

214 BALANCED REACTIONS IN STEEL MANUFACTURE:

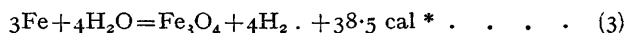
These are balanced reactions, of which the first has been worked out fairly fully, and the composition of the gases which are in equilibrium with iron and ferrous oxide at different temperatures is as follows:—

Temp.	CO.	CO ₂ .	Ratio $\frac{\text{CO}}{\text{CO}_2}$.
° C.	Per cent.		
550	54	46	1·16
650	58	42	1·38
750	61	39	1·56
850	68	32	2·12
900	71·5	28·5	2·51

In Appendix II the author has calculated what the composition would be at higher temperatures, and finds that at 1,500° it would be CO=92·4, and CO₂=7·6, so that if the iron was in contact with any gas containing more than 7·6 per cent. CO₂ it would be oxidized. But the burnt gases in a steel-furnace contain very little CO, and consequently reaction is possible. But the higher the temperature the greater will be the difference between the gases in contact and the gases in equilibrium, so that the higher the temperature the greater the oxidation.

This result can be obtained in another way by the le Chatelier principle, for on giving the reaction heat, it must proceed so as to absorb heat. It has a negative heat of reaction, and must in consequence proceed from right to left, that is, more FeO will be formed. Exactly the same result is obtained with the second reaction, so that neither of these can be the dominant reaction during the melting period.

3. The action of steam on iron gives—



With increasing temperature the amount of hydrogen gets less, and the same result follows from the le Chatelier principle, so that the rate of oxidation is in accord with the slag condition as observed in practical working.

If the loss due to scaling is to be minimized and as little of the charge as possible is to find its way into the slag as oxides, three conditions have to be observed:—

1. Melt down rapidly.
2. Melt down at high temperature.
3. Have a low steam content in the burnt gases.

Nos. 1 and 2 give together hot and quick working. It is often held that during the melting-down period the temperature of the bath must be constant, since there is solid and liquid metal in contact; but this is only true if there is equilibrium, which never holds for steel-melting furnaces. So long as the liquid bath is growing at the expense of the solid scrap there is a difference in temperature between them, and the quicker the rate of melting the greater must this difference be. Pyro-

* Deville, *Liebig Ann.*, 156, 76; Preuner, *Zeit. physik. Chem.*, 1904, 385.

meter observation shows, in fact, that the temperature of the liquid bath is rising steadily during the melting period.

The presence of steam in the burnt gases arises from the combustion of the hydrogen in the producer-gas together with any undecomposed steam which has passed through the producer. The composition of the gas has therefore a direct bearing on the working of the furnace and on the loss of metal due to scaling.

As a result of this reaction the steel has an opportunity of absorbing hydrogen. There is no experimental evidence as to the extent of the solubility of hydrogen in iron in the liquid or solid state. Baraduc-Muller * found that the rate of evolution of hydrogen during solidification was not much greater than the rate of evolution after the steel had become completely solid. If there is little difference in the solubility in the liquid and in the solid state, it is unlikely that hydrogen is ever the cause of blow-hole formation in steel.

Boiling Period.

After melting, the liquid bath has a covering of slag containing FeO and other oxides (which, however, take no part in the subsequent reactions), together with silica. Independently of how these constituents are combined one with the other, the slag can be regarded as an impure solution of ferrous oxide in silica. The addition of iron ore increases the strength of this FeO solution, and since there is no contrary evidence it must be inferred that iron oxide so added cannot act on the steel bath without first going into solution in the slag. The first action of the slag is to oxidize any Si and Mn in solution in the liquid metal; but these reactions need not be considered here, since they do not give rise to gaseous reaction products. After they have been removed, however, the carbon is attacked according to the equation



The FeO is derived from the slag, but there are many reasons for believing that the reaction is by no means confined to the surface layers of metal, but takes place equally throughout the whole mass of liquid. If the slag is scraped off during the boiling period, the metal still goes on boiling vigorously, and can do so for a considerable time although there are only traces of slag in contact with the steel. Clean pieces of Swedish charcoal iron containing 0.16 per cent. carbon lose all their carbon when melted in a magnesia crucible in an electric vacuum furnace.† When a local area in the bottom of an open-hearth furnace gets bad, the boil takes place much more vigorously over that area than elsewhere, and the slag may be projected some distance above the general level through the energetic action. Such facts point to the CO being liberated simultaneously throughout the mass of metal, and since the carbon is in solution, it entails that the FeO must also be in solution in the steel.

On this assumption the FeO is divided between two solvents, the slag and the steel, and the application of the partition law to such a system indicates that the concentration of the FeO in the steel must bear a constant ratio to that of the slag if the molecular condition of

* *Jour. Iron and Steel Inst., Car. Res. Mems.*, 1914, p. 216.

† Yensen, *Bull. Illinois Univers.*, No. 72, p. 41.

216 BALANCED REACTIONS IN STEEL MANUFACTURE:

both solutions be the same. If FeO in the steel be removed from solution, then more FeO will pass from the slag into the steel, until a balance is once more obtained, and if the FeO be continuously removed, then a continuous flow of FeO will come from the slag and will endeavour to replace the loss. If no addition of FeO be made to the slag (in the form of iron ore), then the percentage content will fall continuously.

The mechanism of the carbon reduction in the open-hearth process can now be understood, for as the ore is added to the slag it dissolves as FeO, which is transferred in solution to the bath, and reduced by the carbon there with the production of CO. The reaction will follow the laws of chemical kinetics, so that, stating the concentration of the FeO in the slag as C_{FeO} , the concentration in the steel will be aC_{FeO} , where a is the partition coefficient. If C_C and C_{CO} stand for the corresponding concentrations of the carbon and the carbon monoxide, the reaction velocity will be—

$$\frac{dx}{dt} = K(aC_{\text{FeO}} - x)(C_C - x) - k(C_{\text{CO}} - x) \quad \dots \quad (5)$$

where K and k are constants.

The carbon monoxide which is first given off dissolves in the steel, but whenever the steel becomes saturated the excess gas will escape

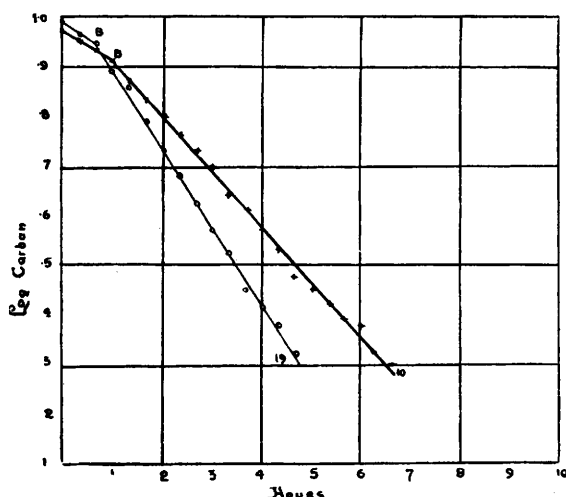


FIG. 1.

into the atmosphere. This is the commencement of the boil. The steel from this moment is therefore saturated with gas, so that the CO term in equation (5) can be neglected. On integrating, this equation takes the usual logarithmic form, and the log of carbon against time should plot a straight line. It is to be remembered at this stage that this will only be true if no external addition is made to the FeO after the reaction starts—that is, if no ore is added to the charge after the boil commences. Fig. 1 gives curves taken from results obtained by the author. Samples were taken every twenty minutes during the course of two acid open-hearth charges from the time the metal was melted

until it was tapped out. It will be seen that the straight line fits the points surprisingly well, considering that in a melting-furnace under steelworks conditions it is impossible to keep other complex influences constant, as the theory assumes.

The curves are interesting in another way, for each really consists of two parts. The first part relates to the loss of carbon before the boil commences, when the bath still contains some silicon and manganese. The commencement of the boil is marked by a distinct angle between the two parts of the curve, and the rate of loss of carbon when the other elements are present is much less than when they are absent.

As the carbon in the bath gets less, the rate at which it is being reduced also gets less, until it ultimately becomes of the same order of magnitude as the rate of the reverse reaction brought about by the presence of the CO. When it becomes equal to the latter, then equilibrium is established and no further carbon is oxidized. When this takes place, equation (5) reduces itself to

$$\text{Constant } \frac{K}{k} = \frac{C_{\text{CO}}}{a \cdot C \cdot \text{FeO} \cdot C \cdot C} \cdot \cdot \cdot \cdot \cdot \cdot (6)$$

How far the attainment of equilibrium is possible in a melting-furnace is a difficult question to decide. The carbon, for one thing, is never constant, but is always dropping slowly, and the time element in practical working necessitates the adoption of other means for controlling the oxides in solution. But the conditions, however they may vary, are always trying to approach equilibrium, and alterations in the external conditions will have the same effect whether it is attained or not.

Since the steel is saturated, the upper term will remain constant in equation (6), and so the lower the carbon in the steel at the final stage, other things being equal, the higher the amount of FeO and vice versa, which accounts for the fact that mild steels are more difficult to deoxidize than higher carbon steels made under the same conditions.

Supposing lime is added to a slag which is in equilibrium with the metal underneath, then the FeO concentration of the slag is reduced and the metal is no longer in equilibrium, but contains excess FeO which will act on the carbon available until equilibrium is once more attained. For this reason CaO can replace ore with advantage towards the end of the boil, but it is obvious that this action cannot take place at the beginning of the boil, since the effect would then be directly opposite and it would retard oxidation. Any diluent, such as manganese ore, magnesia, etc., would act exactly in the same manner.

The influence of temperature is very important, and in the author's opinion it is the one method of control which is neglected in practical steel-making. It is not sufficient to tap a charge which leaves no ladle skull and possesses an excess of heat which is irregular and varies from charge to charge. Much more than that is implied by "temperature control." It is the production of charges of steel which have been worked in the furnace, and which have been cast with a constant and known amount of superheat over the temperature of solidification.

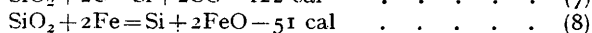
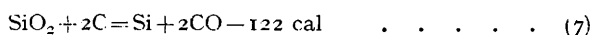
In Appendix I the calculations are given which show that for a variation of 50 degrees in the finishing temperature a decrease of more than 33 per cent. is possible in the amount of FeO which the steel carries in solution. The author has already shown the great influence which

218 BALANCED REACTIONS IN STEEL MANUFACTURE :

this fact has on the number of non-metallic inclusions present in the finished steel.* The reduction in the FeO content of the steel with rising temperature reacts correspondingly on the slag, with the well-known result of thickening it. High temperature working gives siliceous slags.

Reduction of Silicon.

With a highly siliceous slag in contact with iron and carbon, reduction of the silica may take place in two possible ways :—



and in both an increase in temperature will lead to a greater reduction and the formation of more silicon.

From the results of a large number of estimations the author has found that in acid open-hearth working the reduction of silicon during the finishing stages, when the carbon is in the region of 0.15 to 0.20 per cent., is practically negligible. It is within the limits of chemical error. In acid electric-furnace work, on the other hand, it is quite appreciable, and it is possible to reduce 0.2/0.3 per cent. direct from the slag. In crucible melting, the killing of the melt results from the reduction of the silica of the clay pot, but crucible charges are usually high in carbon, and it is much more difficult to kill low carbon charges in this manner. The experiments of MacWilliam and Hatfield† showed that this reduction may be brought about in open-hearth furnaces, but it is noticeable in their figures that when reduction takes place the carbon is about 0.40 per cent.

It is fairly evident, therefore, that it is the carbon which reduces the silica and not the iron. The reverse reaction in equation (8) is important when additions of silicon are made later for deoxidation purposes.

Manganese behaves similarly, and need not be considered separately.

Carbon Monoxide.

The presence of CO in solution in iron entails a further reaction with the FeO—



—a reaction which has been studied over a considerable range by Baur and Glässner‡ for solid Fe and FeO. Their results, however, will not enable us to arrive at quantitative conclusions regarding the equilibrium of the same materials when they are in a state of solution. Qualitative deductions in accordance with experimental facts can, however, be made. This equilibrium is independent of pressure, and the ratio of $\frac{\text{CO}}{\text{CO}_2}$ under reduced pressure is therefore constant. This is shown by the results of Baraduc-Muller§ in the composition of gas drawn off an

* *Jour. Iron and Steel Inst.*, 1918, 1, p. 289.

† *Ibid.*, 1902, 1, p. 54.

‡ *Zeit. physik. Chem.*, 1903, 43, 461.

§ *Jour. Iron and Steel Inst., C.S.M.*, 1914, p. 216.

ingot in four periods between the time of casting and the solidification of the metal :—

No.	CO.	CO ₂ .	Ratio $\frac{\text{CO}}{\text{CO}_2}$.
1	43·2	5·2	8·3
2	56·8	4·0	14·2
3	40·8	4·8	8·5
4	24·8	2·8	8·8

Excepting No. 2, the constancy is extremely good when the difficulties of the experiment are remembered.

A lowering of the temperature of working greatly decreases the ratio (see Appendix II). Thus in cast iron *—

Cast. Temp.	Ratio $\frac{\text{CO}}{\text{CO}_2}$.
1,428	30·2
1,348	13·7
1,264	7·2

The bearing which this has will be considered in the next section.

The Formation of Blow-holes.

It is a general law that the solubility of gases in liquids increases as the temperature is lowered, but at the freezing-point the solubility is much less in the solid state than in the liquid condition. As a result, all gases will show strongly the effects of primary segregation—that is, the concentration of the solution in the last portions to solidify. If during the progress of this concentration the limit of solubility is reached, then the excess gas will escape and blow-holes will be formed. At the finishing stages in the open-hearth furnace, as previously explained, the steel is saturated with CO and the amount of gas will depend only on the temperature. If this is constant, then all steels will start with the same amount of gas in solution. Starting, then, with a quantity of liquid steel containing CO and CO₂, and neglecting for the moment all other reactions except (9), cooling will result in more CO₂ being formed at the expense of the CO. But the steel in the solid state may have a very limited solubility for CO₂, and if this be exceeded, blow-holes will be formed at the instant of solidification. The formation of blow-holes not only depends on the quantity of dissolved gas but also on the variety of gas. No attention has hitherto been paid to this possibility, and to explain all the peculiarities in the relations between these gases and steel it is only necessary to assume that steel in the solid state has a much greater solubility for CO than for CO₂.

When equilibrium is established according to equation (9)—

$$K = \frac{C_{\text{CO}_2}}{C_{\text{FeO}} \cdot C_{\text{CO}}},$$

* *Journ. Iron and Steel Inst., C.S.M., 1916, p. 66.*

220 BALANCED REACTIONS IN STEEL MANUFACTURE :

where Cx is the concentration of X. When there is much ferrous oxide in solution, the ratio $\frac{CO_2}{CO}$ will be correspondingly great, and when the steel solidifies, if the amount of CO_2 is greater than the metal can hold in the dissolved state, blow-holes will be formed. If on the other hand the ferrous oxide be removed, the amount of CO_2 will shrink until the ratio $\frac{CO_2}{CO}$ corresponds to give the correct value of K, and on solidification the saturation limit may never be attained. It is important to notice that the total volume of gas (expressed as c.c. per gram of metal) may remain quite unaltered by the reduction of the FeO , so long as direct reduction of the gases does not take place. How well this accords with the experimentally determined volumes of gas by different observers will be seen by the following results. Boylston,* using all the well-known deoxidizers, found—

Average for deoxidized metal	126 c.c. per 100 grams
Average for oxidized metal	125 „ „

Goerens,† using quite a different method for the estimation of the gas, gives the mean of two charges in a basic open-hearth furnace, the samples being taken from the bath before and after deoxidation—

Average before deoxidation	67 c.c. per 100 grams
Average after deoxidation	88 „ „

Baker,‡ from two similarly melted charges of crucible steel—

Steel without blow-holes	132 c.c. per 100 grams
Steel with blow-holes	67 „ „

With regard to the latter, the two charges were melted in separate pots at the same time, and it is admittedly difficult to determine similarity of condition during melting so far as gas content is concerned.

It may, however, be taken as proved that deoxidation does not necessarily mean the diminution of the total gas in solution.

Since deoxidized steel contains less FeO , the gas given off should have a higher $\frac{CO_2}{CO}$ ratio than oxidized steel, and the results of Goerens again enable this to be confirmed. Taking samples from two electric furnace charges after the removal of the phosphorus slag and again after deoxidation with ferro-silicon and ferromanganese, and extracting the gas, it was found—

				$\frac{CO_2}{CO}$ Ratio per cent.
				$\frac{1}{8.8}$
Before deoxidation	7.3
After deoxidation	21.3

In the first charge the manganese was 0.08 per cent. and in the second 0.13 per cent. at the time of taking the first sample, showing that the

* *Jour. Iron and Steel Inst.*, C.S.M., 1910, p. 157.

† *Ferrum*, 12, p. 78.

‡ *Jour. Iron and Steel Inst.*, C.S.M., 1902, p. 224.

former was in a more highly oxidized state than the latter, and consequently it gives a greater difference after deoxidation. The theoretical deductions are strikingly confirmed.

As calculated in Appendix II, the composition of the gas in equilibrium with solid iron and FeO at the solidifying temperature, taken as 1,500° C., is roughly $\text{CO}_2=7.8$ per cent., $\text{CO}=92.4$ per cent., so that even if pure CO_2 were given off from the solidifying steel it would immediately be reduced again to CO by reaction with the solid iron until the composition of the gas approached this value. The fact that the gas liberated from an ingot burns with the blue flame of CO does not imply that it was given off as such during the solidification.

Estimation of Gases in Steel.

In steel, from what has previously been said, the gas content in the solid state will be proportional to the gas content in the liquid solution, but the determination of the exact composition and quantity of this gas presents grave practical difficulties.

Two methods only so far have been used—the extraction of the gas by heating the sample in a vacuum (Baker, Boylston, Donaldson, etc.) and the fusing of the sample in a vacuum with tin and antimony, which have practically no dissolved gas themselves (Goerens). In the first method, any gas which is evolved, which does not possess the composition necessary for equilibrium according to equation 7 for the temperature of the experiment, will tend to react with the steel until it does possess that composition. Thus the composition found must have been modified in a quite indeterminate manner by reaction taking place at a lower temperature. The sum of the volumes of CO_2 and CO, however, gives the exact volume of the mixed gases at the temperature of solidification. The composition may not be the same.

With regard to the second method, the carbon contained in the steel is insoluble in the alloy and floats to the surface, where it remains, at the same time reducing the CO_2 in accordance with the reaction—

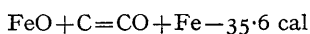


This reaction not only varies with the temperature, but also with the pressure of the gases, so that the results obtained only give the volume of the gas originally contained exactly, when expressed as CO_2 equivalent. That is, the volume of CO_2 plus $\frac{1}{2}$ (volume of CO) gives exactly the volume of mixed gases originally contained by the steel.

How far the composition is altered depends on the rate of evolution, so that the effect is merely to mask the differences in composition by an uncertain amount. Qualitative deductions can, however, still be drawn from the results, and it is the object of this paper to show how such deductions give an insight into the complex conditions existing in liquid steel during manufacture.

APPENDIX I.

The heat of reaction at ordinary temperatures for the reaction



is -35.6 cal, and the heat of reaction at the temperature of a melting-furnace, 1,600° C., can be calculated in the following manner:—

VOL. XIV—T10

222 BALANCED REACTIONS IN STEEL MANUFACTURE:

From Nernst's theorem, using the accepted symbols--

$$Q = Q_0 + \beta T^2$$

$$\frac{dQ}{dT} = 2\beta T = C_p - C_r.$$

There are no measurements of the molecular heat of ferrous oxide, since it has never been isolated pure, but Richards gives the value at 0° C. of the specific heat of

$$\text{Fe}_2\text{O}_3 \text{ as } 0.1456$$

$$\text{Fe}_3\text{O}_4 \text{ as } 0.1447$$

so it can be assumed that the specific heat of FeO is in the neighbourhood of 0.145, which gives a molecular heat of 10.45.

Mol. heat of carbon at 17° C.	1.92
„ CO „	6.71
„ Fe „	6.15

(These values are calculated from Kaye and Laby, *Physical Constants*.)
From these results,

$$C_p - C_r = 12.37 - 12.86 = -0.49 = 2\beta T,$$

and since the values were calculated at 290 Abs.—

$$\beta = -9.0 \times 10^{-4}$$

At $T = 290^\circ$ Abs., $Q = -35,600$, so that at $T = 1,873$, $Q = -38,700$. The difference is therefore negligible, and no appreciable error is introduced by taking the values at ordinary temperatures.

To find the difference in the value of the equilibrium constant K —

$$\frac{d}{dt} \log K = -\frac{Q}{RT^2} \dots \dots \dots (11)$$

and on integrating—

$$\log \frac{K_1}{K_2} = -\frac{Q}{R} \left\{ \frac{T_1 - T_2}{T_1 T_2} \right\}.$$

The ratio between the value of K at $1,600^\circ$ C. and K at $1,550^\circ$ C. is consequently

$$\log \frac{K_1}{K_2} = \frac{38,700 \times 50}{2 \times 2.30 \times 1,873 \times 1,823} = 1.24$$

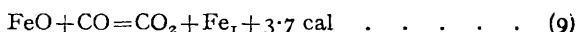
$$\frac{K_1}{K_2} = 1.33.$$

Since $K = \frac{C_{\text{CO}}}{C_{\text{FeO}} \cdot C_{\text{C}}}$, an increase in K implies an increase in CO or a diminution in the product of the bottom terms. The steel is, however, saturated with CO, and, like all gases in solution, the saturation strength must diminish very considerably with a rise in temperature. At the finishing stage, pigging back is usually started when the carbon is in the neighbourhood of 0.17 to 0.20, so that the carbon concentration

is practically constant and independent of other conditions. An increase in the value of the equilibrium constant of 33 per cent., as found above, means a reduction in the amount of ferrous oxide in solution of more than 33 per cent.

APPENDIX II.

The reaction



can be treated in exactly the same manner as the previous reaction in Appendix I, but it presents some peculiar features. To begin with, the log K from Baur and Glässner's results plotted with $1/T$ does not give a straight line, which implies that Q varies with temperature to an appreciable extent.

The heat of reaction at ordinary temperatures is +3,700 cal and the molecular heat of CO_2 is 8.9. This gives, as before—

$$2\beta T = C_r - C_p = 17.16 - 15.05 = 2.11, \\ \therefore \beta = 3.6 \times 10^{-3}.$$

This value is unusually high. At 825°C . the heat of reaction Q_{825} is

$$Q_{825} = 3,400 + \beta(1,098)^2 = 7,750 \text{ cal.}$$

The equilibrium constant K has the following values—

750° C.	1.56
900	2.51

which, calculating back by means of equation 8, Appendix I, gives

$$Q_{825} = 7,650 \text{ cal.}$$

This agrees very well with the previous value, found by quite a different method.

Substituting $Q_0 + \beta T^2$ in the integration of equation (11), Appendix I, the value of K at different temperatures will be—

1,200° C.	5.8
1,300	7.5
1,400	9.5
1,500	12.1
1,600	15.2

The gas given off from a steel ingot immediately after solidification gave a ratio for K of 11.0,* and at lower temperatures 3.1 to 4.2. In the former case the temperature cannot have been far removed from the temperature of solidification, which was in the neighbourhood of $1,475^\circ$, and in the latter case the temperatures were probably about 700 to 800°C . These figures show the great importance of equilibrium conditions, and support the contentions of the author regarding the methods of estimating the gases in solution in steel.

* Baraduc-Muller, loc. cit.