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[1] 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 more than fifty-five 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.

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

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

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.[1] 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"[2] might well be applied to metallurgy. The library of Leyden contains a papyrus which has been described by M. Reuvens,[3] and which is considered by Kopp[4] 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 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,[5] the greatest of the early chemists (he died in 777), who gives a remarkable account

[1] Rossignol, *Les Métaux de l'Antiquité* (1863).
[2] *Lectures*, by Joseph Black, M.D., vol. i. pp. 11, 12 (Edin. 1803).
[3] Reuvens, *Lettres à M. Letronne* (Leyden, 1830), quoted by Prof. Ferguson in an address to the Glasgow Phil. Soc. (1876), p. 19.
[4] *Beiträge zur Geschichte der Chemie*, 1869.
[5] The works of Geber, translated by R. Russell (1686), pp. 74, 78, 220, 234.

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,[1] 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,[2] 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 10 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 knowledge 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 aeriform body. It was not till nearly a century later (1630) that a French chemist, Jean Rey,[3] 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

[1] *De ortu et causis subterraneorum*, p. 519.
[2] *Pirotechnia* (Vinezia, 1540), translated into French by T. Vincent (Rouen, 1627), p. 41.
[3] *Essais de Jean Rey* (reprinted in Paris, 1777), p. 64.

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.[1] Subsequently, in 1669, John Mayo showed that the increase in weight of calcined metals was due to a "spiritus,"[2] derived from the sun's rays.[3] Nevertheless, Boyle heated lead in a small retort,[4] and attributed the increase in weight, as Lemery also did,[5] 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 Becher, 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).

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

[1] MS. register book of the Royal Society.
[2] *Tractatus quinque Medico-Physici*, p. 25 *et seq.* (Oxonii, 1674.)
[3] Prof. Cohen, *Intrody. Lecture, Yorkshire Coll. of Science*, 1901-2.
[4] Collected works, vol. ii. (1744), p. 395, and vol. iii. p. 347.
[5] *Cours de Chymie* (1675), 2nd English edition (1686), p. 107.

admitted by J. R. Mayer[1] in his memoir on the mechanical theory of heat ; and Odling, discussing the experiments on the oxidation of lead, has pointed out[2] 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,[3] 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 eighteenth 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 lead furnished Ste. Clair-Deville,[4] 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, 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. Subsequently, in conjunction with Troost, he gave certain fixed points, such, for instance, as the boiling-points of cadmium and zinc ; and his

[1] "Bemerkungen über die Kräfte der unbelebten Natur," *Liebig's Ann.*, vol. xlii. (1842), p. 233.
[2] *Proc. Roy. Inst.*, vol. vi. (1871), p. 323.
[3] *Edin. Roy. Soc. Proc.*, vol. v. (1866), p. 328.
[4] "Leçons sur la dissociation," and Wurtz, *Dictionnaire de Chimie*, vol. i. (1868), p. 1174.

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 to his memory will be to work in the directions he has indicated.

Deville's experiments on dissociation have rendered it possible to extend to the groups of atoms in chemical systems the laws which govern the fusion and vaporisation of masses of matter, and this has produced a revolution comparable in its importance to that which followed the discovery of the law of definite proportions, for dissociation has shown us that true causes of chemical change are variations of pressure and of temperature. For instance, oxygen may be prepared on an industrial scale from air by the intervention of oxide of barium heated to a constant temperature of 700°, provided air be admitted to the heated oxide of barium, under a pressure of $1\frac{1}{2}$ atmospheres, while the oxygen, thus absorbed, is evolved if the containing vessel be rendered partially vacuous. It will be evident, therefore, that at a certain critical temperature and pressure the slightest variation of either will destroy the equilibrium of the system and induce chemical change.

It will be clear that the measurement of high temperatures has become a question of much moment, and in this direction remarkable progress has recently been made.

The essential difference in the properties of metals produced by a small quantity of foreign matter 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 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.

It is assumed throughout that the student possesses a certain amount of chemical knowledge, but it will be evident that Metallurgical Chemistry is a special branch of chemical science which does not come within the ordinary sphere of the academic teaching of chemistry. It is often urged that metallurgical

practice depends upon the application of chemical principles which are well taught in every large centre of instruction in this country, but a long series of chemical reactions exist which are of vital importance to the metallurgist, though they are not set forth in any British manual of chemistry, nor are dealt with in courses of purely chemical lectures. It is well to insist upon this point, because purely analytical and laboratory methods are so often given in the belief that they are applicable to processes conducted on a large scale and at high temperatures.

It is urged that technical instruction should be kept apart from scientific education, which consists in preparing students to apply the results of past experience in dealing with entirely new sets of conditions, but it can be shown that there is a whole side of metallurgical teaching which is truly educational, and leads students to acquire the habit of scientific thought as surely as the investigation of any other branch of knowledge.

It is, in fact, hardly possible, in a course of theoretical chemistry, to devote much attention to specific cases of industrial practice in which reactions are incomplete because they are limited by the presence of bodies that cannot be directly eliminated from the chemical system. Take, for instance, the long series of reactions studied by Plattner, who published the results of his investigations in his celebrated treatise *Die Metallurgische Röstprozesse*, Freiberg, 1856. A complex sulphide, of which copper is the main metallic constituent, contains some fifty ounces of silver to the ton, and the problem may be supposed, for the present, to be limited to the extraction of the precious metal from the mass in which it is hidden. The student deriving his knowledge from an excellent modern chemical treatise would find the case thus stated :—

"Ziervogel's process depends upon the fact that when argentiferous copper pyrites is roasted, the copper and iron sulphides are converted into insoluble oxides, whilst the silver is converted into a soluble sulphate which is dissolved out by lixiviating the roasted ore with hot water, the silver being readily precipitated from this solution in the metallic state."

It is certain that if an observant, chemically trained student visited a silver extraction works, and possessed sufficient analytical skill to enable him to secure evidence as to the changes that occur, he would find a set of facts which his training had not enabled him to predict, and he would establish the existence of a set of reactions to the nature of which his chemical reading had hardly given him a clue. The process to be considered is a simple one, but it is typical, and applies to a considerable proportion of the silver annually obtained from cupriferous compounds. He would be confronted with a ton or more of finely divided material spread in a thin layer over the bed of a reverberatory furnace. Suppose the material is what is known

as a complex "regulus" as imported into Swansea or produced
at Freiberg, to which are added rich native sulphides. The
mixture then consists of sulphides mainly of iron and copper,
with some sulphide of lead, and contains fifty or sixty ounces of
silver to the ton, and a few grains of gold. It may also contain
small quantities of arsenic and antimony as arsenides, antimonides,
and sulpho-salts, usually with copper as a base.

The temperature of the furnace in which the operation is to be
performed is gradually raised, the atmosphere being an oxidising
one. The first effect of the elevation of the temperature is to
distil off sulphur, reducing the sulphides to a lower stage of
sulphurisation. This sulphur burns in the furnace atmosphere
to sulphurous anhydride (SO_2), and coming in contact with the
material undergoing oxidation is converted into sulphuric
anhydride (SO_3). It should be noted that the material of the
brickwork does not intervene in the reactions, except by its
presence as a hot porous mass, but its influence is, nevertheless,
considerable. The roasting of these sulphides presents a good
case for the study of chemical equilibrium. As soon as the
sulphurous anhydride reaches a certain tension the oxidation of
the sulphide is arrested, even though an excess of oxygen be
present, and the oxidation is not resumed until the action of the
draught changes the conditions of the atmosphere of the furnace,
when the lower sulphides remaining are slowly oxidised, the
copper sulphide being converted into copper sulphate mainly by
the intervention of the sulphuric anhydride formed as indicated.
Probably by far the greater part of the iron sulphide only
becomes sulphate for a very brief period, being decomposed into
the oxides of iron, mainly ferric oxide, the sulphur passing off.
Any silver sulphide that is present would have been converted
into metallic silver at the outset were it not for the simultaneous
presence of other sulphides, notably those of copper and of iron,
which enables the silver sulphide to become converted into
sulphate. The lead sulphide is also converted into sulphate at
this low temperature. The heat is now raised still further with
a view to split up the sulphate of copper, the decomposition of
which leaves oxide of copper. If, as in this case, the bases are
weak, the sulphuric anhydride escapes mainly as such; but when
the sulphates of stronger bases are decomposed the sulphuric
anhydride is to a great extent decomposed into a mixture of
sulphurous anhydride and oxygen. The sulphuric anhydride,
resulting from the decomposition of this copper sulphate, converts
the silver into sulphate, and maintains it as such, just as, in turn,
at a lower temperature, the copper itself had been maintained in
the form of sulphate by the sulphuric anhydride eliminated from
the iron sulphate. When only a little of the copper sulphate
remains undecomposed, the silver sulphate begins to split up,
and the furnace charge must therefore be immediately withdrawn,

or the whole of the silver sulphate would be converted into
metallic silver, partly by the direct action of heat alone, and
partly by reactions such as those shown in the following
equations :—

$$Ag_2SO_4 + 4Fe_3O_4 = 2Ag + 6Fe_2O_3 + SO_2$$
$$Ag_2SO_4 + Cu_2O = 2Ag + CuSO_4 + CuO.$$
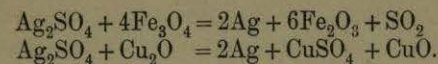
If the charge were not withdrawn, the silver would thus be
effectually removed from the solvent action of water, and the
smelter's efforts would have failed entirely. The charge still
contains lead sulphate, which cannot be completely decomposed
at any temperature attainable in the roasting furnace, except in
the presence of silica, and it is well to leave it where it is if the
residue has subsequently to be smelted with a view to the
extraction of the gold. The elimination of arsenic and antimony
gives rise to problems of much interest, and again confronts the
smelter with a case of chemical equilibrium. For the sake of
brevity it will be well for the present to limit the consideration
to the removal of antimony, which may be supposed to be present
as sulphide. Some sulphide of antimony is distilled off, but this
is not its only mode of escape. An attempt to remove antimony
by rapid oxidation would be attended with the danger of
converting it into insoluble antimoniates of the metals present in
the charge. In the early stages of the roasting it is therefore
necessary to employ a very low temperature, and the presence of
steam is found to be useful as a source of hydrogen, which
removes sulphur as hydrogen sulphide, the gas being freely
evolved. The reaction $Sb_2S_3 + 3H_2 = 3H_2S + 2Sb$ between hydro-
gen and sulphide of antimony is, however, endothermic, and
could not, therefore, take place without the aid which is afforded
by external heat. The facts appear to be as follows: sulphide of
antimony, when heated, dissociates, and the tension of the
sulphur vapour would produce a state of equilibrium if the
sulphur thus liberated were not seized by the hydrogen and
removed from the system. The equilibrium is thus destroyed
and fresh sulphide is dissociated. The general result being that
the equilibrium of the system is alternately restored and
destroyed until the sulphide is all decomposed. The antimony
combines with oxygen and escapes as volatile oxide, as does also
the arsenic, a portion of which is volatilised as sulphide.

The main object of the process which has been considered is
the formation of soluble sulphate of silver. If arsenic and
antimony have not been eliminated, their presence at the end of
the operation will be specially inconvenient, as they give rise to
the formation of arseniate and antimoniate of silver, insoluble in
water, which may necessitate the treatment of the residues by an
entirely different process from that which has hitherto been
considered.

It will have been evident that effecting this series of changes demands the exercise of the utmost skill, care, and patience. The operations beginning at a dull red heat, or a temperature of some 500°, are completed at 700°, within a range, that is, of 200°. Judicious stirring has been necessary to prevent the formation of crusts of sulphates, which would impede the reactions, and, as has been shown, an undue elevation of temperature within a very limited range would, at any stage, have been fatal to the success of the operation. It is difficult to appreciate too highly the delicacy of sight and touch which enables an operator to judge by the aid of rough tests, but mainly from the tint of the streak revealed when the mass is rabbled, whether any particular stage has or has not been reached, and it will be obvious that the requisite skill is acquired solely by observation and experiment. The technical instructor may impart information as to the routine to be followed, and the appearances to be observed, but scientific knowledge of a high order can alone enable the operator to contend with the disturbing influences introduced by the presence of unexpected elements or by untoward variations in temperature. In the training of a metallurgist it is impossible to separate education from instruction, and the above description of a very ordinary operation will show the intimate relations between science and practice which are characteristic of metallurgical operations. Practice is dependent on science for its advancement, but scientific workers too often hesitate to attack metallurgical problems, and to devote the resources of modern investigation to their solution, because they are not aware of the great interest of the physical and chemical problems which are connected with many very simple metallurgical processes, especially with those that are conducted at high temperatures.

Proceeding yet one step further, suppose that the copper smelter takes possession of the residual mass, consisting mainly of oxide of copper, he would smelt it with fresh sulphide ores and obtain, as a slag from the earthy matters of the ore, a ferrous silicate containing some small proportion of copper. The displacement of the copper from this silicate may be effected by fusing it with sulphide of iron, a fusible sulphide of iron and copper being formed which readily separates from the slag. By this reaction some thousands of tons of copper are added to the world's annual production. Proceeding a step further, suppose the smelter to have reduced his copper to the metallic state. If arsenic had been originally present in the ore, and had not been eliminated entirely in the roasting, extraordinary difficulties would be met with in the later stages of the process, in extracting small quantities of arsenic which resist the smelter's efforts. Copper, moreover, containing above 1 per cent. of arsenic cannot be "overpoled," as the presence of arsenic hinders the action of gases on the copper. The amount of arsenic which

the copper smelter has to remove may vary from mere traces up to 1 per cent., and if the copper is destined for the use of the electrical engineer, he will insist on its being as pure as possible, for the presence of traces of arsenic would materially increase the electrical resistance of the copper, and would be fatal to its use in submarine telegraphy. If, on the other hand, the copper is intended for the maker of locomotive fire-boxes, he will encourage the retention of small quantities of arsenic, as it is found to actually increase the endurance of the copper up to 0·4 per cent., and the smelter will in such a case have no inducement to use the special methods for the removal of arsenic with which he is familiar. It may all seem simple enough, but the modern process of copper smelting has been laboriously built up, and has a long and interesting pedigree which may be traced to at least the eighth century, when Geber described the regulus "coarse metal" as being "black mixed with livid," and our familiar "blue metal" as being "of a most clean and pleasant colour," and indicated the reason for the difference.

It must not be supposed, even when commercially pure copper lies on the furnace bed, ready to be transferred to moulds, that its turbulent career of reactions is over. It might be thought that the few tenths per cent. of impurity, dissolved oxide, and occluded gas are so far attenuated by distribution that their interactions must be insignificant. This is far from being the case. The bath of metal is seething from its reactions until the copper is solid, and then polymerisation begins. There may not be a sharply defined critical range of temperature within which the metal can alone be successfully worked, which varies, as regards its starting-point, with the kind of impurity present, as is the case with steel; but evidence of molecular change in the solid metal is afforded by the pyrometric curves of cooling, to which subsequent reference will be made in this work, and by the singular behaviour, as regards electrical resistance, of various samples of copper, in which chemical analysis hardly reveals a difference.

The above description of a very ordinary set of operations will serve to indicate the general nature of the problems with which the metallurgist has to deal.