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Metallurgical Calculations.

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THE HEAT BALANCE SHEET OF THE BLAST FURNACE.

Twenty-eight years ago, Sir Lothian Bell first constructed a satisfactory heat balance sheet for a blast furnace. His observations were largely, and his experience altogether, confined to the reduction of the argillaceous siderite ores of the Cleveland district, England, and although he made numerous attempts to draw general conclusions from the data at hand, applicable to iron smelting in general, yet many of his deductions remain true only for the particular ores and manner of working characteristic of the Cleveland district.

No treatment of this subject, however, can be based otherwise than upon Bell's researches, following the lines laid down in his "Principles of the Manufacture of Iron and Steel."

HEAT RECEIVED AND DEVELOPED.

The items on this side of the balance sheet are:

- (1) Combustion of carbon to carbonous oxide (CO).
- (2) Combustion of carbon to carbonic oxide (CO²).
- (3) Sensible heat of the hot blast.
- (4) Heat of formation of the pig iron from its constituents.
- (5) Heat of formation of slag from its oxide constituents.

(1) and (2) *Combustion of carbon in the furnace.* There is but one satisfactory way to determine with exactness the amounts under this heading. From the balance sheet, the total amount of carbon passing into the gases is obtained; from the analysis of the gases, the weight of carbon per unit volume of gases is calculated; the first divided by the second gives the volume of gases per unit weight of pig iron produced. The amount of CO and CO² in these gases is then obtained by use of the gas analysis, and if from the total CO and CO² in the gases there be subtracted the CO and CO² contributed *as such* by the solid charges, the difference is the CO and CO² which have been formed in the furnace. The heat evolved in the formation of these quantities can then be calculated.

Illustration: In Problem 51¹ it was calculated that per 1,000 kilos. of pig iron produced, 534.09 kg. of carbon went into the gases; also that the analysis of the gases showed 0.20736 kg. of carbon in each cubic meter of gas. The quotient indicated, therefore, 2575.6 cubic meters of gas produced per ton of pig iron. From the analysis of the gases there was in this volume,

$$\begin{aligned} 2575.6 \times 0.231 &= 595.0 \text{ m}^3 \text{ of CO} \\ 2575.6 \times 0.148 &= 381.2 \text{ m}^3 \text{ of CO}^2 \end{aligned}$$

whose weights were

$$\begin{aligned} 595.0 \times 1.26 &= 749.7 \text{ kg. CO} \\ 381.2 \times 1.98 &= 754.8 \text{ kg. CO}^2 \end{aligned}$$

The balance sheet shows, however, 49.1 kg. of CO² contained in the limestone flux used, which can be assumed as entering the gases bodily. Subtracting this we have 705.7 kg. of CO² formed in the furnace, and 749.7 kg. of CO, containing respectively

$$\begin{aligned} 705.7 \times \frac{12}{44} &= 192.5 \text{ kg. of C in CO}^2 \\ 749.7 \times \frac{12}{28} &= 321.3 \text{ kg. of C in CO} \end{aligned}$$

The heat generated in the furnace by the oxidation of carbon is, therefore,

$$\begin{aligned} 192.5 \times 8100 &= 1,559,250 \text{ Calories} \\ 321.3 \times 2430 &= 780,760 \text{ "} \end{aligned}$$

$$\hline 2,340,010 \text{ "}$$

If this carbon could have been entirely burnt to CO², there would have been generated

$$513.8 \times 8100 = 4,161,780 \text{ Calories}$$

Showing that only 56 per cent of the calorific power of the carbon was developed in the furnace; the other 46 per cent exists as potential calorific power in the waste gases, and part of it is really put back into the furnace as sensible heat in the hot blast.

There is a little doubt as to how to consider the CH⁴ in the gases; that is, whether the heat of its formation should be reckoned in as developed in the furnace. This would be (C, H⁴) = 22,250, or 1,854 Calories per kg. of carbon contained therein. Its presence in the gas probably results largely from the distillation of the fuel at a high temperature, and the heat required to disunite the CH⁴ from the solid fuel is probably as great as is represented by its heat of formation from carbon and hydrogen. The item is, therefore, a doubtful one, and as far as we know, we may be coming about as near to the truth by omitting it altogether as by counting it in. If we wished to add it in the illustration just given the calculation would be:

$$\begin{aligned} \text{Volume of CH}^4 &= 2575.6 \times 0.005 = 12.88 \text{ m}^3 \\ \text{Weight of C} &= 12.88 \times 0.54 = 6.9 \text{ kg.} \\ \text{Heat of formation} &= 6.9 \times 1,854 = 12,793 \text{ Cal.} \end{aligned}$$

It should be emphasized that in this calculated heat of oxidation of carbon in the furnace, no account has been taken whatever of *where* in the furnace this heat is generated. Above all, the mistake should not be made of supposing that the 780,760, Calories produced by formation of CO represents the heat generation at the region of the tuyeres; nothing could be further from the truth. A great deal of carbon is burnt to CO at the tuyeres, and some above the tuyeres, but a goodly proportion of this CO oxidizes by abstracting oxygen from the charge and becomes CO². It would not be incorrect, however, to divide the heat of oxidation of carbon in the furnace into two parts, viz.: to assume all the carbon as first forming CO, and part of this CO afterwards forming CO², corresponding to the amount of the latter formed in the furnace. If this were done, we would have

$$\begin{aligned} 513.8 \text{ kg. C to CO} &= 513.8 \times 2430 = 1,248,535 \text{ Cal.} \\ 449.2 \text{ kg. CO to CO}^2 &= 449.2 \times 2430 = 1,091,475 \text{ "} \end{aligned}$$

$$\hline 2,340,010 \text{ "}$$

This analysis gives us the information that of the total heat generated by the oxidation of carbon in the furnace, somewhere about one-half is generated by its burning to CO, and the other half by the further oxidation of CO to CO²; and we also know that the larger part of the former takes place at the tuyeres, and all of the latter takes place during the reduction of the charges in the upper part of the furnace.

If we know, however, or have calculated the amount of the blast received by the furnace, or, more properly speaking, the amount of oxygen in the blast, then the heat generated by oxidation of carbon at the tuyeres becomes known. In the previous illustration, taken from Problem 51, we can also take from the same problem the weight of oxygen in the blast, 557.7 kilos. This would burn $557.7 \times 0.75 = 418.3$ kg. of carbon to CO at the tuyeres, generating there

$$418.3 \times 2430 = 1,016,410 \text{ Calories,}$$

or 44 per cent of all the heat generated by oxidation of carbon in the furnace, leaving 1,323,610 Calories as generated above the tuyeres by the agency of the oxygen of the charges. These figures tell us just where and how the principal items of heat were generated in this particular furnace, and the similar calculation may be made for any blast furnace for which we have the necessary data.

(3) *Sensible heat in the hot blast.* To calculate this item, we need to know the weight or volume of the different constituents of the blast and their temperature. The question at once arises, as to what base line of temperature shall be chosen. It is most convenient to choose 0° C., since that is

¹ See this journal, April, 1906.

not over 15° from the average temperature in the largest iron producing countries. However, any other prevailing temperature may be taken as the base line, involving merely a little more calculation, since our specific heats are reckoned from 0° C. The temperature ought, moreover, to be taken as near to the tuyeres as possible, to properly take into account the effect of cooling of the blast in the bustle and feeder pipes, from radiation and expansion. The blast consists of air proper and moisture, the former with a mean specific heat between 0° and t° C of $0.303 + 0.000027t$, in kilogram calories per cubic meter, or in ounce calories per cubic foot, the latter with a similar mean specific heat of $0.34 + 0.00015t$. Since the moisture at times amounts to as much as 5 per cent of the blast, it should be calculated separately.

Illustration: With the outside air at 30° C., and saturated with moisture (raining), calculate the heat carried into a blast furnace by blast carrying in 1859.1 kilos. of nitrogen, the temperature of the heated blast being 600° C. Barometer 720 millimeters of mercury. Temperature base line 0° C.

Solution: One cubic meter of the moist blast, as taken into the blowing cylinders, carries all the moisture it can hold, the tension of which is therefore 31.5 millimeters. The tension of the air proper present is therefore $720 - 31.5 = 688.5$ millimeters, and each cubic meter of moist air carries

$$\frac{31.5}{720} = 0.0438 \text{ cubic meter of moisture, and}$$

$$\frac{688.5}{720} = 0.9562 \text{ cubic meter of air proper.}$$

Whatever the temperature of the blast, the moisture and air proper will be in this same proportion whenever its temperature is over 30° C. If the temperature were 0° C. the moisture would be mostly condensed, but for the purposes of calculating the heat brought in we may assume the moist air to be at 0° C., with its moisture uncondensed. That volume of blast which would be 1 cubic meter at 0° and 760 mm. pressure, would, therefore, bring in, at 600° C., the following quantity of heat:

$$\begin{array}{l} \text{H}^2\text{O } 0.0438 \times [0.34 + 0.00015 (600)] \times 600 = 11.3 \text{ Calories} \\ \text{Air } 0.9562 \times [0.303 + 0.000027 (600)] \times 600 = 179.7 \text{ "} \\ \hline \text{Total } 191.0 \text{ "} \end{array}$$

Since the nitrogen present in this is

$$0.9562 \times 1.293 \times \frac{10}{13} = 0.9511 \text{ kg.}$$

the heat brought in per 1859.1 kg. of nitrogen is

$$191.0 \times \frac{1859.1}{0.9511} = 373,344 \text{ Calories.}$$

An amount equal to over one-third of all the heat generated by combustion of carbon at the tuyeres.

(4) *Heat of formation of pig iron from its constituents.* The pig iron contains several per cent, some 5 to 10 altogether, of carbon, silicon, manganese, phosphorus, sulphur and other elements. The energy of their combination with the iron is a somewhat indefinite quantity, and in no case can be considerable. Berthelot states the energy of combination of carbon with iron as $(\text{Fe}^3, \text{C}) = 8,460$, which would be 705 Calories per kilogram of carbon, and another investigator (Ponchière) states the heat of combination of phosphorus with iron to be zero. In the present state of uncertainty it is hardly allowable to add in any other than the heat of combination of the carbon in the iron, and leave out that of the other elements.

(5) *Heat of formation of the slag from its constituent oxides.* Here we touch upon a quantity of more than insignificant proportions, yet which is not yet quantitatively known with satisfactory accuracy. The main constituents of the slag

are SiO_2 , Al_2O_3 , CaO , MgO and CaS , which are provided by clay, limestone and iron sulphide. If we allow, on the other side of the balance sheet, for the heat necessary to de-hydrate clay, drive carbonic acid off carbonates, and break up iron sulphide and enough CaO to furnish Ca for CaS , we are then entitled, on the other hand, to place in the heat evolution column the heat of combination of aluminium silicate with lime and magnesia, the heat of formation of CaS and its heat of solution in the silicate slag. The heat of formation of CaS is 94,300 Calories, or 2,947 Calories per kilogram of sulphur; its heat of combination with a silicate slag is unknown. The heat of combination of lime with aluminium silicate has been determined only for the proportions 3CaO to $\text{Al}_2\text{Si}_2\text{O}_7$, that is, for 168 parts of CaO uniting with 222 parts of aluminium silicate. This has been determined in Le Chatelier's laboratory as $(3\text{CaO}, \text{Al}_2\text{Si}_2\text{O}_7) = 33,500$ Calories, which is 200 Calories per unit of CaO combining, or 150 calories per unit weight of $\text{Al}_2\text{O}_3 + \text{SiO}_2$. The calculation would be made on the basis of the amount of lime (plus lime equivalent of magnesia present), if it were present in a smaller ratio than 168 to 222 of silica and alumina, and on the basis of the silica and alumina, if their ratio to the summated lime were less than 222 to 168. It is probable that in the near future these quantities will be known more accurately.

One item of heat received by the furnace has not been mentioned, because of its usual absence, viz.: heat in hot charges. Very rarely roasted ore comes hot to the furnace, in which case its sensible heat must be counted in, else the thermal sheet of the furnace will be that much out of balance.

HEAT ABSORPTION AND DISBURSEMENT.

The items on this side of the balance sheet are:

- (1) Sensible heat in waste gases, including water vapor only as vapor.
- (2) Sensible heat in outflowing slag.
- (3) Sensible heat in outflowing pig iron.
- (4) Heat conducted to the ground.
- (5) Heat conducted and radiated to the air.
- (6) Heat abstracted by cooling water, tuyeres, etc.
- (7) Heat for de-hydrating the charges.
- (8) Heat for vaporizing water from charges.
- (9) Heat absorbed by decomposition of carbonates.
- (10) Heat absorbed in reduction of iron oxides.
- (11) Heat absorbed in reduction of other metallic oxides.
- (12) Heat absorbed by decomposition of moisture of the blast.

(1) *Sensible heat in waste gases.* The amount of these gases is known only from the carbon contained in unit volume, by analysis, and the known weight of carbon entering and leaving the furnace. If there is much fine coke carried over by the blast, allowance must be made for the carbon in it, because this would not be represented in the gas analysis. The analysis of completely dried gas is that usually obtained, because if the gas is measured without drying, an uncertain amount of moisture is condensed, and, therefore, it is usual to dry before measuring and analyzing. The amount of moisture in the gases is either assumed as that driven off from the charges, as shown by the balance sheet, or else is determined directly by drawing the gases through a calcium chloride tube or other desiccating apparatus. Several tests should be made to get a fair average, because much more will be in the gases immediately after charging than immediately before. Dust must be excluded from the drying tube by filtering the gases through dry asbestos. The average temperature of the gases should be known over a considerable period; a thermo-couple in the down-comer gives this most accurately and more uniformly than if inserted above the stock line in the furnace.

The weight of moisture per unit volume of dry gas is then converted into volume at standard conditions by dividing by 0.81 (1 cubic meter = 0.81 kg; 1 cubic foot = 0.81 ounce avoirdupois). The sensible heat of the gases is then calculated, using 0° C. as the base line, and the proper mean specific heats

of the gases per unit of volume. The water vapor will here be considered simply as a gas, and its sensible heat above water vapor at 0° only calculated. This leaves the latent heat of vaporization of this water to be considered as a separate item (606.5 calories), that is, as heat absorbed by reactions in the furnace, thus putting it on exactly the same footing as the CO^2 in the gases which has been expelled from carbonates in the furnace. By so proceeding much uncertainty as to the heat in the water vapor is avoided.

If the amount of flue dust is considerable its quantity should be ascertained, and the heat in it also calculated and added in to the heat in the moist gases. Its specific heat may be approximated as so much carbon, iron oxide and silica, the proportions of each of these present being known.

(2) *Sensible heat in outflowing slag.* The weight of slag produced is seldom taken directly, but can be reckoned up with all needful accuracy from the balance sheet of materials entering and leaving. Its temperature and specific heat, solid and liquid, melting point and latent heat of fusion, are unfortunately almost always unknown factors. The one datum which is needful, however, is the total heat in a unit weight of liquid slag as it flows from the furnace, and this is not a difficult quantity to obtain. A rough calorimeter with a reliable thermometer and containing a carefully weighed quantity of water, may be easily constructed. Some liquid slag is run directly into it, and by observing the rise of temperature and afterwards filtering out, drying and weighing the granulated slag, a satisfactory determination can be arrived at. This is corrected to 0° C. by using an approximate specific heat, say 0.20, for the range of final calorimeter temperature to zero. In this connection it is important to note that the calorimetric determinations of Akerman on blast-furnace slags, give the heat in the *just-melted* slag, whereas slags flowing out of a furnace are considerably, some 200° to 500° C., above their melting point, and therefore contain some 50 to 150 Calories more heat than that given by Akerman for a slag of similar composition. Since Akerman's values run from 350 to 400 Calories, the actual heat in the outflowing slag may be between 400 and 550 Calories. Akerman himself states that an average of twenty-seven Swedish furnaces gave 530 Calories as the actual heat in unit weight of outflowing slag, and Bell uses 550 in most of his calculations on Cleveland (England) furnaces.

(3) *Heat in outflowing pig iron.* The heat in *just-melted* pig iron is evidently too small a quantity to use in this connection. The heat in the outflowing pig iron at 200° to 500° above its melting point will be 50 to 100 Calories greater. The former quantity is about 245 calories; the latter will be 300 to 350. Bell takes 330 for Cleveland furnaces; Akerman states 250 to 325 for Swedish furnaces. We may conclude, then, to use 300 Calories for a coke furnace running cool, and up to 350 Calories for a very hot furnace.

(4) *Heat conducted to the ground.* This is a very uncertain quantity. It varies with the kind of ground, and is more nearly a constant per day than per unit of pig iron produced. It is, therefore, expressed per unit of iron produced, larger for small furnaces run slowly than for large furnaces run fast. It is less when running rich ores and greater with poor ores, other things being equal. As nearly as can be assumed we would put this item as lying between 60 and 200 Calories per unit of pig iron made. Bell uses 169 on one Cleveland furnace, but it is certainly less than 100 in some charcoal furnaces using pure ores and fuel, and consequently with a small heat requirement.

(5) *Heat conducted and radiated to the air.* This item is likewise more nearly a constant quantity per day for a given furnace, and is therefore less per unit of iron produced the faster the furnace is run. It may vary between 60 and 250 Calories per unit of pig iron, the former in furnaces of low heat requirement per unit of iron produced, the latter in those of high heat requirement. If the amount were calculated it

would figure out as a time function, and would require the temperature of the outside shell, that of the air, the velocity of the wind, and the total outside surface, in order to calculate by the principles of heat radiation and conduction, the amount radiated per day. No one has done this yet for any one furnace, and, in brief, items (4) and (5) of this schedule are usually grouped together and determined simply by difference, their sum aggregating from 100 to 500 Calories per unit of pig iron, averaging 100 to 150 for charcoal furnaces of low heat requirement, 200 to 450 for Cleveland furnaces (Bell), and 300 to 500 for large, modern furnaces with thin walls and great height.

(6) *Heat abstracted by cooling water.* In the old-fashioned heavy masonry, cold blast furnace, this item was zero. With the advent of hot blast, the water needed for cooling the tuyeres entered as a heat abstracting factor. It is greater the harder a furnace is blown, but does not increase proportionately with the output. The heat lost by tuyere-cooling water may be 50 to 100 Calories per unit of pig iron made. That for cooling of bosh plates and the outside of the crucible in modern furnaces, may vary all the way up to 200 Calories. These two items are very large in a modern furnace, but are necessary expenditures of heat energy in order to preserve the lines of the furnace during fast running. For any particular furnace they may be determined with all needful accuracy by measuring the amount of water pumped or used for these purposes and its temperature before and after using.

(7) and (8) *Drying and de-hydrating charges.* Water goes into the furnace as moisture and as combined water of the charges. To convert the moisture, such as is evaporated by a current of moderately warm air, into vapor requires 606.5 Calories per unit of water. This allows merely for its vaporization in the furnace, and not for any sensible heat which it may carry out of the furnace at the temperature of the waste gases. This latter item is properly considered in with the sensible heat of the waste gases. The common practice of saying that it takes 637 Calories to evaporate the moisture of the charges is wrong, because this amount would convert water at 0° to vapor at 100° , and, therefore, would include part of what is properly the sensible heat of the waste gases. On the other hand, it is equally wrong to say that this heat of vaporization should be counted in as sensible heat in the hot gases; it would be just as logical or, rather, equally illogical, to count the latent heat of vaporization of CO^2 as sensible heat in the gases.

To drive off water of hydration from hydrated minerals in the charge requires an additional amount of chemically-absorbed heat. As far as is known, this is small for the water driven off hydrated iron oxides, so small as to be a doubtful quantity and safely left out; but if it comes from clay the large amount of 611 calories is absorbed in merely separating it from its chemical combination ($2\text{H}^2\text{O}$, $\text{Al}^2\text{Si}^2\text{O}^7$) = 22,000 Calories, which would require $611 + 607 = 1,218$ Calories to put into the state of vapor each unit weight of water entering the furnace chemically combined in clay. (This does not concern the ordinary moisture in moist clay, expelled at 100° C., but only the combined water in the dry clay). Where much clay occurs in the ores this quantity becomes important, and its amount explains some of the difficulties met in working clayey charges, particularly since a large part of this chemically combined water is expelled only at a red heat, and, therefore, cools greatly the hotter zones of the furnace.

(9) *Decomposition of carbonates.* Raw limestone, or dolomite, is the usual flux of the blast furnace, and its carbonic acid is evolved at temperatures between 600° and 800° . Whether some of this is subsequently decomposed by contact with carbon and reduced to CO , is immaterial to the balance sheet, because more than enough CO^2 escapes from the furnace to represent the CO^2 of the flux, and we charge the furnace only with the formation of the CO and CO^2 actually found in the gases, less the CO^2 from fluxes. Bell charges up

the heat absorbed also in the assumed reaction $\text{CO}^2 + \text{C} = 2\text{CO}$, but this is an error, because it is doubtful how much of the CO^2 is thus decomposed. and the question, in its last analysis, is one of heat *distribution* in the furnace, and does not concern the totals of heat absorbed or evolved. We can, therefore, omit the item of decomposition of this CO^2 (as likewise, and for analogous reasons, the heat evolved in carbon deposition in the upper part of the furnace — $2\text{CO} = \text{C} + \text{CO}^2$), and need consider only the heat required to expel the CO^2 from carbonates. This is:

(CaO, CO^2)	= 45,150 Calories	= 1,026 Calories per kg. CO^2
(MgO, CO^2)	= 29,300 " "	= 666 " "
(MnO, CO^2)	= 22,200 " "	= 500 " "
(FeO, CO^2)	= 24,900 " "	= 566 " "
(ZnO, CO^2)	= 15,500 " "	= 352 " "

By using the above figures, in connection with the known composition of ore and fluxes, the heat required to decompose carbonates can be correctly calculated.

(10) *Reduction of iron oxides.* The heats of formation of the various oxides of iron are:

(Fe, O)	= 65,700 Calories	= 1,173 Calories per kg. iron
(Fe^3 , O^4)	= 270,800 " "	= 1,671 " "
(Fe^2 , O^3)	= 195,600 " "	= 1,746 " "

And, therefore, just these quantities of heat are required per unit weight of iron reduced from these compounds. If the ore is a carbonate the heat absorbed in driving of CO^2 from FeCO^3 can be first allowed for, and then the heat required for reduction of the FeO calculated on the weight of the reduced iron. If some FeO goes into the slag it will be as FeO, and if the ore was Fe^3O^4 , or Fe^2O^3 , the reduction of unit weight of iron from the state of Fe^2O^3 , or Fe^3O^4 , to the state of FeO, absorbs respectively 573 or 498 Calories, as may be readily deduced from the heats of formation of the three oxides concerned. If FeS is present its heat of formation is

$$(\text{Fe}, \text{S}) = 24,000 \text{ Calories} = 429 \text{ Calories per kg. Fe.}$$

If the iron is charged partly as silicate, such as mill or tap cinder, an additional amount of heat will be required for reduction, equal to that needed to separate the iron oxides from their combination with silica. The heat of formation of the bi-silicate slag only has been determined:

$$(\text{FeO}, \text{SiO}^2) = 8,900 \text{ Calories} = 148 \text{ Calories per kg. SiO}^2.$$

And since the cinders concerned contain relatively more iron than this, we can best make allowance for the heat required to set free the silica. It is necessary, therefore, to take the amount of silica in the iron cinder charged, and allow, as necessary for its decomposition into FeO and SiO^2 , 148 Calories for each unit weight of SiO^2 contained.

(11) *Reduction of non-ferrous oxides.* Silicon is usually present in pig iron, its reduction from silica requiring:

$$(\text{Si}, \text{O}^2) = 180,000 \text{ Calories} = 6,413 \text{ Calories per kg. Si.}$$

There is a little doubt about this (Berthélot's) figure; more recent determinations, not yet published, point rather to 196,000 and 7,000 Calories respectively.

Manganese is often present in the ores as MnO^3 , Mn^3O^4 , or MnO^2 , and going partly into the slag as MnO. The heat absorbed in reduction to manganese is:

(Mn, O)	= 90,900 Calories	= 1,653 Calories per kg. Mn
(Mn^3 , O^4)	= 328,000 " "	= 1,988 " "
(Mn, O^2)	= 125,300 " "	= 2,278 " "

For the MnO produced and going into the slag, the reduction from Mn^3O^4 , or MnO^2 , per unit weight of contained manganese, absorbs 335 or 625 Calories respectively.

Sulphur generally comes from the reduction of FeS, requiring 667 Calories per kg. of sulphur; but care must be taken not to allow for this heat twice, since if reckoned once under the head of iron reduction it must not be reckoned on the balance sheet a second time under sulphur. One reduction of FeS liberates both constituents.

Phosphorus may be reduced in large quantity in making basic

iron. It probably comes mostly from calcium phosphate, in which case we must reckon on not only the heat of oxidation of phosphoric oxide but also its heat of combination with lime:

$$\begin{aligned} (\text{P}^2, \text{O}^5) &= 365,300 \text{ Cal.} = 5,892 \text{ Cal. per kg. of P.} \\ (3\text{CaO}, \text{P}^2\text{O}^5) &= 159,400 \text{ " } = 2,410 \text{ " " " contained.} \end{aligned}$$

Making a total heat requirement of 8,302 Calories to separate unit weight of phosphorus from phosphate of lime, and leave free lime. In a furnace making a pig iron with several per cent of phosphorus, this item becomes quite large.

Calcium occurs in the slag as CaS, its reduction from lime requiring

$$(\text{Ca}, \text{O}) = 130,500 \text{ Calories} = 3,263 \text{ Calories per kg. Ca.}$$

Other elements than the above rarely occur in pig iron in notable quantity. If rare ones occur, their heat of reduction can be sought in thermochemical tables. Those of tungsten, titanium, molybdenum and chromium are, however, not at present known.

(12) *Decomposition of moisture in the blast.* This is to be counted as vapor of water, the heat required to decompose, which is:

$$\begin{aligned} (\text{H}^2, \text{O}) \text{ vapor} &= 58,060 \text{ Cal.} = 3,226 \text{ Cal. per kg. H}^2\text{O.} \\ &= 29,030 \text{ " " " H}^2. \end{aligned}$$

It is not correct to allow here for the sensible heat in this water vapor coming in with the hot blast, because that heat should go on the other side of the balance sheet as heat delivered to the furnace. Neither is it correct to subtract the heat of combination of the oxygen of this moisture with carbon to form CO at the tuyeres; because, although that combination actually does take place, yet the heat thereby evolved properly belongs also on the other side of the balance sheet, and is there properly taken care of as part of the heat of oxidation of carbon in the furnace.