CHAPTER XI.

THERMO-CHEMISTRY.

THE great importance of thermo-chemistry in relation to metallurgy is so evident that it is absolutely necessary for the student to have such knowledge as will enable him to consult with advantage the original memoirs of Andrews, Berthelot, Julius Thomsen, Nernst, and others. In this country comparatively little attention has been devoted to thermo-chemistry in relation to metallurgical teaching, but in France admirable work has been done, notably by Ditte,[1] in bringing within the reach of students the results of the labours of Berthelot and of St Claire Deville.

Ostwald reminds us that chemical energy is the least known of all the various forms of energy, as we can measure neither it nor any of its factors directly; the only way of obtaining information regarding it is to transform it into another species of energy. It passes most easily and completely into heat, and the branch of science which treats of the measurement of chemical energy in *thermal units* is called thermo-chemistry. The quantities of heat evolved or absorbed measure the decrease or increase of chemical energy in so far as other energy is not involved in the process. The ordinary equation of the chemist $C + O = CO$ is far from representing the whole truth, for in fact C unites with O to form an entirely new body (CO), which may be liquid, solid, or gaseous, but it never has the same potential energy as was possessed by the bodies from which it was formed. The equation should therefore be $C + O = CO + q$ *heat units*.

It must be remembered that only the final result of a chemical process can be measured. The calorimeter is the instrument used in thermo-chemical measurement. First as regards the "calorie" employed. The student will remember that the calorific power of carbon in the form of charcoal as determined by the aid of the calorimeter is given on p. 248 as being 8080, that is, 8080 units (grammes) of water will be heated from 0° to 1° by the complete combustion of 1 unit (1 gramme) of carbon. The calorie hitherto employed in this book is, however, too small for use in thermo-chemical measurement. The heat required to raise 1 kilogramme of water is the unit employed in this chapter. It must be borne in mind that *the quantities of energy and heat given in thermal equations refer to such quantities of the substances as amount to their formula weight in grammes.*

Hence the thermal equivalent of carbon burnt to carbonic anhydride is 97. The calorific power of charcoal being 8080, it may be well to show how the number 97 is deduced. In the equation $C + 2O = CO_2$, 12 grammes of carbon (its equivalent weight) are used. 8080 represents the unit of carbon, hence $8080 \times 12 = 96,960$; but the thermo-chemist, as above stated, employs 1000 grammes as the unit of water instead of 1 gramme, and the sum becomes $\frac{96,960}{1000} = 96 \cdot 960$, or in round numbers, 97.

The various forms of calorimeter are fully described in the works to which reference is given at the end of this chapter. The form of the calorimeter is modified to suit the particular conditions of the experiment, but the limits of this book will only permit a brief reference to the methods by which the calorimetric determinations given in the accompanying table were made. (See Folding Plate placed at the end of this chapter.)

The calorimeter employed by Berthelot is a thin cylindrical vessel of platinum, of about 600 c.c. capacity. If, for instance, the problem is to determine the heat evolved by the reaction between two liquids, these would be placed in flasks of very thin glass of about 300 c.c. capacity, provided with short necks, marked with the calibration line at the base of the neck. These receptacles are allowed to stand near the calorimeter until they acquire a constant temperature, which is carefully measured. The difference in temperature between their contents should not exceed $\frac{1}{10}$th of a degree. The contents of one flask would then be poured into the inner chamber of the calorimeter and rapidly stirred with the thermometer, the temperature is then noted, and the contents of the second flask are added to the liquid already in the calorimeter, and careful thermometric observation is made to ascertain whether the admixture has been attended with a lowering or an elevation of temperature. The above description has merely been given to indicate the general nature of the method, but treatises on calorimetry must be consulted with reference to the precautions to be observed when solids and liquids react, or when the reaction between gases and liquids has to be studied.

Bomb Calorimeter.—The instrument of which a description will now be given is the one in use at the Royal School of Mines. It often happens that the metallurgist has to deal with reactions which are attended with vivid combustion—the reaction, for instance, between solids and gases—the product of which is

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[1] *Leçons sur les Métaux*, Paris, 1891.

gaseous, and in such cases closed combustion-chambers are employed, and the heat is not measured directly by a thermometer, but is transferred, through the walls of the combustion-chamber, to water contained in a receptacle in which the combustion-chamber is placed. There are various forms of such combustion-chambers, but the one most serviceable to the metallurgist is the modification of Berthelot's bomb calorimeter devised by M. Mahler, and the following description shows the nature of the appliance and the method of using it. The apparatus consists essentially of a shell or bomb B (figs. 181 and 182), forged out of high-class mild steel, having a capacity of 654 c.c. (say 40 cubic inches), and weighing about 4 kilogrammes (or $8\frac{4}{5}$ lbs.) with its accessories. The shell B, which is 8 millimetres ($\frac{5}{16}$-inch) thick, is nickelised on the outside, and enamelled inside, so as to withstand the corrosive and oxidising action of combustion, but the coating of enamel does not sensibly interfere with the transmission of heat. The shell is closed by a screw cap, tightened on to a lead ring; and the cap is provided with a conical screw cock (*x*, fig. 182) for the introduction of oxygen. A platinum rod, attached to the cap, holds the capsule C, on which is placed the fuel to be tested, and the latter is ignited by being brought in contact with a spiral of iron or platinum wire F, heated by an electric current. It may be well to assume that the material is either carbon or hydrocarbon, which is to be burnt in oxygen.

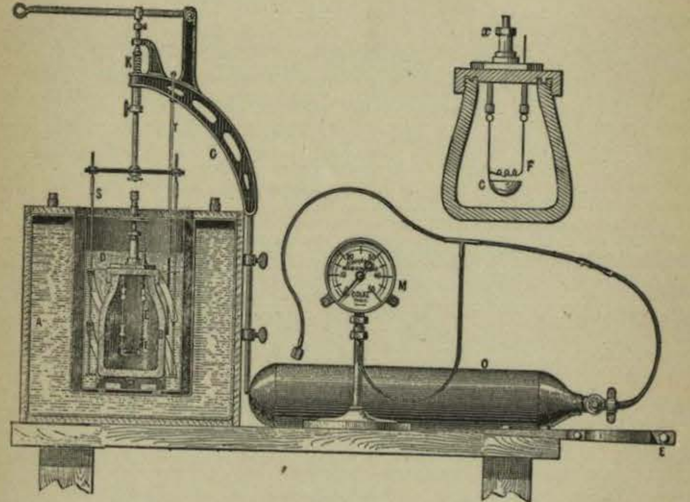

FIG. 181. FIG. 182.

The sample to be tested is introduced into the steel bomb, which is then closed, and charged with oxygen under pressure, and the whole apparatus is immersed in the water of the calorimeter. If the fuel be then ignited by the aid of a wire heated to redness by an electric current, it will burn completely and almost instantaneously, the water formed by the combustion of the hydrogen being condensed on the inside surface of the bomb. The heat disengaged by the explosion is transmitted to the water of the calorimeter, and may easily be estimated. The pressure of oxygen is determined by the condition that combustion must always be complete, and that an excess of oxygen is indispensable.

For testing a solid or liquid fuel, a gramme of the substance is placed in the capsule and the cap is screwed down tightly. Oxygen, under pressure, is allowed to enter by the cock, until the manometer M shows that a suitable pressure is obtained, generally from 20 to 25 atmospheres. Care must be taken, especially with coal in a finely divided state, to prevent the sample from being displaced, in which case there would be danger of part escaping combustion, and for this reason the sample is generally compressed into a pellet. The shell thus prepared is placed in the calorimeter D, which contains a known quantity of water, when the thermometer T is adjusted, and the helicoidal agitator S set to work for a few minutes to bring the whole apparatus to the same temperature, when all is ready for the observation. In order to prevent irregular loss of heat by the calorimeter D, it is placed upon three small pieces of cork within a large, metallic, double vessel of water A, covered externally with a thick layer of felt and provided with a thermometer. This vessel serves also as a support for the bracket G, from which the stirrer S is suspended, and to which the handle and spring K, for working the stirrer, are fixed. O is the vessel containing the supply of oxygen, and E is a clamp in which the bomb may be fixed and prepared for the experiment.

The temperature is noted every minute for four or five minutes, and then the charge is fired by electricity. Although the combustion is almost instantaneous, the transmission of heat to the water requires a few minutes. The temperature is noted, first half a minute, and then one minute, after the ignition, and afterwards every minute until the thermometer begins to fall, which shows that the maximum temperature has been reached, after which the observations are continued for about five minutes more. The principal elements of the calculation are thus afforded, and especially the one correction necessary, which is due to the loss of heat sustained by the calorimeter before reaching the maximum temperature. The agitator S must be worked regularly during the observation, at the conclusion of which the shell is removed from the calorimeter, the cock is opened, and then the shell itself. The inside of the shell is washed with a little distilled water, so as to collect the acid liquid formed during the explosion. The amount of acid is determined by titration.

It is advisable, when experimenting on substances poor in hydrogen, like coke, and consequently incapable of furnishing by combustion sufficient water to form nitric acid, to put a little water at the bottom of the bomb.

For determining the calorific value of a gas of constant volume, a vacuum is made in the bomb, the exact cubic contents of which is known. The bomb is filled with the gas; a fresh vacuum is produced by exhaustion until the pressure is only a few millimetres of mercury, and the bomb is filled with the gas at the atmospheric pressure and temperature of the laboratory, and the operation is completed in the same manner as with solid and liquid fuels.

The significance of the thermal data given in the table facing page 404, which has been obtained by one or other of the calorimetric methods, will now be considered.

It is assumed that the student is familiar with the theory of the granular structure of matter, and with the molecular theory of gases. He must also know that the atoms of every element have valencies of their own, and, further, that there may be distinct movements and reactions between the atoms arranged in a molecule. The question naturally arises—Why do certain reactions take place, while others do not? Berthelot held "that every chemical change which can be accomplished without the aid of a preliminary action or the addition of energy from without the system necessarily occurs if it is accompanied by a disengagement of heat." Viewing a reaction generally, he held that if external energy is not imparted to a system, the tendency will be to form that compound the production of which is accompanied by the evolution of the maximum quantity of heat. It is true that changes resulting in a positive calorific effect occur more often than those accompanied by negative ones, but it is well known that, of two or more possible reactions, the one which is accompanied by the evolution of most heat is not always the one which actually occurs. Decompositions accompanied by negative calorific effects are more frequent at high than at low temperatures. In this connection it must be remembered that heat is not the only form in which energy can be lost by a changing chemical system, as the change may give rise to electrical phenomena. A redistribution of atoms in the molecule may take place; and although the energy is not lost to the system, it may not be possible for it to directly appear as heat. In some cases the only outward sign of change is the passage of an element from a normal to an allotropic modification.

Van't Hoff[1] has pointed out that modern chemical theory had two weak points: it expressed itself neither as to the relative

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[1] *La Chimie dans l'espace* (original edition).

position of the atoms nor as to their movement. It is known that many active organic bodies lose their activity by being heated; and this fact, which is recognised as being of much importance in organic chemistry, can hardly be without significant relations in the inorganic reactions with which the metallurgist has to deal.

The atoms in the molecule have, as has already been stated, movements of their own; and, as Lother Meyer has urged, "if these movements of the atoms are to be considered, then we must investigate what part in the observed calorific effects is to be attributed to them, and how much is due to the potential energy of the hypothetical force of affinity. It is doubtful, however, whether the atoms do possess powers of attraction, and consequently potential energy; it is more probable that the whole of the kinetic energy the atoms give out is already their own as such." But suppose atoms do possess "potential energy" of their own to which they owe their "affinities," then when the system undergoes change which satisfies the affinities of the atoms without the addition of energy from an external source, this change must be attended by a "locking up" of energy which must have been kinetic, and consequently there is less kinetic energy available in the system to appear as heat, so that, although in a particular reaction but little heat may be evolved, there may nevertheless be a considerable degradation of chemical energy.

In chemical operations generally, and especially in metallurgical ones, there is another consideration of much importance. If two compound bodies react one upon the other, the presence of the products of the reaction will bring it to an end, and a state of equilibrium will be established, so that both the original and the newly formed substances are present in definite quantities that remain the same so long as the conditions of temperature and pressure do not undergo further change. If this is the case, the reaction can only be resumed if the products are eliminated from the system as fast as they are formed. In "wet" chemical processes this removal is effected by the precipitation of a product, or by its evolution as a gas. In metallurgical operations conducted by the aid of fire the products are often gaseous, and are swept away by the draught of the furnace. In other cases the fusion of the products enables this separation to be effected, as the products either flow away or arrange themselves in layers under the influence of gravity.

Again, in very many metallurgical processes, reactions are rendered incomplete by the limitations imposed by the presence of bodies which cannot be speedily eliminated from the system, and the result may be to greatly retard the completion of an operation. The time has come when the principles of dynamic chemistry must be applied to the study of metallurgical problems if they are to be correctly understood, and it is, moreover, necessary to remember the part played by the surface separating the different aggregates in contact with one another. When, for instance, a reaction has to take place accompanied by the evolution of gas, there must be space into which the gas can pass, and the rate at which change takes place will obviously depend on the state of division of the mass.

One of the most remarkable points in the whole range of chemistry is the action engendered between two elements capable of reacting, by the presence of a third body. It may be that merely a trace of a third body is necessary to induce reaction, or to profoundly modify the structure of a mass. H. Le Chatelier and Mouret have pointed out that in certain cases it is inaccurate to say that the third body causes the reaction to take place, because, after it has destroyed the intermolecular resistances which prevented the reaction taking place, the third body ceases to intervene. This is apparently the case when platinum sponge effects the union of oxygen and hydrogen, or, conversely, when very hot platinum splits up water vapour into its constituent gases. Future investigation will, it is to be hoped, show whether the platinum does not exert some direct action in such cases. We can no longer neglect the study of such questions from the point of view of their practical application. The manufacture of red-lead presents a case in point. In "drossing" molten lead, the oxidation of the lead is greatly promoted by the presence of a trace of antimony, and, conversely, in the separation of silver from molten lead by the aid of zinc, H. Roessler and Endelmann have shown that aluminium has a remarkable effect in protecting the zinc from loss by oxidation, and, further, the presence of one-thousandth part of aluminium in the zinc is sufficient to exert this protecting action on that metal.

An examination of the following thermal equations and the remarks which precede them will show how frequently, in conducting metallurgical operations, demands are made upon energy, in the form of heat, from a source external to the particular "chemical system" which is undergoing change. It has been urged that if it is the energy of the external heat which dissociates a compound, and enables a reaction to take place, then chemical equilibrium such as is revealed by experiments on dissociation is really equilibrium between the energies of affinity and of heat. It follows, as M. Duhem[1] has pointed out, that the third law of thermo-chemistry is greatly weakened, if not rendered absurd, by the necessity for bringing external heat to a chemical system. This law states that "Every chemical change which is accomplished without the intervention of external energy tends towards the production of a body which evolves the most heat." If it be necessary to import external heat, the law admits of being reduced

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[1] Duhem, *Introduction à la Méchanique Chimique*, Paris, 1893, p. 79.

to the useless expression, "Every reaction which does not absorb heat evolves it."

But the more ardent members of the school of Deville, which rendered such splendid services to metallurgy and to physics, did not advocate the employment of the mechanism of atoms and molecules in dealing with chemical problems, but simply accumulated evidence as to the physical circumstances under which chemical combination and dissociation take place. They did not even insist upon the view that matter is minutely granular, but, in all cases of change of state, made calculations on the basis of work done, viewing "internal energy" as a quantity which should reappear when the system returns to the initial state; and they viewed chemical combination and dissociation as belonging to the same class of phenomena as solidification, fusion, condensation, and evaporation. As yet, the study of chemical equilibrium is not sufficiently advanced to afford a basis for building a theory of metallurgy; and if there is evidence of the existence of atoms and molecules, it is not advisable to ignore their existence when dealing with metallurgical problems.

There is one important theorem developed by M. Moutier which must not be overlooked. He has shown that under a given pressure there is only one temperature at which transformations are reversible. If the conditions of equilibrium are such that the transformation occurs below the critical temperature, it is attended with evolution of heat, while, on the other hand, if the transformation occurs above this temperature, it is attended with absorption of heat. Take the case of a mixture of carbonic anhydride, lime, and calcium carbonate, exposed to such a pressure and temperature that the system is in equilibrium. It is stable; more carbonic anhydride cannot combine with the lime, nor can fresh calcium carbonate be decomposed. But destroy the equilibrium by an elevation of temperature, carbonic anhydride and lime will be the result, but the reaction is attended with absorption of heat. On the other hand, destroy the equilibrium by lowering the temperature, lime and carbonic anhydride will combine, and the reaction will be attended with an evolution of heat. According to this law, the occurrence of a definite chemical change will not be determined by the fact that much or little work would be done (law of maximum work), but by the relation between the temperature and pressure to which the substances are subjected. This and other theorems of Moutier apply, however, only to reversible reactions, and the student should be warned that the theorems as to the conditions of chemical equilibrium lead in many cases to the expectation of reactions or transformations which are not found to occur exactly as anticipated. Thus reactions occur suddenly at an abnormally high temperature, and with explosive violence, whilst the theory of chemical equilibrium indicates that reactions should tend to check themselves, and that, therefore, there should be no tendency to explosion. Other cases are presented by the phenomena of surfusion, supersaturation, and delayed ebullition. It would thus appear that a position of *unstable* or *false* equilibrium may be established; but if the equilibrium be destroyed, it may be by a further rise in temperature, by the presence of a minute trace of impurity, or even by a mechanical shock, the change is propagated rapidly through the mass.

Thermo-chemists are reproached for having neglected the study of reactions at high temperature, for the measurement of which, until recently, no simple methods were available, but now, as has been shown in these pages, that high temperatures can be measured with facility, it is to be hoped this reproach may be removed. When this is done, it will be interesting to compare the new thermal equations representing reactions at high temperatures with those now in use. Such an investigation will be very tedious, but there are many reactions at high temperatures the study of which can be undertaken, though they present great difficulty.

The student may fairly ask why a series of equations are presented which are confessedly based on numbers that were obtained from experiments conducted at temperatures differing from those employed in practice. The answer is that these equations do enable him to know the quantity of heat that will be required to obtain a certain result, and also indicate the probable temperature at which an operation can be effected. A reaction, the final result of which is represented by a minus number which is large when considered in relation to the quantity of material involved, generally means that a high temperature is necessary to effect it, but much will depend upon the melting-points of the members of the particular chemical system.

A reaction between sulphide of lead and sulphate of lead is attended with a large absorption of heat (– 180 large units), the mass involved being considerable. The reduction of ferric oxide by carbon is attended with an absorption of heat (– 112 large units). Both these reactions require very high temperatures; the mass in the latter case is relatively small, but the melting-point of the reduced iron is high.

The ordinary atomic equation

$$Fe_2O_3 + 3C = 2Fe + 3CO$$

shows that the reduction of one ton of ferric oxide should be effected by four and a half hundredweights of carbon, leaving the CO produced to reduce still more ferric oxide. The thermal equation, with its very large minus number (– 122), prepares the student for the fact, well known to the blast-furnace manager, that the reduction of one ton of ferric oxide in accordance with the above equation is a very difficult operation, which would require a large amount of fuel; and, moreover, the student is led to expect that the reaction represented by the above equation is evidently not the one that does happen, for he will see that the reaction

$$Fe_2O_3 + 3CO = 2Fe + 3CO_2,$$

which is accompanied by a disengagement of heat (+4·6), is probably the main reaction that takes place in the blast-furnace.

Whenever an equation shows that a reaction is accompanied by the evolution of much heat, it is safe to conclude that it will take place either at a low temperature or will be effected with ease.

Thermal Equations.—In using these, the student must bear in mind that all compounds that have to be decomposed will absorb as much heat during decomposition as they evolved while they were being formed, so that it is necessary to take the algebraic sum of each side of the equation, and to algebraically subtract the total heat required to effect all the decompositions from the total heat evolved from all the combinations. The difference will be the total quantity of heat evolved or absorbed, according to its particular sign. If the answer has a plus sign, then there is an evolution of heat; if a minus one, then there has been absorption of heat. For example, take the following equation:—

$$2PbSO_4 + PbS = 2PbO + Pb + 3SO_2.$$

Here two molecules of lead sulphate and one molecule of lead sulphide have to be decomposed, whilst two molecules of lead oxide and three molecules of sulphurous anhydride are formed. Then

Total Heat required for Decomposition.		Total Heat evolved by Combination.	
$PbSO_4$	$2 \times 216·2 = +432·4$	PbO	$2 \times 51·0 = 102$
PbS	$1 \times 17·8 = +17·8$	SO_2	$3 \times 71 = 213$
	$+450·2$		$+315$

Total heat evolved by the members of the system = + 315·0

Total heat originally evolved when the members of the old system were formed . . . = + 450·2

Difference, or the quantity of heat as would be measured by the calorimeter . . . = – 135·2

It will be seen that this reaction is accompanied by an absorption of heat, and is thus endothermic.

But it must be remembered that this calculation, to be rigorously accurate, ought to be corrected to the exact temperature at which the reaction occurs. The folding plate gives the numbers obtained by heating up the chemical system to the temperature at which reaction occurs, then allowing the reaction to take place, and subsequently cooling the system to the initial temperature. Unfortunately, sufficient data as to the specific heats of various bodies at high temperatures have not as yet been accumulated to enable this to be done, but the correction to be made is as follows :—

Let M_1, M_2, etc., be the respective masses of the reacting bodies,
M_a, M_b, etc., be the respective masses of the products of the reaction,
S_1, S_2, etc., S_a, S_b, etc., be the mean specific heats of the different masses, over a range of the temperature, t, of the water in the calorimeter to the temperature, T, of reaction,
$T =$ the "temperature of reaction," or that temperature at which the reaction can proceed,
$N =$ number of heat units as measured under the standard conditions in the calorimeter,
and let C be the true value required.

Then $C = N + (T - t)\,[(M_1S_1 + M_2S_2 + \text{etc.}) - (M_aS_a + M_bS_b + \text{etc.})]$.

In turning to the modern aspects of metallurgical practice, we shall see that the whole range of the metallurgist's field of study is changing. It is no longer possible for him to devise a series of operations on the evidence afforded by a set of equations which indicate the completion of an operation; he has, as has already been suggested, to consider the complicated problems which have been introduced into chemistry from the sciences of physics and mechanics. He has, in fact, no longer to deal merely with atoms and molecules, but with the influence of mass. If metallurgists are to advance their industrial practice, they must think in calories, and thus supplement the ordinary atomic "tools of thought." They will then be able to suggest what reactions can, under given conditions, take place; to indicate those which will be completed; and to avoid those that are impracticable.

In order that the application of the preceding observations may be evident, it will be well to consider briefly the two main operations upon which metallurgical practice is based.

These are (1) the reduction of oxides by carbon and by hydrogen (see *ante*, p. 315), and (2) the oxidisation of metals by an oxidising agent, usually air (*ante*, p. 312).

First, as regards the reducing action of carbon, it has already been shown that the heat of combination of carbon and oxygen into carbonic anhydride, CO_2, is 97 *large* calories, but in the blast-furnace, in the presence of excess of carbon, carbonic anhydride is converted into the main reducing agent, carbonic oxide, by the very well-known reaction $CO_2 + C = 2CO$.

The carbonic anhydride, in combining with carbon to form carbonic oxide, becomes doubled in volume. If, however, the equation be completed by the addition of the thermal equivalents

$$\begin{array}{lll} CO_2 + C & = & 2CO \\ 97 & & 29 \times 2 = -39, \end{array}$$

it will be seen that this reaction—one of the fundamental ones in the whole range of metallurgy—is really accompanied by an absorption of heat; that is, it is **endothermic**, and would, by Berthelot's law, be impossible if heat external to the chemical system were not available. In the blast-furnace there is such external heat, which acts in two ways: (1) by "depolymerising"—that is, simplifying the atomic constitution of the carbon, which can then combine with the oxygen of the CO_2, with evolution of more heat than from carbon in its normal condition; or (2) by dissociating the carbonic anhydride, thus setting oxygen free which is in a specially favourable condition to combine with the carbon, and so form the main reducing agent, carbonic oxide. In the case of the reduction of iron, the reaction

$$\begin{array}{lllll} Fe_2O_3 & + & 3CO & = & 2Fe + 3CO_2 \\ 199{\cdot}4 & & 3 \times 29 & & \quad 3 \times 97 = +4{\cdot}6 \end{array}$$

is **exothermic**, that is, attended by evolution of heat, but there is another reaction in which solid carbon plays a part,

$$\begin{array}{llll} 2Fe_2O_3 & + & 3C = & 4Fe + 3CO_2 \\ 2 \times 199{\cdot}4 & & & \quad 3 \times 97 = -107{\cdot}8. \end{array}$$

This is strongly endothermic; how, then, can the reduction of oxide of iron by the occurrence of this reaction be explained? The calorific power of carbon varies with its mode of aggregation; in the diamond form it evolves 94 calories in burning to CO_2, while the amorphous variety yields 97 calories. It may be the heat of the furnace depolymerises the carbon; and if it is brought to such a molecular condition that the heat of formation of carbonic anhydride from it is 117 instead of 97, then the endothermic equation would become an exothermic one. This is not at all an extravagant supposition, for it has been estimated that if carbon could be burnt as gaseous carbon, the heat of formation of carbonic anhydride would be no less that 136·0. We have, moreover, no knowledge, as yet, of the molecular form of the liberated iron. There is, however, another point to be considered: metallic iron will, as is well known, decompose carbonic anhydride, becoming oxidised itself, and forming carbonic oxide. The equation is

$$\begin{array}{lll} Fe + CO_2 & = & FeO + CO \\ \quad\;\; 97 & & 66{\cdot}4 \quad 29 = -1{\cdot}6. \end{array}$$

It will be seen, on comparing this with the last equation but one, that the amounts of heat are very nearly balanced, + 4·6 in the one case and $-1·6$ in the other; and when this is the case, the inverse reaction may very readily be brought about by comparatively slight variations in the external conditions.

Two interesting cases may be borrowed from the metallurgy of zinc and of lead respectively. The reaction

$$\begin{array}{llll} 2ZnO + C = 2Zn + CO_2 & & & \\ 2 \times 86·4 & & 97 = -75·8 & \end{array}$$

occurs in the presence of excess of carbon, which splits up the carbonic anhydride formed; but it is strongly endothermic, as is also the reaction $ZnO + CO = Zn + CO_2 = -18·4$: the latter is, however, less endothermic than the former. It is nevertheless the fact that when zinc oxide and carbon are introduced into a retort which is strongly heated, zinc is reduced in abundance (this is the main method adopted in the metallurgy of zinc), carbonic anhydride together with some carbonic oxide being the result. How is this reduction to be explained? Possibly the carbon, under the influence of external heat, loses its condensed form and assumes one analogous to that in which carbon exists in carbonic oxide, so that during the passage from the system $ZnO + C$ to $CO + Zn$ all the heat is absorbed. The part played by the external heat is twofold: it furnishes the energy necessary to depolymerise the carbon, it may also modify the specific heats and heats of formation of the bodies in presence of each other. Dissociation also plays an important part (*see ante*, p. 393).

It will be evident that of the two reactions given above, the one in which carbonic oxide and oxide of zinc react is endothermic ($-18·4$), but less so than that in virtue of which carbon acts on the zinc oxide ($-75·8$). The passage from one set of reactions to the other may be effected by the presence of even a minute quantity of air entangled in the mixture of ore and carbon introduced into the retort. First, the oxygen in the air may form with the carbon some carbonic anhydride, and then some carbonic oxide, which reacts on the oxide of zinc. The carbonic anhydride, CO_2, which is the product of this reaction, is again converted by the excess of carbon present into carbonic oxide. The carbonic anhydride yields double its volume of carbonic oxide; hence the accumulation of carbonic oxide is very rapidly effected, even though its production originated in only a "trace" of air, an important factor in the mechanism of reduction.

A state of equilibrium between the zinc oxide and carbonic anhydride does not become established, because carbonic anhydride is dissociated at the high temperature which exists.

Oxide of lead heated with carbon gives only carbonic anhydride; in fact, the reaction $2PbO + C = 2Pb + CO_2$ is so slightly endothermic that but little external aid is needed to change the conditions and render the reaction exothermic.

With regard to endothermic reactions generally, Victor Meyer gives a word of warning. He says[1]: "Decompositions accompanied by negative calorific effects are more frequent at high than at low temperatures. This fact is usually expressed by saying that the heat represents the work necessary for the decomposition of the compound, or yields the kinetic energy required, which in the decomposition is converted into potential energy. A fundamental difference between decompositions requiring a red heat and associated with a negative calorific effect, and those taking place at the ordinary temperature, does not exist; for in both cases the particles of the materials possess kinetic energy, a part of which, with consequent lowering of the temperature, is utilised in bringing about the decomposition. It is therefore at least inconsistent to regard decompositions of this kind taking place at high temperatures in a light different from quite analogous decompositions taking place at a lower temperature, and, in fact, to consider the former as abnormal, and to try by various artifices to explain them away. The fact to be recognised is that chemical changes requiring for their completion the aid of heat can take place under various conditions, and that such changes do take place more frequently, and the more easily the more heat there is to be disposed of, consequently at higher temperatures, but that such changes do not take place exclusively at high temperatures."

Decompositions associated with negative calorific effects take place usually very easily in association with others producing heat, so that in the total effect more heat is produced than is used. This may be well illustrated by a series of reactions on which an important metallurgical process (Claudet's) depends. Zinc iodide is used to separate silver from silver chloride, dissolved in brine, the equation being

$$\begin{array}{llll} ZnI_2 \times 2AgCl = ZnCl_2 + 2AgI \\ 60·6 \quad 2 \times 29·4 \quad 112·8 \quad 2 \times 13·8 = +19. \end{array}$$

The separation of chlorine from silver by the iodine of iodide of zinc is quite in accordance with the fact that a greater amount of heat is liberated by the formation of chloride of zinc than silver chloride. In the second stage of the process, zinc again takes the iodine from iodide of silver, the heat of formation of zinc iodide being greater than that of silver iodide.

$$\begin{array}{ll} 2AgI + Zn = 2Ag + ZnI_2 \\ 2 \times 13·8 \qquad\qquad 60·6 = +33. \end{array}$$

It is well to repeat that in the following equations the figures representing the thermal values are preceded by the plus or minus sign. This is a conventional mode of representation of the fact that heat has been gained or lost during the formation of the particular compound. In calculating the thermal value of

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[1] *Modern Theories of Chemistry*, p. 442.

any given set of reactions as represented by an equation, it is necessary to algebraically subtract the thermal value of all compounds that are decomposed, and, conversely, to algebraically add the thermal values of the bodies formed.

The elements are assumed to be in the normal state of aggregation unless it be otherwise stated, so that although an equation may be written $CuS + 3O = CuO + SO_2$, it must be understood that it is oxygen in its normal condition that is employed, and not nascent oxygen. The heats of aggregation are only known in a very few instances.

The heats of formation given in the following tables are mainly derived from the results found in the *Annuaire du Bureau des Longitudes*. The numbers therein given have been adapted to agree with the chemical notation in use in this country. They are, it is believed, the most trustworthy that can be set before the student, and with their aid he will be able to obtain an insight into the thermal conditions which prevail when some of the principal metallurgical operations are being conducted. The thermal equations given on page 397 will provide the student with a basis for such work. It will be observed that the synopsis of typical processes, page 405, contains reference numbers to these sets of distinctive thermal processes. It must, at the same time, be admitted that the basis for thermo-metallurgy is at present a somewhat slender one, as most of the data which have as yet been obtained are derived from "wet," and not "dry" reactions. It is well, therefore, to bear in mind the warning of Mendeléeff against "extracting exact consequences of importance to chemical mechanics" from the present store of thermo-chemical data. He points out[1] "that the majority of the determinations were conducted in weak aqueous solutions, and, the heat of the solution being known, were referred to the substances in solution." It must be remembered, however, it is probable that during both solution and dilution the water acts independently in a chemical sense on the substance dissolved, and that "physical and mechanical changes proceed side by side with chemical changes . . . . and for the present it is impossible to distinguish the thermal effects of the one and of the other kind of change . . . . purely chemical phenomena are inseparable from mechanical phenomena."

HEATS OF FORMATION OF SOME GASEOUS COMPOUNDS.

Reaction.	Product.	Heat Evolved.	State of Product.
S + 3O	SO_3	+ 91·8	Gaseous.
,,	SO_3	+ 103·6	Solid.
S + 2O	SO_2	+ 71·0	Gaseous.
2H + O	H_2O	+ 58·2	,,
	H_2O	+ 69·0	Liquid.
C + 2O	CO_2	+ 97·0	Gaseous.
C + O	CO	+ 29·0	,,
2H + S	SH_2	+ 4·6	,,

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[1] *The Principles of Chemistry*, vol. i., 1891.

HEATS OF CHANGE OF THE ISOMERIC ELEMENTS.

Name.	Heat Evolved.
Oxygen, changing to ozone (16 grammes) .	− 9·9
Sulphur, octahedral to insoluble variety . .	0·0 at 18° < 0 at 112°
,, insoluble amorphous to the soluble amorphous variety . . .	+ 0·08
,, soluble amorphous to the octahedral .	− 0·08
,, prismatic to octahedral . . .	+ 0·08
,, plastic to octahedral. . . .	+ 0·40
Selenium, vitreous to metallic variety . .	+ 5·6
Tellurium, crystalline to amorphous variety .	+ 24·2
Phosphorus, white to red crystalline ,, .	+ 19·2
,, ,, ,, amorphous ,, .	+ 20·7 + 9·3 and − 1·0, according to the modification.
Arsenic, amorphous to crystalline variety .	+ 1·1
Carbon, amorphous (charcoal) to diamond .	+ 3·4
Silicon, amorphous to crystalline variety . .	+ 8·1
Gold, precipitated from the bromide, to the physical state of gold precipitated from the chloride	+ 3·2
Iron, about 650°	− 0·28
,, ,, 850°	− 0·34

THERMAL EQUATIONS FOR THE PRINCIPAL METALLURGICAL OPERATIONS.

I.

Mercury.

$HgS + 2O = Hg + SO_2$
8·2 71 = + 62·8

$4HgS + 4CaO = 4Hg + 3CaS + CaSO_4$
4 × 8·2 4 × 132 3 × 92 318·4 = + 33·6

II.

Copper.

$Cu_2S + 3O = Cu_2O + SO_2$
20·2 42 71 = + 92·8

$CuS + 3O = CuO + SO_2$
10·2 37·2 71 = + 98·0