some time before being introduced into the furnace. The internal dimensions of the calcining furnaces are usually 30 feet by 12 feet, or 21 feet by 12 feet. The charge is 3 to 6 tons of ore, the calcination occupying 12 to 24 hours. The doors are then closed, and the temperature raised in order to decompose the sulphates. The gas evolved may consist of 10.6 per cent. of sulphurous and carbonic anhydrides, 9 per cent. of oxygen, and 80 per cent. of nitrogen.

The furnaces, in which the fusion for regulus is effected, are so arranged as to give a high temperature, and the fireplace is consequently large in comparison with the laboratory portion. The bed consists of a series of layers of compressed sand cemented

with metal-slag. It is about 15 to 20 inches in thickness, and slopes in all directions towards a tap-hole. There is a door in proximity to the flue, and through this door the slag is skimmed without allowing the air to pass over the regulus and oxidise it. In front of the tap-hole is a perforated receptacle, which can be lowered by a crane into a tank full of water. The bed is about 14 feet long, the distance between the top of the bridge and the roof being 23 inches. The charge is usually 2 tons of ore. Slags from subsequent operations are added, and fluorspar, if much earthy gangue is present. The materials used in this first fusion for regulus are chiefly oxides and sulphides of copper and iron, and the operation consists essentially in obtaining copper sulphide, thus :—

$$2Cu_2O \ + \ 2FeS \ + \ 2SiO_2 \ = \ \underset{\text{Regulus.}}{2Cu_2S} \ + \ \underset{\text{Slag.}}{2FeSiO_3}$$
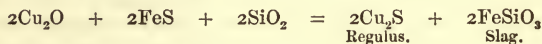
The sulphides must be in excess, otherwise copper will be absorbed in the slags, and copper will be obtained.

The calcination* of the regulus is effected in a furnace similar to that used for the first calcination. The charge is $3\frac{1}{2}$ to $6\frac{1}{2}$ tons of regulus. The reactions taking place are similar to those in the first calcination. The process occupies twenty to thirty-six hours, and 12 per cent. of the sulphur is eliminated.

The second fusion is conducted in a similar manner to the first fusion for coarse-metal. The charge is 2 tons of calcined coarse-metal and 12 cwt. of slag and oxidised ores. The regulus obtained consists of white-metal (75 per cent. of copper), or blue-metal (60 per cent. of copper), or pimple-metal (81 per cent. of copper). The slag is a silicate of iron, with about 4 per cent. of copper. The reactions are similar to those that obtain in the first fusion for regulus. Blue-metal contains some sulphide of iron, and pimple-metal contains an excess of the oxidised copper compounds. When very impure ores are dealt with, it is often found advisable to allow a little coarse copper to form as bottoms.

The roasting of these different varieties of regulus is conducted in a reverberatory furnace with a deep hearth. The process is prolonged as much as possible, and thus the arsenic and antimony may be caused to escape before the actual reducing action commences. When the pasty mass has collected at the bottom of the furnace the temperature is raised, and the reaction between

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* Copper smelters call these operations *calcination*, but *roasting* would be more accurate.

the sulphide and the oxide takes place, metallic copper being formed. The chief reactions may be expressed thus—

$$Cu_2S + 2Cu_2O = 6Cu + SO_2$$
$$Cu_2S + 2CuO = 4Cu + SO_2$$
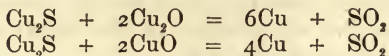
This impure copper, blister-copper, is refined in furnaces similar to those used for fusion, except that the bed is deeper and the fireplace larger. The charge consists of about 10 tons of blister-copper in the form of pigs, which are loosely stacked, and an abundant supply of air is provided, so as to oxidise the metal as much as possible. The temperature is raised gently to the melting-point of copper; it is then moderated in order that the fusion may be prolonged and oxidation occur. The melting occupies five to six hours, and the moderate heating is continued for five to six hours more, in order that the iron, antimony, arsenic, &c., may be completely oxidised. The temperature is then raised much higher for three to four hours more, when the oxidised products form a thin slag, containing a considerable quantity of copper oxide. This is raked off, and the surface covered with a layer of the purest anthracite or charcoal. A long pole of wood, green wood by preference, is pushed beneath the surface of the molten metal and held down by a suitable metal bar. The violent evolution of gas from the wood causes the metal to splash up amongst the carbonaceous covering, and this, with the gases from the wood, reduces, to the metallic state, the copper oxide that exists dissolved in the copper to the extent of 4 per cent. A small amount of the oxide must be left, and the workman judges, from a sample that he takes from time to time and tests by breaking in a vice, whether it is still "dry" or at "tough-pitch," that is, ready for market, or "overpoled." If the last, he removes the carbon covering, and exposes the metal to the action of the air.[*]

Smelting of Gold and Silver Ores in Colorado.—The old works of the Boston and Colorado Smelting Company at Black Hawk have disappeared, and the modification of the Swansea system adopted, which was fully described by Dr. Egleston [†] in 1875, has been so far changed in the method now practised at

[*] Fuller information on the Welsh method of copper smelting will be found in the following works :—Percy, *Metallurgy*, vol. i. (London, 1861), p. 314; Vivian, *Copper Smelting: Its History and Processes*, 1881; Howe, *Copper Smelting*, Washington, 1885; Le Play, *Procédés Métallurgiques employés dans le Pays de Galles*, Paris, 1848; Rivot, *Principes généraux du Traitement des Mineraux métalliques*, Paris, 1871.

[†] *Trans. Amer. Inst. M.E.*, vol. iv. p. 276.

the Argo works, near Denver, as to be scarcely recognisable, excepting so far as the general principles are involved. The following is a short sketch, borrowed from Mr. R. Pearce's Presidential Address, delivered at the meeting of the American Institute of Mining Engineers, in June 1889.

About 200 tons of ore is smelted per day, the ores including a great variety of copper, silver, and gold ores from Colorado, as well as from other Western States and Territories, and averaging 40 to 60 oz. of silver and $\frac{1}{2}$ to 1 oz. of gold per ton, and 2 to 3 per cent. of copper. About 90 per cent. of the ore contains no copper, the other 10 per cent. furnishing that metal in sufficient quantity to make up the general average to 2 to 3 per cent. Half the ore, 100 tons per day, is roasted in furnaces or in kilns, but the operation is not complete in either case, as sulphur is always allowed to remain to the extent of 5 to 7 per cent. The other 100 tons are smelted without roasting. The roasted ore and siliceous ores are mixed so as to yield a slag containing 40 per cent. of silica and a regulus (ore metal) containing 40 per cent. of copper and 400 oz. of silver and 6 oz. of gold per ton. The capacity of each furnace is about 25 tons of ore per day, with 2 tons of rich slags added from other operations. In this smelting 13 tons charged yield 1 ton of ore-metal. This regulus always contains a certain amount of lead, but the proportion rarely exceeds 10 per cent.

In the next stage of the process, the charge consists of a mixture of two-thirds of roasted ore-metal and one-third of unroasted ore-metal, together with rich siliceous silver ore, in quantities sufficient to prevent corrosion of the furnace by the iron in the regulus. The concentration-furnace in which this operation is effected stands 3 feet above the level of the ore-furnace, so that the rich slag from the former may, when skimmed, flow directly into the latter, where it is reduced to the condition of ordinary ore-furnace slag. This effects a great saving in the cost of re-smelting these rich slags. The white-metal obtained contains 700 to 800 oz. of silver and 10 oz. of gold per ton, together with 60 per cent. of copper, each ton representing 20 to 21 tons of ore. The white metal is now ready for the extraction of the silver, which comprises the following operations :—

Rough roasting.
Fine grinding.
Fine roasting for silver sulphate.
Lixiviation, and the precipitation of the silver.
Refining and melting of the cement silver.

The white-metal is crushed so as to pass through a screen of 6 meshes to the inch, and roasted for twenty-four hours. The bulk of the sulphur is driven off, and oxide of copper is formed, the mass still containing sufficient sulphur for the subsequent operation of roasting for silver sulphate. After cooling, the roasted material is ground fine under edge-rollers and passed through a 60-mesh screen. It is then ready for fine roasting or conversion of the sulphide into a sulphate.

This operation, based on principles pointed out by Ziervogel, lasts about five hours. The first stage is conducted at a low temperature, and lasts about an hour and a half, copper sulphide being oxidised with evolution of heat. In the second stage, at a slightly increased temperature for an hour and a half, the material increases in volume, and assumes a porous appearance from the formation of copper sulphate. In the third stage, the temperature is further increased for an hour or until the silver is completely changed into sulphate. If cuprous oxide is present at this stage, it will, during the operation of lixiviation with water, cause the reduction of the silver sulphate to metallic silver. The charge is consequently vigorously stirred, and turned over, in the fourth and last stage, in order to completely oxidise any cuprous oxide. The results of the operation are very materially affected by arsenic, by antimony, and, above all, by bismuth, metals which form insoluble silver compounds. The lixiviation of the roasted regulus is effected in tubs, and nothing but hot water is required. The solution, charged with silver sulphate, is allowed to flow over copper plates for the precipitation of the silver, a process requiring but little attention. The solution enters tank No. 1, charged with silver, and leaves tank No. 2, charged with copper, and without a trace of silver. It finally flows over scrap iron for the precipitation of the copper. In the precipitated silver, some copper is found in the form of cuprous oxide or as metal. This is removed by prolonged boiling with water containing a small quantity of sulphuric acid, into which air is injected by a small steam-jet. The copper sulphate formed is carefully washed out of the silver, which is then dried and melted into bars of an average fineness of 999.

The residues from the silver extraction contain about 40 oz. of silver and 10 oz. of gold per ton, and 65 per cent. of copper as cupric oxide. They also contain lead and bismuth as sulphates and iron as ferric oxide. They are mixed with pyritic ores containing gold, pyrites rich in sulphur and poor in silver, and siliceous gold ores, and are smelted direct for regulus with 65 per

cent. of copper, and 10 to 15 oz. of gold and 80 oz. of silver per ton. The slag, which is similar in composition to that from the ore-furnace, is thrown away.

The regulus is treated so as to obtain a rich copper-gold alloy. This process involves two operations—(1) a combined roasting and smelting, and (2) a refining of the crude alloy. The aim of the process is to concentrate the gold contained in the regulus into a rich gold- silver-copper alloy, containing also the bulk of the impurities existing in the regulus. This process is similar to the Swansea method of making "best selected copper." At Argo, about 12 tons of slabs of regulus, residue metal, are placed on the hearth of a large reverberatory furnace, and melted after partial oxidation. In the last stage of the melting, a reaction takes place between the oxide and sulphide, and a certain amount of metallic copper is liberated. This contains nearly all the gold, together with any foreign metals present in the regulus. The charge is tapped into sand-moulds, and the first few pigs nearest the tap-hole are found to have, under the enriched regulus, plates of this impure copper, commonly known as metallic bottoms. The proportion of these to the whole tap of regulus, or pimple-metal, is about 1 to 15. The bottoms contain 100 to 200 oz. of gold to the ton, and about 300 oz. of silver. They are subjected to processes of refining and separation, whereby the gold is recovered.

The pimple-metal, if the operation has been properly conducted, contains 0.1 to 0.2 oz. of gold per ton, 90 oz. of silver, and 77 per cent. of copper. It is crushed, roasted, ground fine, and again roasted to form silver sulphate. In fact, it is treated by the Ziervogel process in precisely the same manner as the rich silver regulus ; but, as it contains no gold, a separate set of furnaces is used. The residue consists almost entirely of copper oxide with less than 10 oz. of silver per ton. It is dried, packed in barrels, and sold to the manufacturers of sulphate of copper, or is reduced to black copper by melting with small coal slack in a reverberatory furnace.

Freiberg Process.—The smelting works at Freiberg,[*] in Saxony, were originally established to treat the ores obtained from the mines of the district. At the present time, ores from all parts of the world are also smelted. There are also two works, of which

* Descriptions of the various operations conducted in these works will be found in the following books :—*Freibergs Berg- und Hüttenwesen*, Freiberg, 1883 ; *Festschrift zum hundertjähr. Jubiläum der k. Bergakademie zu Freiberg*, Dresden, 1866 ; Percy, *Lead*, p. 203 *Silver and Gold*, p. 543 ; *Arche, Die Gewinnung der Metalle*, part i., 1888.

the more important is situated about three miles from the town of Freiberg, the other being somewhat more distant.

The ores treated consist chiefly of the sulphides of lead; but silver and copper are always present in the mixture of ores which constitutes the furnace-charge. The plant also includes furnaces for the treatment of ores of zinc, arsenic and antimony fume. As an incidental process, sulphuric acid is made both by the ordinary lead-chamber method, and by a process in which the gases containing the sulphurous anhydride are stated to be passed over perforated clay slabs covered with platinised asbestos. Bismuth is also extracted from the portions of the cupellation hearths in which is collected the greater part of the bismuth that was originally contained in the lead treated. Provision is also made for the extraction of copper, nickel, and cobalt present in the ores. The relation borne by the respective sections to each other and to the general plan of operations is indicated by the accompanying diagrammatic scheme (Fig. 79). The various departments of the work are kept distinct, and the treatment, as a whole, centres round the smelting of the lead ores, the various residues from the treatment of other ores, frequently rich in the precious metals, being added to the lead-smelting charge. It is in this latter treatment that the distinctive features of the Freiberg smelting-process are found, the lead ores being smelted in admixture with the copper ores and argentiferous and auriferous residues. For this purpose the Pilz water-jacketed furnaces (Fig. 64) are used. They were originally introduced about the year 1865 to replace the older types of blast-furnace which had long been employed. The extraction of silver by the classical Freiberg amalgamation process, conducted in barrels, was also abandoned about this period, and was replaced by the method still in use, by which the precious metals are collected in the smelted lead. The main features of this process are as follows:—In order to impart the necessary degree of strength and coherence to enable them to be treated in the blast-furnace, as well as to obtain them in pieces of a size adapted to such treatment, the ores are first roasted at a temperature sufficiently high to clot the mass. This is effected by subjecting a suitable mixture of ores to an oxidising roasting in a long-bedded reverberatory furnace. The sulphur of the ore is in this way oxidised, and the metals are left chiefly in the form of oxides. Towards the end of the roasting the temperature of the furnace is raised to a degree sufficient to partly fuse the oxidised charge then present; the roasted material can in this state be withdrawn from the furnace into sheet-iron wheel-barrows, in which it is allowed to solidify. The

FIG. 79.

solidified material is afterwards broken up into pieces of the desired size, and classified according to the completeness with which the roasting has been effected, as indicated by the presence or absence of unroasted sulphide. It is then smelted down in the Pilz furnaces, in admixture with coke and brown coal. Large quantities of iron are present in the material charged into the furnace, and cold blast has therefore to be employed to prevent too great a reduction of that metal and the consequent formation of unfused masses of reduced iron in the furnace. The products of this smelting are (1) lead; (2) a regulus, or mixture of fused sulphides of lead and copper; (3) a slag; and (4) a lead fume. A small quantity of speise, containing nickel and cobalt, is also occasionally obtained. The lead produced contains the greater part of the precious metals originally present in the charge, together with some copper and other impurities. Such lead has always to be subjected to a refining process before being desilverised by the method in use at the works, and, if very impure, a secondary refining process of liquation has also to be used. To avoid the necessity of this the charge is usually maintained as free from impurities as possible, the percentage of the copper being at the same time kept low. The slag from the ore-smelting always contains lead in too large a quantity to admit of its being thrown away. It has therefore to be re-treated, and, as the lead obtained from this source is always very impure, any impure materials that it may be necessary to deal with are generally treated simultaneously with the slag, provided they are not too rich in the precious metals. The percentage of copper admissible in the furnace-charge for this slag-smelting is also greater than in that for the treatment of the ore. The ore-slag is treated in admixture with materials poor in silver and in lead, in a manner similar to the method adopted when smelting the ore. The products are the same as before—lead, speise, regulus, slag, and fume. The lead, however, is much less in relative quantity, and more impure than that obtained from the ore-smelting; speise is a more frequent product, the regulus obtained is richer in copper, and the slag is so poor in silver and lead that it may be thrown away.

The further treatment of these various products is as follows:—

Lead.—The slag-lead, and occasionally the ore-lead, is first submitted to a liquation process, which consists in melting the lead at as low a temperature as possible, on the sloping bed of an ordinary reverberatory furnace in a deoxidising atmosphere. By this means the lead melts and flows into a sump or hollow at the foot of the sloping bed of the furnace, leaving the greater por-

tion of the copper it originally contained, together with iron and other impurities, the melting-points of which exceed that of lead, on the furnace-bed. Nearly all the silver present in the lead charged into the furnace, and with it the gold, passes into the liquated product, owing to the low melting-points of the silver-lead and gold-lead alloys there present. This liquated lead, together with the ore-lead, is then submitted to an oxidising fusion in a reverberatory furnace, the result being that the arsenic, antimony, tin, and other impurities present, which had failed to be eliminated by the liquation process, are oxidised, and a portion of the lead being simultaneously oxidised and fused, they pass into this oxide scum, and can be removed with it. Owing to the varying degree of oxidisability of the several impurities, the fused litharge obtained at different stages of this process contains relatively larger or smaller quantities of the various impurities. These litharges, after removal from the furnace, are kept separate, and are known by the name of the more important impurity they contain. Each of them is after-wards reduced by itself in a small blast-furnace, the product being in each case a readily-marketable hard lead, the impure litharge being first fused with a small percentage of carbon to reduce a portion of the lead, and in this way to collect any silver that may be present in the reduced lead formed. Any copper, too, that may have passed into the liquated lead is also oxidised, but the bismuth remains with the lead. Small quantities of the precious metals always pass into the fused oxide layer on the surface of the lead, but by far the larger proportion of that originally charged into the furnace remains with the purified lead. This lead is then treated by the ordinary Pattinson process, the lead being first melted at a low tempera-ture and then allowed to cool gradually, the lead crystals poor in silver being separated from the richer molten portion. This treatment is repeated in the ordinary manner until the lead contains o.1 per cent. of silver. Instead of continuing to treat this lead by the Pattinson process, the Parkes process of desilveri-sation by the aid of zinc is employed for the purpose of extracting the remaining silver and gold, the lead from this treatment being dezincified by an oxidising fusion, after which it is ladled into moulds and is ready for the market. The rich Pattin-sonised lead is cupelled in cupellation-furnaces of the German type, with non-absorbent marl beds. The cupellation is so con-ducted that the lead, being charged into a hearth of large size, is oxidised until the residual material contains about 80 per

cent. of the precious metals. This requires a higher temperature for its further treatment, and it is therefore removed from the large furnace to a similar but much smaller one, in which the remaining portion of the lead is eliminated, the fused gold and silver being granulated by pouring into water, the granules dried, and the gold and silver parted by the aid of sulphuric acid.

The litharge, if of a yellow colour, is reduced to the metallic state by a reducing-fusion in a small Pilz furnace, but any red litharge that is produced is sold as such. The beds of both the large and the small cupellation-furnaces show green spots at the places where the final products, rich in gold and silver, collected; the bismuth, not being removed by oxidation until nearly all the lead has been oxidised, passes into these portions of the marl-beds, colouring them green. These green patches are carefully removed, dissolved in hydrochloric acid, and the bismuth oxychloride is precipitated by dilution with water. This is either sold as such after purification, or else is reduced to the metallic state by fusion in crucibles with iron. The other portions of the marl cupellation beds, being rich in lead, are on this account added to the various smelting-charges.

Zinc.—The argentiferous zinc ores are roasted, the sulphurous anhydride evolved being collected and converted into sulphuric acid. The desulphurised ore is then mixed with charcoal, and placed in the retorts, which are heated in a regenerative furnace by gaseous fuel. The zinc distils over, and is collected in fire-clay receivers, and, after refining in a special reverberatory furnace, is sent to market. The residues left in the retorts contain the precious metals, and are charged into the Pilz furnaces with the lead-ores.

The zinc rich in silver and gold obtained by the Parkes process is distilled in an ordinary Morgan furnace, which consists of a hooded crucible contained in a wind-furnace. This completes the lead-smelting process proper, both the gold and silver present in the original materials treated having been collected, and the desilverised lead obtained in a form in which it is ready for the market.

The *cupriferous regulus* resulting from the ore-smelting contains usually but a few per cent. of copper, and consists chiefly of the sulphides of iron and lead. It may be mentioned that it is necessary to have considerable quantities of iron present in the furnace-charge, partly on account of the desulphurising action of the reduced metal, and partly because considerable quantities of zinc are usually present, and the zinc-oxide, passing into the slag,

would render it exceedingly pasty and difficult to fuse, were it not for the counteracting influence of large quantities of ferrous oxide.

This regulus, if its composition is such that this treatment is admissible, is roasted in kilns, the sulphurous anhydride produced being utilised in the manufacture of sulphuric acid. When roasted the regulus is added to the slag-smelting charge; the greater portion of the lead-oxide contained in the roasted regulus is then reduced to the metallic state, and a second regulus is produced, which is poorer in lead but richer in copper than was the one resulting from the ore-smelting. This regulus is too rich in copper to admit of its being roasted in kilns, the tendency of the pieces of regulus to clot together during the roasting being too great; it is therefore roasted in "stalls" which are built of brick, and much resemble ordinary cattle-stalls; they are roofless, with low surrounding walls and a slightly sloping bed. On this bed wood is placed, the regulus to be roasted being piled up on it, and then covered over with a compact layer of finely divided roasted pyrites or regulus. The stalls are placed in rows side by side, and back to back, a tunnel being left between every two such rows. Into this tunnel the gases resulting from the roasting are drawn through perforations in the back walls of the stalls, and are led away to the sulphuric-acid chambers. The combustion is started by lighting a small fire in a grate outside the stall; this kindles the wood, the heat evolved by the combustion of the sulphur in the regulus being afterwards sufficient to continue the process without the addition of any other fuel. This roasted second regulus is then treated as before, until a regulus is produced which contains about 35 per cent. of copper.

Instead of this repeated roasting and treatment with the slag-charge, the regulus, after having been roasted, may be treated in a cupola, together with lead-slags and other fluxing and reducing additions. The product is a comparatively rich regulus, the lead originally present being reduced to the metallic state, taking with it the silver, the enriched regulus retaining but little of the precious metals. When enriched to the degree mentioned above, the regulus is brought, by a single roasting in an ordinary Welsh reverberatory furnace, to a "white" or "pimple" metal containing about 75 to 80 per cent. of copper. This is not further treated at the Müldenhütte, the principal works at Freiberg, but is sent to the Halsbrücke works, where it is roasted sweet, and the copper converted into copper sulphate by treating the roasted material with sulphuric acid. Any lead and gold that

may have been present remain undissolved, as does also the greater portion of the silver, the small quantity that passes into solution being reprecipitated by metallic copper. The undissolved lead residue is added to the blast-furnace treatment.

Speise.—This is a comparatively rare product. The nickel and cobalt it contains are concentrated by a process resembling that for the concentration of the copper in the regulus, the speise being first roasted and then re-melted with fluxes, such as lead-slags, and with reducing agents, in a small blast furnace. Metallic lead is obtained, which contains the greater portion of the precious metals originally present in the speise, and the latter is much richer in nickel and cobalt after this treatment than it was before. In this concentrated state it is sold to outside works, where it is treated by the wet process, the residues, which contain the gold and silver of the speise, being bought back by the Government works.

The *ore-slag* is treated in the manner that has been described, the resulting slag, poor in lead, being thrown away. This contains about $2\frac{1}{2}$ per cent. of lead and 0.0045 per cent. of silver, the zinc-oxide also present occasionally reaching some 20 per cent.

The *fume* contains large quantities of lead-oxide, together with zinc-oxide and arsenious anhydride, which is collected and sold after a further sublimation. The oxides of lead and zinc remain on the bed of the furnace, and are added to the blast-furnace charge.

Thus, the general scheme of treatment is as follows :—The ores are mainly those of lead, copper, zinc, and silver. The products are, lead, zinc, bismuth, silver, gold, arsenic, as metals, and copper, mainly recovered as sulphate. Besides these, there are also incidental products, such as sulphate of iron and sulphate of manganese. Nickel and cobalt are recovered as arsenides—that is, in the form of speise; and the arsenic is recovered partly as metal, but mainly as powdery arsenious anhydride, and as red, yellow, and white arsenical glass.

The ores come partly from surrounding mines, and partly from foreign sources, the latter being smelted mainly for the copper, silver, and gold they contain. Almost all the ores are argentiferous. The principal portion of each charge consists of lead-ores, and these are divided into galenas with 30 per cent. or more of lead, and poor lead ores with 15 to 20 per cent. In the mean they contain generally 40 per cent. of lead, and 0.015 per cent. of silver. The following, however, is a general statement respecting the ores :—

							Lead.	Silver.	Sulphur.
							per cent.	per cent.	per cent.
Galenas (1)	.	.	.	.	.	.	79	0.011	
,, (2)	.	.	.	.	.	.	74	0.012	
,, (3)	.	.	.	.	.	.	65	0.012	
,, (4)	.	.	.	.	.	.	80	0.008	
Poor lead ores	.	.	.	.	.		26	0.060	
							27	0.020	
Quartzose ores	.	.	.	.	.		—	0.026	
							—	0.050	
Quartzose and pyritic ores			.	.	.		—	0.010	16
							—	0.015	13
Pyritic ores	.	.	.	.	.	.	—	0.540	20
Sulphuretted ores	.	.	.	.	.		—	0.600	31
							—	0.240	30
							—	0.035	35
Lead ores with arsenic		.	.	.	.		23	0.450	Arsenic.
							39	0.100	16
							Zinc.		
Zinc-blende	.	.	.	.	.	.	38	0.044	
							40	0.020	

The lead in the ore is only paid for when it reaches 15 per cent., additional payment being made for every 5 per cent. above 20 per cent.—that is, for 25, 30, 35, and so on. Those ores in which only the silver or gold is of a value sufficient to cause them to be paid for are called " Dürrerze," and the class is subdivided into —pyritic, 20 to 40 per cent. sulphur; quartzose, 10 to 19 per cent. sulphur; and spathose, o to 9 per cent. sulphur.

The sulphur is paid for when it exceeds 24 per cent., and every additional 5 per cent. is paid for. Each per cent. of copper is paid for, but fractions of 1 per cent. are not taken into account.

The zinc-ores must not contain more than 5 per cent. of lead, and in ores that are not described as zinc-ores, only 3 to 4 per cent. of zinc may be present.

The copper-ores contain from 1 to 15 per cent. of copper, arsenical-ores from 10 per cent. arsenic, zinc-ores from 30 to 40 per cent. zinc, sulphur-ores from 25 per cent. sulphur.

The arsenic in an ore is paid for when it reaches 10 per cent., and fractions of 5 per cent. are accounted for.

Gold is paid for from 0.0005 per cent. and upwards, and silver 0.004 per cent. and upwards.

The weighing takes place in the presence of representatives of the mine and of the works. About 5 cwt. is weighed at a time. The accuracy of the weighing depends on the richness of the ore;

0.01 to 0.05 per cent. silver accurate to 10 lbs., 0.50 to 5 per cent. silver accurate to 0.1 lb., 5 per cent. and upwards, accurate to 0.02 lb.   Ores rich in gold are always weighed to 0.02 lb.

Sampling.—A small scoopful is taken from every 2 cwt. and is thrown into two or more wooden dishes, according to the amount weighed off.   The ore is then put into the ore-house, and a board is inserted in the ore-heap, showing the character of the ore, its quality, &c.   The moisture is determined by heating 75 grammes in a copper shovel; the calculation of the moisture is accurate to $\frac{1}{2}$ per cent.   The mixing takes place in the ore-house.   The various ores are spread out in layers, the thickness of which depends on the nature of the material, layer over layer.   Then a definite portion is cut off one end of the heap, and the ore so removed is thrown up into a conical heap, which is then considered to be sufficiently mixed.

Roasting.—A charge for roasting and smelting may contain 2500 cwt. roasted material from the Gerstenhöfer furnaces, 600 cwt. roasted residues from kilns and arsenic furnaces, 3000 cwt. raw ore, 200 cwt. residues from zinc-smelting.

Heaps of from 6000 cwt. to 7000 cwt. supply four roasting-furnaces for a week and a half; one furnace will treat 180 cwt. a day. The roasting-furnace is a single-bedded reverberatory, upwards of 40 ft. long and about 10 ft. broad; it has eleven doors on each side, and one, which is used for roasting pure galena, has fifteen doors on each side.   It is worked from both sides at the same time. The fire-bridge is hollow, and the bed consists of a layer of fire-bricks, made from two parts of raw and one part of burnt clay; they contain 60 to 70 per cent. of silica.   These bricks rest on common bricks supported by an iron plate, resting in turn on pillars.   If the hearth, or fire-bridge, becomes worn the work is not stopped, but, by means of a long iron ladle, a ball consisting of one part of clay and two parts of poor quartz-ore, is inserted.   This is beaten down so as to repair any defective place.

Each charge of ore consists of 34 cwt., and there are five such charges on different parts of the furnace-bed at one time.   The charge near the fire-bridge is allowed to clot, and is then removed. The other charges on the furnace-bed are then advanced towards the fire-bridge the distance of two doors at a time.   The fire-place is divided in the centre, so that really there are two fire-places, or grates, to each furnace, as the breadth is too great to permit one fireman to stoke the whole.

These long-bedded calcining furnaces are in connection with long brick chambers for the condensation of the fume, the collection of which takes place every six months, when some 2700 cwt. to

3000 cwt. of material is collected, containing—0.01 to 0.02 per cent. silver, 10 to 28 per cent. lead, 40 to 50 per cent. arsenious anhydride. The sulphurous anhydride from these flues cannot be used, as the gases are far too dilute and impure.

The charge for roasting generally consists of—galena 30 to 40 per cent.; poor lead ore 20 to 30 per cent.; poor quartzose ore 10 to 15 per cent.; and residues 5 to 10 per cent.

The cost of roasting each hundredweight of ore is as follows:—Fuel, $1d.$; transport, $0.7d.$; wages, $2.5d.$; wear and tear, $0.1d.$; tools, $0.5d.$; total, $4.8d.$

The roasted ore still contains from 5 to 7 per cent. of sulphur when the semi-fluid charge is withdrawn from the furnace into barrows of sheet-iron. The roasted charge is tipped out when solid, and broken into pieces about the size of the fist, and sorted by sight into (1) well roasted, (2) ordinary, and (3) badly roasted, according to whether much or little undecomposed galena is seen to be present. The men are paid accordingly.

There are several large Pilz furnaces, each with eight tuyeres, and one small one with four tuyeres. The following is a charge for the ore-smelting:—Ore, 450 cwt.; pyritic ore, 80 cwt.; roasted residues, 40 cwt.; slag, 550 cwt.; quartzose ore, 20 cwt.; total, 1140 cwt. This gives 88 cwt. of argentiferous lead, containing 0.4 to 1 per cent. of copper, and 20 cwt. of regulus, and very often a speise forms as well. In charging, the coke is thrown towards the centre, and the larger pieces of ore to the side.

If an obstruction or "bear" forms in the furnace, it is usually a ferruginous one; but it may contain much zinc-sulphide, and it generally forms at the top of the boshes. In order to remove it, bricks are removed below the bear, and the obstruction is knocked away while hot. The bear often has the form of a ring. The hearth of the furnace is built upon an iron plate. Then follow three layers of common bricks placed flat, and then two layers of fire-bricks, these together being about 16 in. thick. Then follows another layer, 16 in. thick, of the fire-bricks already described. The pressure of the blast is about $10\frac{3}{4}$ to $13\frac{1}{4}$ inches of water when smelting ore, and 7 to 10 inches when smelting slag. For driving the blast there is a twenty-horse-power water-wheel, used during the day for the liquation-and refining-furnaces, and during the night for the blast-furnaces; it also drives a small water pump. There is also a twenty-horse-power steam-engine for the blast- and liquation-furnaces, a fifteen-horse-power steam-engine for the blast-furnaces and smithy, and an eight-horse-power steam-engine for the blast-furnaces and steam-lift.

In twenty-four hours each blast-furnace smelting ore treats about 1400 cwt. to 1500 cwt. The charge would consist of—roasted ore, 600 cwt. to 700 cwt.; slag from previous smelting, 500 cwt. to 560 cwt.; and other additions, 250 cwt. to 300 cwt. This charge requires some 115 cwt. to 120 cwt. of coke, or about 1 cwt. of coke to 12 cwt. of the ore-charge. The result of the smelting is about 115 cwt. of lead, and 36 cwt. of lead regulus.

The charge described above is worked by five men at each furnace. They work in shifts of twelve hours. Below, one smelter and three assistants; above, one charger. The wages amount to about ½d. for each cwt. of ore.

The hearth is allowed to fill until some of the regulus is seen to come out with the slag, which is tapped continuously from one or other of two tap-holes.

The lead contains	.	.	0.5 to 0.6	per cent. of silver
The lead regulus .	.	.	25.0 to 30.0	,, ,, lead
			6.0 to 15.0	,, ,, copper
			0.2 to 0.25	,, ,, silver

The slags contain 0.3 per cent. of copper, 4 to 5 per cent. of lead, 0.003 to 0.004 per cent. of silver.

Smelting the Rich Slag.—The slags may be viewed as three equivalents of monosilicate with one equivalent of bisilicate, and slags that do not contain more than 0.001 to 0.002 per cent. of silver, and 1.5 per cent. of lead are thrown away.

The charges in slag-smelting are very varied. The following are examples :—

(1) Slag 900 cwt.; plumbiferous material 45 cwt.; broken-up hearths 12 cwt.; which yielded 52 cwt. of poor lead, 85 cwt. of coke being required.

(2) For every 2 cwt. of a mixture of 5 cwt. roasted regulus from slag, 12 cwt. roasted ore-regulus, 2 cwt. roasted copper-regulus, 5 cwt. roasted liquation residues, is added 4½ cwt. of slag from galena-smelting, and 4 cwt. of common slag.

(3) Three cwt. of ore-slag, 3 cwt. of various residues rich in lead, 1½ cwt. once-roasted ore-regulus, 0.5 cwt. of coke. To this charge there is added, in the working-day of twenty-four hours, 12 cwt. of marl, 12 cwt. of hearth, and 12 cwt. of lead-skimmings.

(4) Twelve cwt. of slag, 25 cwt. of twice-roasted regulus, 40 cwt. of slags from the smelting of the litharge.

Products of the Slag-Smelting.—Slag-lead containing 0.4 per cent. of silver, regulus containing 10 to 20 per cent. of lead, or

regulus containing 20 to 30 per cent. of copper, poor slag containing 0.0015 per cent. of silver and 1.5 to 2 per cent. of lead.

Sometimes a speise of nickel and cobalt is also formed. The regulus is only about one-third of the amount of lead produced. The slags often contain 9 per cent. of oxide of zinc. The regulus is broken up and roasted in kilns, or stalls, and is then added to a smelting charge similar to that by which it was formed, or is concentrated in a Pilz furnace, or goes to a reverberatory for concentration with silica and barium-sulphate.

Smelting the Speise.—The charge in 150 cwt. of speise, 675 cwt. ore-slag, 4 cwt. impure litharge, 44 cwt. lead residues, 5 cwt. hearth, 40 cwt. fluor-spar, 75 cwt. coke. The products are 54 cwt. of lead, 121 cwt. concentrated speise.

The speise is concentrated by continuous and alternate roastings and smeltings, until it contains 20 per cent. of nickel, when it is sold. The poor lead goes to the liquation-furnace. The regulus is roasted in kilns and stalls, then fused to concentrate it, until it contains 30 per cent. of copper; it is then called " copper " regulus. It is afterwards treated in a reverberatory to form simple metal. Incidentally, large quantities of impure lead and substances containing lead-oxide are produced.

The process employed for the reduction of the lead from such substances consists of a reducing-fusion. One such substance, the litharge derived from the rich argentiferous lead, contains about 78 per cent. of lead. The furnace used is a small Pilz furnace with four tuyeres. The charge in twenty-four hours is, 1500 cwt. litharge, 450 cwt. lead-slags, 50 cwt. slags from a previous smelting, 130 cwt. coke. The products are, (1) a variety of lead, which, according to its purity, is either first liquated and then refined, or is taken to the Pattinson pots, and (2) a slag containing 10 per cent. of lead. Part of this slag goes to the next charge, and part to the first ore and slag smelting.

Liquating the Impure Lead.—This is done at Freiberg on the inclined bed of a reverberatory furnace, 500 cwt. being treated daily. The copper, with some lead, remains solid in the form of liquation-residues. The lead, before the liquation, contains 0.5 per cent. copper, afterwards it still retains 0.07 per cent. The residues are about 5 per cent. of the total lead ; they consist principally of lead with 15 to 18 per cent. of copper, and are added to the slag-smelting in the Pilz furnace.

The scum from the Pattinson pots is also treated in this reverberatory, in admixture with lignite. When antimonial lead is liquated the temperature must be kept low, but a little

wood must be kept kindled in the well of the furnace to prevent the lead solidifying.

If the lead contains 1.5 per cent. of silver, it is cupelled at once—that is, it is added to lead that has been already enriched by the Pattinson process. If it is impure, the lead is refined and Pattinsonised.

In refining, the lead is fused in an oxidising atmosphere on the bed of a reverberatory furnace. The products are a variety of different kinds of litharge to which the name of "*Abstrich*" is given. They are nothing but impure litharge, and as the nature and proportion of the impurities vary greatly, the appearance is very dissimilar; some are dark-grey and stony, others are light-yellow and are crystalline in structure:—(1) Powdery tin *Abstrich*; (2) fused tin *Abstrich*; (3) arsenical *Abstrich*; (4) antimonial *Abstrich*; (5) impure litharge *Abstrich*; (6) pure litharge *Abstrich*. There is a fractional oxidation of the various impurities, the tin and arsenic going first. The time required to refine 40 cwt. of lead is about fifty hours.

The products, in the case of lead smelted from ore, are as follows:—10 cwt. of tin *Abstrich*, or about 3 per cent. of the total lead, containing 11.3 per cent. of tin, 14.4 per cent. of arsenic, 2.8 per cent. of antimony; 20 cwt. arsenical *Abstrich*, or about 5 per cent. of the total lead, containing 8.5 per cent. of antimony, 8.9 per cent. of tin, 8.7 per cent. of arsenic; 10 cwt. of antimonial *Abstrich*, about 3 per cent. of the total lead, containing 6.8 per cent. of antimony, 1.3 per cent. of tin, 4.4 per cent. of arsenic; 10 cwt. impure litharge, about 3.2 per cent. of the total lead, containing 3.1 per cent. of antimony, $\frac{1}{2}$ per cent. of tin, 2.0 per cent. of arsenic.

In refining lead produced from the smelting of slag, very similar varieties of *Abstrich* are obtained, except that they are not so rich in tin, as when lead from ore is refined. At the Halsbrücke Works, a hollow pipe through which steam is passed is sometimes used as a mechanical stirrer when refining. In desilverising the tin *Abstrich*, about 90 cwt. of slag-lead is placed on the bed of the refining furnace and then, on that, 15 cwt. of the *Abstrich*, mixed with 4 per cent. of coal; the charge is melted down in three hours, and then another 15 cwt. of *Abstrich* and 4 per cent. of coal is added, and so on until the furnace is full. The desilverised *Abstrich* is taken off (the silver passing into the lead) and run down in a small Pilz furnace.

The lead is refined and Pattinsonised. The antimonial *Abstrich* is desilverised in the same manner, except that 24 cwt. of it is

added instead of 15 cwt., as it melts easier. The arsenical *Abstrich* and impure litharge are directly revivified by being run down in a small Pilz furnace for metallic lead, the lead obtained being then refined. The impure lead is added in part as a plumbiferous addition to the Pilz furnace smelting ore.

The desilverised tin *Abstrich* is smelted in a Pilz furnace, the charge being 100 parts of *Abstrich* to 100 to 150 parts of poor lead-slag, 50 per cent. of slags from the same working, and 20 per cent. of limestone. The lead obtained is revivified and poled in a Pattinson pot. The various kinds of *Abstrich* obtained are desilverised over and over again, until they contain comparatively no silver. The composition of the hard lead obtained from the stanniferous *Abstrich* is very varied. One variety contains 18 per cent. of tin, 10 per cent. of antimony, and 2 per cent. of arsenic.

The desilverised antimonial *Abstrich* is smelted in a Pilz furnace with slag and 10 per cent. of limestone. In twenty-four hours, 100 cwt. to 150 cwt. are sent through. The hard lead is liquated and poled, and contains about 10 per cent. of antimony, 3 per cent. of arsenic, and 1 per cent. of tin. Each refining-furnace is worked by one refiner and two assistants.

Pattinson Process as conducted at Freiberg.—In this process, the silver is concentrated in fluid lead by straining off crystals of lead which separate from the bath. The pots have a thickness at the bottom of 2.36 to 2.76 inches, and 1.9 inch at the sides. They are 5 feet in diameter at the top, and 2 feet 9 inches at the bottom. They hold about 15 tons, and last about 500 crystallisations. Each pot has a separate fire ; there are sixteen pots, sometimes worked in two batteries of eight pots each. They are worked by the one-third system. Each pot is kept at a determined percentage of silver, and assays are made daily. When fresh lead is added, it is introduced into the pot containing the same percentage of silver. At Freiberg it is usually the third pot from the left. The rich lead contains from $1\frac{1}{2}$ per cent. to 2 per cent. of silver, and the poor 0.0018 per cent. The scum from pots 1 to 4 is liquated by itself, and similarly those from pots 5 to 8, and from 9 to 15 by themselves. In a case in which the enrichment had not been carried far enough, the following were assays of the contents of the pots :—(1) 1.07 silver, (2) 0.80 silver, (3) 0.42 silver, (4) 0.33 silver, (5) 0.30 silver, (6) 0.26 silver, (7) 0.18 silver, (8) 0.11 silver, (9) 0.08 silver, (10) 0.04 silver, (11) 0.02 silver, (12) 0.012 silver, (13) 0.007 silver, (14) 0.0035 silver, (15) 0.0015 silver, (16) 0.001 silver. The poor lead never contains more than 0.05 per cent. of copper, 0.2 per cent. of iron, and traces of arsenic and antimony. The fuel

used is a mixture of lignite and small coke. To each battery of sixteen pots there is one fireman, and to every two pots there are two men. There is also one lead ladler. The men work for eleven hours, but the fireman works for twelve hours.

Cupellation at Freiberg.—The hearth is formed of 48 cwt. of fresh marl mixed with $\frac{1}{2}$ cwt. of clay. The marl is of three kinds :—

	I.		II.		III.
Calcium carbonate . . .	50	...	68	...	66
Magnesium carbonate . .	13	...	27	...	6
Iron carbonate . . .	2	...	2	...	2
Clay	14	...	3	...	25

Any pyrites present is carefully removed.

The greatest depth of the hearth from a line on a level with the tuyeres ought to be not more than 7.8 inches. The fire-resisting material with which the roof is lined consists of one part of clay and two parts of silica ; 100 cwt. to 200 cwt. of lead is placed on the damp hearth, and this is covered with sawdust and chips ; the roof is then put on, the wood lit, and the roof luted on with clay; the fire is kindled, and the blast turned on ; the lead melts down in sixteen to eighteen hours. The temperature is gradually raised, and lead is added, 700 cwt. being the total charge. The litharge, as it forms, is removed until the remaining lead on the bed contains 60 to 80 per cent. of silver. This is taken out, and the extraction of the silver completed on a similar but much smaller hearth. If the red litharge obtained contains less than 0.02 per cent. of silver, it is sold. It is said that if the lead contains 0.2 per cent. of bismuth no red litharge will be produced. At the end of the process, where the concentrated lead and silver settle on the hearth, there is a dark spot which indicates the presence of bismuth, and which is broken away and the bismuth subsequently extracted, this portion of the hearth having been previously hollowed to collect the rich lead. There are two men attending to each furnace, and they are paid a little over a penny for every hundredweight of lead treated. It takes 120 to 140 hours to cupel 700 cwt. of lead. The silver obtained is granulated by running it into water. It is about 990 fine, and is sent to the Halsbrücke works to have the gold parted from it.

Solution of the Regulus.—The concentrated copper regulus is sent to the Halsbrücke works, where it is roasted nearly sweet. It still contains about 1 per cent. of sulphur. It is then passed through a rather fine sieve, and the larger pieces are crushed and re-roasted. The roasted regulus is dissolved in sulphuric acid in

wooden vats lined with hard lead. The sulphate of copper is crystallised out, and, after purification by re-crystallisation, is sold. Such copper-sulphate as does not crystallise out but remains in solution is removed by scrap-iron. The solution of copper-sulphate before crystallisation is made to pass over metallic copper, in order to remove any silver it may contain. The residue, after the treatment of the regulus with sulphuric acid, contains the lead, and most of the silver originally present in the regulus treated. This is sent back to the Pilz furnace, with a view to concentrate the silver in the lead produced from the lead ores.

Wet Processes for Treating Argentiferous Copper Ores. —In certain cases copper pyrites is converted into copper sul-
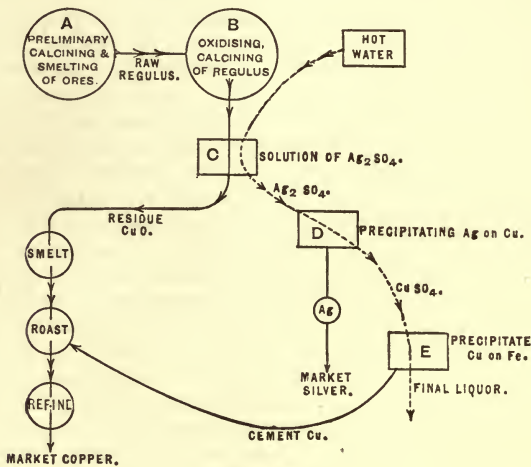
FIG. 80.

phate by the action of air and moisture. The sulphate is dissolved in water, and the copper precipitated from the solution by iron. When, however, argentiferous ores are dealt with, containing much copper but not much lead, the processes are more complicated. The principal processes in vogue are :—

1. Ziervogel's process, which consists in submitting the regulus to an oxidising roasting, yielding cupric oxide and silver sulphate. The latter is dissolved in water and precipitated on copper. The cupric oxide is recovered from the residues by smelting (Fig. 80).

2. Augustin's process, which consists in submitting the regulus

to an oxidising and subsequently to a chloridising roasting, yielding cupric oxide and silver chloride. The latter is dissolved in hot brine and precipitated on copper. The cupric oxide is recovered from the residues by smelting (Fig. 81).

3. Longmaid's or Henderson's process, which is applied to the ore after roasting, and which consists in dissolving the copper and silver from the ore roasted with salt by water and dilute hydrochloric acid. The copper is precipitated by scrap iron, and the silver is recovered by the Claudet process (Fig. 82).

4. In Claudet's process the silver is precipitated as silver iodide from a solution of copper and silver chlorides by zinc iodide
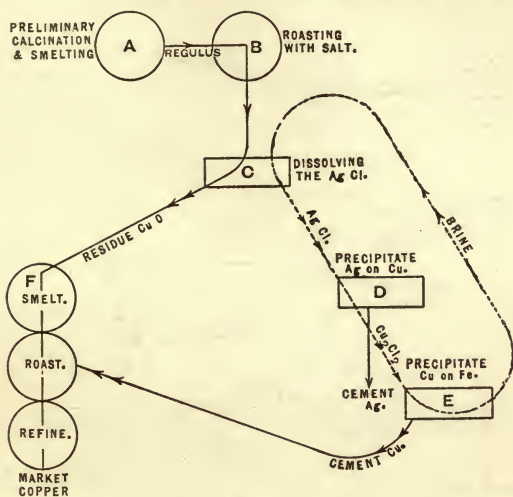
FIG. 81.

regenerated during the process, zinc being used to precipitate the silver.

These four processes are illustrated by the accompanying schemes, Claudet's process forming part of the scheme (Fig. 82).

The plant used in the Ziervogel process is illustrated in Fig. 83.

The charge of roasted material is placed in tubs A, provided with false bottoms, and hot water is introduced through the pipe b until the liquors begin to flow through the tap c. The pipe b is then closed, and acidulated hot water is admitted through the pipe a. The silver sulphate solution flows into a long tank, divided into two compartments B, C, whence it is distributed into

precipitating tubs D, provided with false bottoms on which cement copper is placed, with copper bars above it. Most of the silver is precipitated, and the liquors pass to a trough E, on the bottom of which is a layer of pieces of sheet-copper, and thence to the tubs F, also containing a little copper. The desilverised liquors are conveyed by the gutter g to a leaden pan, and again utilised. The precipitated silver is treated with sulphuric acid in the tubs H, and finally washed with hot water. The liquors rise through L, and are conducted by the trough M over metallic copper into tanks containing scrap-iron. The water from the
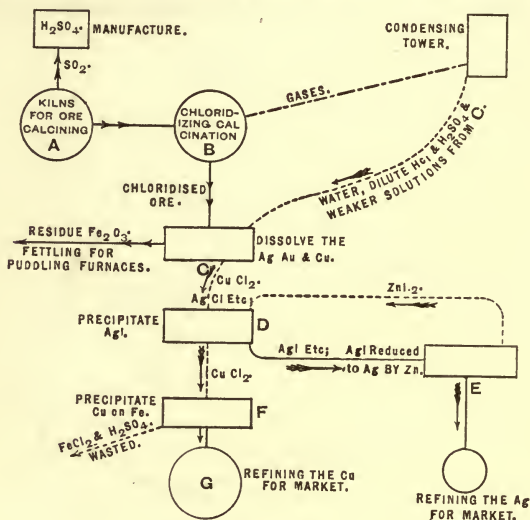
FIG. 82.

final washing is run off at N, and conducted to a lead-lined tank. The silver is moulded into blocks and refined.

Chlorination of Gold Ores.—Plattner's method of extracting gold from its ores by means of chlorination is based on the fact that chlorine gas transforms gold into soluble gold chloride without sensibly attacking the earths or metallic oxides with which the gold is mixed.

The ore is crushed and roasted with salt, 5 to 9 lbs. of salt per ton of ore having been added. Any lead, bismuth, or silver present is thus converted into chloride. The iron sulphide present, however, will first be converted into iron sulphate, and this

must be decomposed to form ferric oxide by raising the temperature of the roasting furnace. The base chlorides are soluble in water, and are removed by treating them in wooden vats. The residue is then acted upon in a moist state in wooden pitch-lined vats by gaseous chlorine. The gold is thus converted into chloride, but the ferric oxide remains unchanged. The gold chloride is dissolved in hot water, and precipitated by ferrous sulphate solution in another set of wooden vats. The insoluble residues left in the "gassing" vat are now treated with sodium hyposulphite solution in order to remove the silver chloride, which may be precipitated by means of calcium sulphide, and reduced by heating in air.
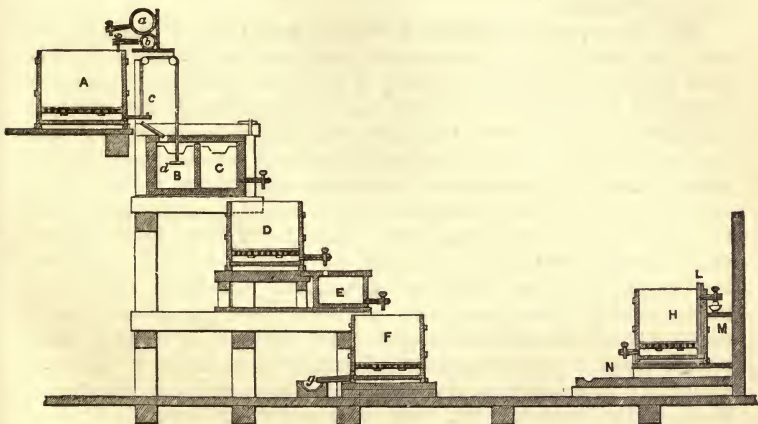
FIG. 83.

Numerous modifications of the chlorination process have been introduced, and large sums of money have been sunk in the formation of companies to work the processes. Only indifferent results have, however, been obtained.

Dr. Mears, of Philadelphia, was the first to lay stress on the influence of pressure in increasing the solvent action of chlorine. With certain ores, however, it has been found that as good results are obtained without pressure as with the highest pressure.

The largest chlorination plant in the world is at the Mount Morgan mine in Queensland. According to M'Dermott and Duffield,* the ore averages 5 oz. of gold per ton, and 1500 tons

* *Losses in Gold Amalgamation*, London, 1890, p. 30.

is worked per week, while the tailings contain only 3 dwt. per
ton.   The process consists in drying, crushing between rolls,
roasting, and working in revolving barrels by the aid of chloride
of lime and sulphuric acid.   The total cost is 30s. per ton.   The
ore is roasted for two and a half hours, and worked in wooden
barrels $5\frac{1}{2}$ feet in length.   Each barrel takes a charge of 1 ton of
ore, with 30 lbs. of chloride of lime, 33 lbs. of sulphuric acid, and
80 gallons of water.   The gas pressure does not exceed 20 lbs.
per square inch at its maximum development.   The barrels are
slowly revolved for two hours, and the charge is then filtered on
gravel and sand beds, and the solution precipitated by filtration
through charcoal filters, which are subsequently burnt in a rever-
beratory furnace.

Wet Process for Treating Nickel and Cobalt Ores.—The
wet methods for the extraction of nickel and cobalt from a com-
plex regulus or arsenide consist, in the first place, of a roasting
operation having for its object the volatilisation of the sulphur
and arsenic, and, it may be, antimony and the conversion of the
iron, nickel, cobalt, and other metals present into oxides.   Ferric
oxide formed in this manner at a high temperature is but little
soluble in acids, whilst the other oxides may be readily dissolved.
On treating the roasted material repeatedly with hydrochloric
acid or with dilute sulphuric acid, a residue is obtained contain-
ing but little ·or no cobalt or nickel, and consisting mainly of
ferric oxide.   Some iron will, however, have passed into solu-
tion.   Should the solution contain lead, bismuth, or copper, these
metals may be precipitated by sulphuretted hydrogen; but it is
customary to precipitate the copper at a later stage of the opera-
tions.   The bismuth, too, may be precipitated from a hydro-
chloric acid solution by dilution with water.

The next operation consists in the precipitation of the iron.
Any ferrous oxide which may have passed into solution is con-
verted into ferric oxide by careful addition of chloride of lime,
followed by the addition of lime, which precipitates the iron.
Arsenate of iron is, at the same time, also precipitated if arsenic
is present.   Should the temperature of the solution exceed 40° C.
some nickel and cobalt are precipitated, as, also, is some copper.

Instead of an addition of lime as the precipitant, caustic soda
or sodium carbonate is occasionally employed to prevent the pre-
cipitation of calcium sulphate when working with sulphuric acid
solutions.   Care must be taken to avoid using an excess of the
precipitant as the precipitation is a fractional one, and as soon as
the iron has been precipitated oxides of the other metals present
begin to be thrown down.

WET PROCESS FOR EXTRACTING NICKEL AND COBALT.

A. Calcined ores or speise of nickel and cobalt.

B. Granite jar containing HCl. Steam passed in.

C. Precipitation of iron and arsenic by milk of lime after peroxidising the ferrous oxide by $CaOCl_2$. Steam passed in.

D. Filter.

E. Solution. Pumped up to F.

F. Precipitation of copper sulphide by sulphuretted hydrogen.

G. Filter.

H. Ni and Co solution. Pumped up to J.

J. Solution carefully mixed with metallic iron, chalk, and chloride of lime. Steam passed in. Sulphuretted hydrogen evolved.

K. Filter.

L. Stock tank. Solution pumped up to M.

M. Dividing tank. Heated to 40°. Co precipitated by $CaOCl_2$.

N. Filter.

Residue Co_2O_3 to market.

O. Nickel ppt. by milk of lime.

Ppt. reduced to metallic nickel.

The next stage of the process consists in the precipitation of the copper. This is effected by raising the temperature of the solution to 70° C., and then precipitating the copper by the careful addition of either calcium carbonate, milk of lime, or a solution of soda. If an excess of the precipitant is employed, nickel will be thrown down. When a test with potassium ferrocyanide shows that the whole of the copper has been thrown down, the cobalt is precipitated from the filtered solution by the careful addition of a solution of chloride of lime to the perfectly neutral, hot, and not too dilute filtrate. If too much chloride of lime is added the precipitate becomes nickeliferous, and this must be carefully avoided. The nickel is next precipitated, either by calcium carbonate, milk of lime, or soda. The nickel hydrate is filtered, dried, heated with sodium carbonate, to decompose any calcium sulphate that may be present, washed with acidulated water, and finally dried and reduced by carbonaceous materials to the metallic state.

This process, being dependent on the fractional precipitation with the same precipitants of the several metals present in the ore or metallurgical product under treatment, is frequently subject to slight alterations of procedure, and the following is a description of the process as carried out at a works in the United Kingdom :—

About 3 cwt. of fine ore or speise A, that has been thoroughly roasted, is charged with hydrochloric acid in granite jars, into which steam is passed. The mass is kept boiling for twelve hours. It is allowed to settle, and run off into tubs C. Steam is conducted into the tubs, and when the liquid begins to boil, bleaching powder (chloride of lime) is added to peroxidise the iron, and the mass is allowed to boil for about three hours. The arsenic and iron come down together. If no iron be present in the solution some must be added. The liquid is then run off through filters D, to underground tanks E, whence it is pumped to tanks F, in which the mass is treated with sulphuretted hydrogen. Adjoining these tanks, of which there are six, there are also three lead retorts, in which sulphuretted hydrogen is produced. In these tanks, the copper is precipitated and the nickel and cobalt solution is strained through filters G, and drains into a second underground tank H. It is then pumped into a tank J, and there successively mixed with iron, chalk, chloride of lime, and water from tubs placed above the tank, with a view to precipitate, first, any copper that may have passed into solution during filtration, and then the iron which has taken the place of the copper. The charge is first boiled by the aid of steam pipes so as to expel the sulphuretted

hydrogen. It is then run off to a tank L for stock. It is next pumped up into a dividing tank M, and heated with chloride of lime, the cobalt being precipitated as oxide at a temperature of 40°. The solution containing nickel is allowed to run off into another tank O, in which milk of lime is added, and the nickel precipitated as hydrated oxide. The liquid is allowed to run off as waste. The oxides are pumped into presses, and the water is drained off. The nickel oxide is dried on the roof of a muffle, heated, and crushed. It is then mixed with charcoal, and heated in a crucible in a reducing furnace for eight or twelve hours. A rough powder is obtained, and in this form the metal is sold, or the nickel oxide is mixed into a paste with flour and water, which is heated and cut into cubes. These cubes are placed in crucibles with charcoal, and heated to a temperature above the melting point of copper. The nickel oxide is reduced by the charcoal and by the carbonised flour. The metal does not melt, but preserves the form of cubes. The cobalt oxide is removed from the dividing tanks to stone jars, and treated by a process similar to that described, so as to remove the last trace of nickel. The cobalt is finally sent to market in the form of oxide.

System of Teaching Metallurgy.—As the choice of a particular course of metallurgical study is of much importance to the student, it will be well to consider the various systems which have been adopted for teaching the subject.

First, there is the one that long prevailed in the Royal School of Mines of this country, which, from its foundation in 1851 to within the last few years, trusted to lectures and ordinary laboratory work, supplemented, since 1880, by visits to some metallurgical district.

Second, there is the system which receives its fullest development in the Berg-Akademie at Freiberg, in Saxony, where the subject is studied theoretically in the lecture-room and laboratory, the main feature of the course being the attendance of the students, during a considerable portion of their time, in one or other of the celebrated works of the district in which the school is situated.

Third, there is the widely different plan adopted in certain American schools, notably at the School of Mines, Columbia College, New York, and at the Massachusetts Institute of Technology, Boston, where, in addition to lectures and laboratory work, the students actually conduct operations, often on a considerable scale, with small metallurgical plant.

This is the system which the author unhesitatingly prefers, provided that the importance of laboratory work and research is

not lost sight of. An industrial district is not, in his opinion, the best situation for the chief metallurgical and mining school of a nation. Such an institution derives great advantages from being placed in a metropolitan centre of education ; but, apart from the question as to locality, it may be urged that an attempt to derive practical knowledge mainly from ordinary metallurgical works is attended with very distinct disadvantages. It is difficult to bring home to young mining engineers the fact that failures in mines and works quite as often result from errors in judgment as from the poverty of the ores, or defects in the processes, and upon this point Prof. R. H. Richards,* of Boston, well observes that the great advantage of teaching students by the aid of small metallurgical plant consists in their " finding out by their own experience that little losses taking place everywhere in the course of their work mount up enormously in their final account of stock . . . . . large works cannot afford to spoil a furnace-charge to show a student what happens from a little carelessness, and a well-regulated establishment may go on a long time without such a slip, and a student may be months at a works without finding out what is the key to its successes." At the School of Mines, Royal College of Science, this system of teaching with the aid of small plant is gradually being adopted, and there can be no question that the actual use of such appliances is most advantageous to the student, and that it enables him to acquire a better idea of the relations of metallurgical art to the sciences than is possible from mere theoretical work. As a type of such appliances the stamps for crushing quartz, and the concentrator, known as the Frue vanner, designed by Mr. R. E. Commans for the author's laboratory, have been placed as the frontispiece of this book.

The total height of the stamps is about 12 feet, and they are capable of treating from 1½ to 2 tons of material in the course of a day. By the aid of this plant it is easy to determine what is the most effective speed to give to the stamps when working upon ores of various hardnesses and compositions. A wide range of problems connected with the concentration of minerals may be studied, and considerable insight may be obtained into the difficulties of collecting the precious metals by amalgamated metallic plates. The degree of success of each operation is, of course, controlled by the results of assays.

This system of teaching with the aid of small plant is gradually being adopted by the author, whose laboratory at the School of Mines is already fairly well equipped. It is not, of course,

* _Trans. American Inst. Mining Engineers_, 1879, vol. vi.

urged that such a metallurgical laboratory would in any sense be a substitute for the works in which alone the professional education of a metallurgist can be fully developed, and no such claim is made on behalf of the engineering laboratories of which the country now possesses so many.   Their success abundantly justifies their existence, and all the arguments which have been urged in favour of the kind of training they afford, may be applied to mining and metallurgical laboratories.

It is to be hoped that the growth of such laboratories will be fostered in this country, and that other institutions will follow the example of the Technical School of Sheffield, which will possess a small Siemens regenerative furnace, in which the problems connected with the production of steel may be worked out, and the efficiency of the several methods of applying gaseous fuel may be compared.

CHAPTER X.

ECONOMIC CONSIDERATIONS.

Object of the Metallurgist.—Viewed in its commercial aspect, the object of the metallurgist is to render science subservient to manufacturing art, or, what is equivalent, to make science remunerative. If, as has been well observed, we hope to urge on practical metallurgists the importance of combining scientific with practical knowledge, it must be demonstrated that the combination will be of pecuniary advantage to themselves, as they can have no inducement for investing capital to carry into practice an invention, however beautiful and attractive in a scientific point of view, apart from the consideration of gain. This being the case, it will be well for the student to bear in mind a few of the principles by which the relations of capital and labour are guided, and the economic conditions under which metallurgical works are carried on.

Capital and Labour.—In the early stages of the metallurgical art, when the metals were extracted from their ores either by the direct action of heat, or by the aid of simple reactions, man was, as Gruner shows, in a measure the sole mechanical agent in this industrial art ; but when machines and appliances were devised, the agency of man became less apparent. In order to obtain these machines, Capital is necessary, and capital has been defined as "accumulated work," stored, that is, from some period anterior to that in which it has been brought into play. This accumulated work also demands payment when it is utilised, and this payment is the interest received by the capitalist who furnishes the equivalent of work. Manual labour is still necessary, and its influence is always considerable, even though it bears a less direct relation than formerly to the cost price of the product. It must be remembered, however, that there has always existed between capital and labour, between the employer and the employed, antagonism which it is very difficult to entirely banish. The utmost care should nevertheless be devoted to reducing it to the smallest possible limits, and as the condition of operatives

has materially improved during the last quarter of a century, it is certain that the efforts that have been made on their behalf have not proved fruitless.

Both masters and workmen should remember that industrial enterprise rests on three principal elements, knowledge, capital, and labour, although it is difficult to determine the relative importance of these elements. In uncivilised nations, labour is almost the sole element in the selling price of the manufactured product. In modern works, the selling price of the product is composed of widely different elements : cost of material, interest on capital, cost of direction, wear and tear of machinery, and price of labour. But, as no modern works can be carried on without capital, it will be well to consider this element first. The risks to which capitalists, who invest money in mining or metallurgical undertakings, are exposed, are too often imperfectly appreciated. The element of uncertainty is greater in mining than in metallurgy, but even in the latter industry, notwithstanding the observance of due care, the results are often disappointing. As M. Soupart * has recently pointed out, during the last twenty-five years in Belgium, in Hainaut and Namur alone forty-three smelting companies were established, and of these thirty-nine have been in liquidation and eleven have ceased to exist. In the province of Liége, fifteen companies have resulted in nine liquidations, and in two complete failures; a sum estimated at £2,400,000 has been entirely lost. Similar examples might have been borrowed from metallurgical enterprise in other countries. The failure is owing in most cases to rapid changes in the conditions under which the industry is conducted, to the adoption of new appliances and processes, and to the legitimate competition of rival works. It may fairly be asked what would have become of the labouring population if capitalists had elected to invest their capital in Government securities which, while affording no possibility of a high rate of interest, were at least safe. It would seem, therefore, that if capitalists are exposed to such great risks, they should unquestionably, in the event of success, receive the greater part of the profits.

Now, with regard to the remuneration of technical knowledge as distinct from that of either capital or labour, there is less difficulty as to its place. It should obviously be less than that of the capitalist, for, however indispensable knowledge may be, the possessor does not risk the loss of it, although knowledge is

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* *Rapport présenté au Groupe XI. Exposition universelle de Paris,* 1889. Brussels, 1889.

capital of a kind, and the personal responsibility involved in its application may be very great.

Finally, the operative brings to the common stock labour which may be considered to be current work as distinguished from accumulated work or capital. He, however, risks nothing; he changes his field of labour easily, and consequently cannot be entitled to as high a reward as either capital or knowledge.

To sum up, capital, intellectual work, and manual work, are the three factors of every metallurgical product, and misunderstandings that result in disaster are in nearly all cases due to the existence of false ideas respecting the relative values of these three factors.

The cost of labour in a modern steelworks, such as Dowlais, with an army of ten thousand people, does not exceed 25 to 30 per cent. of the total expenditure, and in an ordinary ironworks the proportion is not more than 15 to 20 per cent. It will, however, be evident that in addition to the actual sum paid in wages to the workman, much will depend on his skill, intelligence, and care. The importance of manual labour is therefore not measurable simply by the sum set down to labour in the accounts by which the selling price of the product is regulated. Cognisance must also be taken of the method of organisation of the labour and of the activity with which it is effected. It is therefore necessary to examine the methods of remunerating the workmen, and of organising the work.

Work may be paid for by the hour or day, by contract, or by piecework.

Payment by the day is the simplest of all methods, and has been very widely adopted. It consists in simply fixing the duration of the period of work, and the price to be paid for it. In very small works employing but few hands, the method may be found advantageous, but in large works it will ensure neither an efficient employment of time, nor a satisfactory performance. The supervision, moreover, that it is necessary to exercise, is of a kind that is peculiarly irritating to the men. Further, the method does not take into sufficient account the difference in the ability or industry of the workpeople. It should be adopted only in cases where the nature of the work is constantly varying.

In the system of work by contract, the work is allotted to contractors, who employ workpeople at a daily wage under their own immediate supervision. In this case, the supervision is perhaps more irksome than in the former, as the contractor, being an interested person, will be more exacting than an ordinary foreman.

Piecework is the system generally adopted. This consists in paying the workmen, in proportion to the amount of work executed, at a settled rate. It is the only system that conduces both to the interest of the employer and the employed. The first and most considerable difficulty consists in fixing the price of the piece, or the unit of work, and the adjustment of the contract affords abundant opportunity for the exercise of forbearance and equity on the part of the employer. The arrangement is more complicated where, instead of agreeing with a single workman, it is necessary to entrust work to several workmen associated as partners. It is then impossible to divide the work equally, for some of the workmen are more experienced than others. In this system it is also difficult to ensure that the work executed is of good quality. This difficulty, however, can be overcome by careful supervision.

Remarkable results have been attained with this system at the Creusot, Terre Noire, and other French steelworks, where the wages have increased 50 to 60 per cent., and the production has been doubled in the space of a few years, and that without increasing the number of hours of work. A special stimulus, too, is given by progressive payments—that is to say, by increased payment for the supplementary tons in excess of the normal outturn of iron or steel.

The adoption of this system of giving premiums has been attended with marked success. At the great Belgian zinc-works of *La Vieille Montagne*, all systems of payment are adopted; but the smelters and mill-men receive, in addition to a fixed wage, a premium calculated on the out-turn, and a special premium is also given for unwonted energy. In some cases, the firemen receive a similar premium, based on the time their furnace lasts without repair. In other cases the workmen receive a premium when they obtain from the ores a greater amount of metal than that which they are calculated to yield. Two-thirds of this premium is paid periodically with the regular wage. The remaining third is retained until the end of the year, and it is not paid then unless the workmen have worked regularly throughout the year.

At the Dowlais ironworks, the system of giving premiums is adopted in some instances—for example, puddlers are paid so much a ton for their work with a supplemental wage if they work a full number of turns during the week. The majority of men in iron and steelworks are paid per unit of work—that is to say, by the ton or quantity of work they turn out.

At the Royal Mint, London, a somewhat peculiar system is adopted. Prior to 1870, the workmen were paid on an average

2s. *8d.* per 1000 accurately struck coins, and when the Mint was not at work they received a small payment amounting to from *6s.* to *10s.* per week. The objections to this system are obvious. When the department was in full work, the men received an average of £2 *15s.* per week, and during the remainder of the year they received allowances insufficient to maintain them, or to prevent their forming other engagements. The result was, on the one hand, that the more improvident among them contracted liabilities and returned to work in debt, and, on the other hand, that the more skilful workmen were induced to accept employment elsewhere, and the Mint lost their services. The rate paid for piecework was therefore slightly reduced, and a uniform payment of £1 per week for the men, and *10s.* to *15s.* per week for the boys, as " subsistence money " as it is termed, was set on foot.

There can be no doubt that the system of premiums renders it possible to retain the services of good workmen, as well as to stimulate and encourage their intelligence. It is the best method of enabling him to share in the profits, and at the same time it indirectly augments those of the employer.

We now come to a question that has been discussed with much interest in recent years. Certain economists and philanthropists urge that it would entirely remove antagonism between capital and labour, if the operatives directly participated in the profits of an undertaking. Others contend that this sharing of profits, far from effecting a better understanding between capital and labour, would only give rise to further troubles. In one shape or another participation of profits has found a good deal of favour on the Continent, where many works have adopted it with generally very beneficial results to all parties concerned. This has notably been the case at the ironworks of Godin, at Guise, France.*

M. P. Leroy-Beaulieu, editor of *L'Économiste française,* states that the system of participation in profits, viewed as a general method of organising labour, is both deceptive and dangerous. It may be possible to admit superior workmen and foremen to participation in profits; but in this country, at least, workmen are not ready for the change. Everything goes well as long as the works are carried on at a profit; but in bad times discontent soon breaks out. The system is not viewed with favour by the workmen themselves. They are perfectly willing to share in the profits, but they object to be answerable for their share of loss, and are even reluctant to contribute to a reserve fund

* *Journ. Iron and Steel Inst.* 1888, No. I. p. 102.

to cover the losses of future bad years. A workman cannot either wait for better times, or turn out products at a loss in order to retain his employment. Moreover, the final participation appears too remote; the workman cannot appreciate the relation that exists between his work and the annual profit.

Among the methods that have been adopted for giving the men a permanent interest in the works, the following may be enumerated :—

1. The method of paying over to the workmen a share in an annual cash bonus.

2. Retention of the share for an assigned period, in order ultimately to apply it, together with its accumulated interest, for the workman's benefit.

3. An annual distribution of a portion of the workmen's share and an investment of the remainder. This third method is adopted at the La Vieille Montagne zinc works, where the results have been found to be most beneficial, and have entirely prevented strikes.

Whatever method be adopted, no effort should be spared to induce the men to exercise the utmost care in the conduct of their ordinary occupations. To illustrate this, Mr. Kenward, the manager of Messrs. Chance's works, near Birmingham, states that in such an apparently routine occupation as superintending a machine punching holes in a metal plate, a thoroughly active workman could realise a surplus wage three times as great as that obtained, under identical conditions, by a less strenuous but not less skilful fellow workman. With due care, a large amount of the waste that occurs in every trade could be avoided. In metallurgical industries, this waste is often apparent, and in some cases the dimensions of the scrap-heaps are a source of wonderment to foreigners who visit this country.

Quite apart from the methods of remunerating labour, much will depend upon the personal relations between employer and employed, and more especially upon the moral example set by the heads of the firm, and upon the amount of care and interest they display in providing for the wants of their people in the way of schools, gardens, savings banks, libraries, and hospitals. In this country the provision made in this respect at such works as Crewe, Elswick, and Dowlais deserves especial commendation. At Crewe there is a well-organised institute, in which competent teachers prepare the younger operatives for the various technological examinations throughout the country. Similar institutes have been founded at many other works.

No doubt where, as in the Royal Mint and other Government

establishments, pensions can be given, they afford the most powerful inducements to industry and fidelity.

It is not necessary here to dwell upon the importance of technical education. The advantages that craftsmanship constantly reaps from scientific knowledge are standing proofs of the necessity for special training. All may be summed up in a few words borrowed from the writings of a former French Minister of Finance, Jules Simon :—

" The practised eye and the sure hand are much, but they do not replace Science. The smith who knows the drawbacks of too rapid oxidation, who knows why throwing water on the surface of fuel increases the heat at the centre of the mass, the puddler who takes into account the effect of an oxidising or reducing flame, and who exposes metals to one or the other at the right moment—such are evidently the best workmen, more skilful for current needs, less disconcerted by an accident, less embarrassed by having to describe an observation, less slaves to routine, and quicker to adopt new processes." He points to the fact that so many of the modern inventions are due to workmen, and justly urges that the more intelligent the workman becomes, the better he will understand the skill possessed by those who direct him, and the more he will appreciate work that differs from his own.

In spite of all the advantages that technical education offers, it must be remembered that many metallurgical works in this country are successfully conducted by so-called practical men ; not the kind of man so forcibly described by Sir Frederick Bramwell,* as one "whose wisdom consists in standing by, seeing, but not investigating, the new discoveries which are taking place around him, the aim and object of such a man being to ensure that he should never make a mistake by embarking his capital or his time in that which has not been proved by men of large hearts and large intelligence ; " nor the man who accepts no rule but the rule of thumb, but practical men possessing technical knowledge of a high order, whose careful observations enable them to use the results of past experience in dealing with circumstances and conditions analogous to those they have met with before, and with which long practice has made them familiar. It would be difficult to overrate the value and importance of such knowledge as theirs, and, when we remember the scale on which smelting operations are carried on, it will be obvious that this kind of knowledge can only be gained in the works, and not in the laboratory or lecture-room, for, however careful metallurgical

* *Brit. Assoc. Rep.* 1872, p. 238.

teaching in a school may be, it is only practical in a limited sense. At the same time, it must be borne in mind that a man trained to scientific methods starts with the enormous advantage of being able to deal with circumstances and conditions that are new to him, and with which, therefore, he cannot be said to be familiar. The technical skill that time and opportunity can alone give him will then rest on a solid basis. It is necessary, however, to guard against undervaluing the teaching of experience unaided by reasoning that we should recognise as scientific, for it is only necessary to witness such operations as the roasting of a large mass of ore on the bed of a furnace, or the forging of many tons of iron under a steam hammer, to appreciate the value of the subtle skill of sight and touch on which success depends.

The relation between scientific and technical men is thus traced, as hitherto there have been misunderstandings on both sides, or, as Dr. Williamson* so well observes, " Men of detail do not sufficiently appreciate the value and usefulness of ideas or of general principles; and men of science, who learn to understand and control things more and more by the aid of the laws of Nature, are apt to expect that all improvements will result from the development and extension of their scientific methods of research, and not to do justice to the empirical considerations of practical expediency which are so essential to the realisation of industrial success in the imperfect state of our scientific knowledge."

While it is no longer necessary to justify the scientific teaching of metallurgy, it is as important as ever that the true relation of Theory and Practice should be clearly understood. It rarely happens that a process can be transferred from the laboratory to the works without important modifications; and it must be remembered that metallurgy is a manufacturing art, and that, when the truth of a theory has been demonstrated, a dividend has to be earned. This would, indeed, often be difficult without the aid of the practical man. Practical men have, however, ceased to undervalue science, and the most practical body of men in the world, in the best sense of the term, the ironmasters of this country, on whom its prosperity so largely depends, formed themselves, in 1870, into an Iron and Steel Institute, of which many of the members possess high scientific attainments, and are distinguished for scientific research.

Turn, then, to the advice given by those who are accustomed to deal with metals on a large scale. In 1873 Sir Lowthian

* Inaugural Lecture, University College, London, 1870.

Bell * stated : " If we would avoid the failure of what may be designated unscientific practice, or the failure of impracticable science, we must seek to combine commercial intelligence with a knowledge of those natural laws which form the only trustworthy groundwork of the complicated processes in which we are engaged."

Again, Sir W. Siemens,† in 1877, said, " It is not many years since practical knowledge was regarded as the one thing requisite in an iron smelter, whilst theoretical knowledge of the chemical and mechanical principles involved in the operations was viewed with considerable suspicion."

As regards the preliminary training in metallurgy, the utmost efforts of the student should be devoted to securing a thorough acquaintance with scientific methods and metallurgical principles, and, at the same time, to gathering as many well-ascertained facts as possible, remembering that applied science is nothing but the application of pure science to particular classes of problems. It consists of deductions from the general principles, established by reasoning and observation, which constitute pure science. No one can safely make these deductions until he has a firm grasp of the principles, and he can obtain that grasp only by personal experience of the processes of observation and of reasoning on which they are founded.

Production of Metals.—According to a diagram prepared by order of the French Minister of Public Works, and shown at the Paris Exhibition of 1889, the world's production of metals in 1887 was as follows :—

	Quantity. Tons.		Value. Francs.
Pig-iron	22,721,000	...	1,155,297,000
Silver	3,383	...	700,500,000
Gold	158	...	629,600,000
Copper	291,000	...	324,908,000
Lead	474,000	...	180,785,000
Zinc	333,000	...	129,795,000
Tin	35,000	...	95,123,000
Mercury	3,794	...	19,780,000

The world's production of coal during the same year amounted to 435,024,000 tons, valued at 3,000,652,000 francs.

The amount of pig-iron produced per head of population in the principal iron-producing countries is as follows :—

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* *Journ. Iron and Steel Inst.* 1873, p. 12.   † *Ibid.* 1877, p. 7.

							lbs.
Great Britain	.	.	.	.	.	.	463
Belgium	.	.	.	.	.	.	282
United States	.	.	.	.	.	.	238
Sweden	.	.	.	.	.	.	207
Germany	.	.	.	.	.	.	187
France .	.	.	.	.	.	.	88
Austria-Hungary	.	.	.	.	.	42

Price of Metals.—In an able paper,* published in 1887, Dr. D. A. Wells contends that depression in trade is largely the result of depression in the prices of metals and other metallurgical products. It is interesting, therefore, to consider past experience in the production and price of metals.

In the case of iron Sir Lowthian Bell fixed the world's production of pig-iron in 1870 at 11,565,000 tons, which increased to 14,345,000 tons in 1872. From that date production remained stationary until 1879, when it was 14,048,000 tons. After 1879 the average make for the ensuing five years was 18,000,000 tons, and in 1883 it rose to 21,063,000 tons, or nearly 50 per cent. more than it was in 1879. While the production of iron increased in the United Kingdom at the rate of 131 per cent. from 1870 to 1884, the increase in the production of the rest of the world during the same period had been 237 per cent.

Under such circumstances the price of pig-iron throughout the world has rapidly declined.

In America, pig-iron was 45 dollars per ton in 1870; in 1885 it was 16 dollars. Cleveland pig-iron was £4 17s. per ton in 1872, £2 10s. in 1880, 37s. 2d. in 1887, and 33s. in January 1888. In 1874 Bessemer steel rails were £12 per ton; in 1887 they were £4. Since 1870 there has been a marked increased production on the same expenditure in capital and labour. In Great Britain, the yield of iron per workman per year was 173 tons in 1870, 194 tons in 1880, and 261 tons in 1884. During the period under consideration, there has been a large substitution of steel for iron. A ship of 1700 tons requires 17 per cent. less material if made of steel than if of wrought iron; at the same time its efficiency is 7 per cent. greater in the former case. Again, on account of the greater durability of steel, a rail of this material has a life probably three times as long as that of an iron one. An iron rail is replaced after eight to twelve years, whilst a steel one lasts for twenty-four years. The consequence is that the British railways require only 200,000 tons annually of steel rails for replacement. If, however, they were of iron, 500,000 tons would be required. The same

* *Contemporary Review*, 1887, p. 523.

period has witnessed a great diminution in the production of puddled iron. This, it has been computed, has resulted, in the ten years from 1875 to 1885, in the loss of £4,667,000 of capital invested in puddling furnaces in England alone.

Other metals have also undergone great fluctuations in price; in most cases there has been a decline. In the case of copper, the increased annual production for the year 1885, compared with 1873, was 97 per cent., the increase being chiefly in the United States, Spain, and Portugal. In 1886 copper reached its lowest price, it having been, at New York, 9½ cents per lb., whilst in 1880 it was 25 cents per lb. In January 1887, Chili bars cost £40 per ton. Many mines had to stop working, for at such prices they could only work at a loss. The great mines alone kept on, but their dividends were considerably reduced. This state of things led to speculation in copper, and endeavours were made to buy up a certain quantity of this metal, to raise the price, and then to sell at a profit. A syndicate was formed in Paris, and large quantities of copper were bought. The first results exceeded all expectations. Copper rose in a short time from £40 to £80. It was then resolved to make the affair permanent, and the syndicate contracted with the leading copper mines to buy their output at a given price. It undertook, in fact, to take 150,000 tons a year, involving an outlay of at least £9,000,000. Besides this, in order to keep up the price and the monopoly, it was necessary for the syndicate to buy all the output of those mines which declined to contract. One of the chief factors in the affair, however, was overlooked. Consumers did not come forward as in previous years. Copper came into the market from all directions, and, owing to the high prices, old sheathing was melted down, meeting the consumption, and copper in many cases was superseded by iron or steel. In short, the stock of the syndicate swelled daily in alarming proportions, and in February 1889 the final crash came, and copper fell to £39. Since this date it has steadily risen, until it is now (September 1890) £57 per ton.

From 1880 to 1885, the world's production of lead increased about 30 per cent., and the price fell in the same proportion. In the latter year, there was great commercial distress among British lead miners and smelters. The price is now about £13 per ton.

Nickel, not many years ago, was a scarce metal of limited uses, but now the annual production amounts to from 800 to 900 tons. This exceeds the demand, and hence it is quoted at a comparatively low figure. The New Caledonian and Canadian ores are capable of yielding an immense supply of this metal; but until

recently there has been no market for it. In January 1887 the price was 2s. 3d. per lb. It is now 3s.

From 1860 to 1864, the demand for tin exceeded the production, and consequently prices ruled high. In 1872 the price was as much as £159 per ton. The large yield of the Australian mines from 1872 to 1878 brought the price down to £52 in the latter year. Since then, however, the Australian output has diminished, but the supply from the Straits has augmented. The demand has also increased, and prices have been £110 in January 1887, £167 in January 1888. It is now £95.

Better plant and the revolution in the price of iron has caused the production of tin plates to be doubled for the same price during the last fifteen years. In 1872 the price per box was 26s., in 1887 it was 13s., and in 1890 15s. 6d.

The price of mercury in 1874 was £26 per flask. In 1884 it fell to £5 2s., and in 1888 it rose to £10 7s. The decline in price of this metal was due to the increased production of California, which yielded 30,000 flasks in 1870, and 80,000 flasks in 1877. The demand for mercury in the treatment of silver ores is diminishing on account of the more general adoption of the lead method for extracting silver.

The annual supply of silver increased from 1872 to 1885 from 50,275,000 oz. to 95,908,000 oz., and during the same period the price of the metal fell very considerably. It is now 4s. 3d. per ounce; but, as the cost of production of the metal does not exceed 1s. 8d. per ounce, it is very probable that its market value will again fall considerably below the present rate. Indeed, its market price might have been expected to fall below the lowest point actually reached had it not been for the artificial stimulus imparted by recent coinage legislation in the United States of America.

This estimate of the cost of production of silver was based on the world's production in 1883, and was prepared by the author for the Royal Commission on the Recent Changes in the Relative Values of the Precious Metals (1887). The metallurgical processes involved in the extraction of silver from its ores, though very complex, admit of being classified under four heads, shown in the following table, which also gives an estimate of the cost of production of silver by each of these processes, as well as the resulting mean cost :—

Section.	Method by which Silver was obtained.	Weight Produced in Ounces.	Cost per Ounce of Fine Silver.	
			s.	d.
1	Refining of native gold . . .	508,000	0	2½
2	Desilverisation of lead . . .	30,726,000	2	0
3	Desilverisation of copper and cupriferous products . . .	7,200,000	1	11
4	Treatment of silver ores . .	49,920,733	1	5
	Total . . .	88,354,733	1	8

This result appeared to the Director of the United States Mint to be far too low, and a considerable portion of his Report on the " Production of the Precious Metals in the United States for the Year 1887," is devoted to a critical examination of it.   Dr. Kimball gives the results of an elaborate inquiry, in the course of which circulars requesting information as to the cost of mining and reduction of silver ores were sent to " all the mines in the United States known, or believed, to be producing gold and silver."   The general conclusion at which Dr. Kimball arrived is that the mean working cost per ounce of silver is 2s. 1½d., and it is remarkable that it should differ so little from the estimate given in the above table, which was made with limited data at command, and dealt with the whole of the silver production of the world.   (See also Report of the Royal Mint, 1888, pp. 23 & 56.)

CONCLUSION.

The foregoing pages will have shown the student that the adaptation of metals for use is an important part of the metallurgic art, which is by no means limited to the extraction of metals from their ores.   The author considers that in the immediate future the most marked technical advance may be expected not from improvements in smelting operations, but from the study of the properties of metals and alloys as influenced by thermal or mechanical treatment, and by the presence of foreign matter.   It may be urged that such questions should be left to the Physicist and to the Engineer, but the Metallurgist must devote attention to them as their practical solution has to be effected by him, and he alone can appreciate the economic difficulties which present themselves.

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