Kinetics of the Carbon-Oxygen Reaction in Liquid Iron*

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Synopsis

Reaction mechanisms of CO evolution in liquid iron-carbon alloys were investigated and the rates of carbon oxidation were measured by blowing oxygen into liquid iron. Since an estimated rate of the homogeneous reaction is extremely rapid at 2000°K, the rate of C-O reaction can be determined by reactant transports from the uniform bulk to the equilibrium area. Mathematical expressions are given to nucleation, growth, and motion of CO bubbles in liquid iron, and reaction rates in open hearths. Measured rates of $C + \frac{1}{2}O_2(g)$ reaction are interpreted on the basis of the present formulation.

I. Homogeneous Chemical Reaction

The theory of absolute reaction rates developed by Eyring¹⁾ provides an estimated rate of a chemical reaction. If the rate of the carbon-oxygen reaction in liquid iron were controlled by the process of "homogeneous one", the rate of this reaction would be approximately

$$-\frac{d[C]}{dt} = \frac{RT}{N_0 h} e^{\times p} \left(-\frac{\Delta H^\ddagger}{RT} \right) \frac{7}{1600} [C][O] \quad (1.1)$$

where $[C]$ and $[O]$ are respectively weight per cent of carbon and that of oxygen in liquid iron, R gas constant, T absolute temperature, N_0 Avogadro number, h Planck's constant, and $\Delta H^\ddagger$ activation energy. Putting $T=2000^\circ K$ and $\Delta H^\ddagger = 28 \text{ Kcal.}$ ²⁾ estimated $-d[C]/dt \cdot [C][O]$ is found to be roughly 10^7 per cent per hour. This result is too large compared to the observed value. The same conclusion has been obtained in Darken's calculation³⁾ for heterogeneous chemical reaction on the surface of carbon monoxide bubbles. It is to be noted that the rate of homogeneous reaction is not dependent on the bath size of the liquid metal (or the contents of the charged metal) as shown in equation (1.1). However, in the case of the heterogeneous reaction the bath size has an inverse effect on the rate. In other words, a large bath size results in a low reaction rate and vice versa.

II. Diffusion Film Theory

The rate of CO formation may thus be rapid in terms of chemical reaction, whether it is homogeneous or heterogeneous. Now the most reasonable process for determining CO formation would be a transfer of the dissolved carbon (C) and oxygen (O) to the existing surface of CO bubbles.

Generally, migration of the materials in liquids is due to diffusion, stirring, and convection, etc., where a uniform concentration rapidly prevails in the liquid state as compared to the solid state. However, there is occasionally a concentration gradient in the liquid near the interface between heterogeneous phases as shown in the solution process of a solid or gas into a liquid. This may be owing to viscous effects of the liquid near the boundary surface. The analogous effect is found in fluid dynamics. For example, in a fluid of Reynolds' number R^* , a solid material of dimension r has the thickness of the boundary layer, influenced by the viscosity of the liquid, Δl , given by

$$\Delta l \cong r / \sqrt{R^*} \quad (2.1)$$

Reynolds' number R^* in the case of CO gas bubbles in liquid iron is evaluated as follows:

$$R^* = \rho v r / \eta \quad (2.2)$$

where ρ is the density of the liquid iron, v the velocity of the bubble, r the radius, η the viscosity coefficient of liquid iron. As far as $v \cong 1 \text{ cm/sec}$, which will be described later, and $r \cong 1 \text{ cm}$, R in (2.2) is roughly 10^3 , since $\rho=7$ and $\eta \cong 10^{-2}$ poise. Consequently, the thickness of the surface layer of a gas sphere with a radius of 1 cm will be roughly 0.03 cm. Similar consideration will be possible also in the case of liquid metal-slag interface or—air flat interface. The latter case has been observed, by Shvartzman, Samarin, and Temkin in their experiments on the rate of carbon oxidation⁴⁾. In this case the thickness is 0.01 cm. The order of magnitude of this thickness is concordant with the theoretical value. Thus, the viscous effect of liquid iron is regarded as an important cause for the concentration gradient of $\underline{C}$ and $\underline{O}$ near the gas bubbles and slag or solid surfaces. Then, this concentration gradient in the narrow region near the surface of the heterogeneous phase (10^{-2} or 10^{-3} cm) may give the respective rate determining steps of many reaction in liquid iron.

The stationary flows of the dissolved carbon and oxygen through the boundary layer are given by³⁾⁵⁾⁶⁾

$$\begin{aligned} J_c &= D_c \frac{N_0 \rho ([C] - [C]_\infty)}{1200 \Delta l} \frac{\text{atoms}}{\text{cm}^2 \text{ sec}}, \\ J_o &= D_o \frac{N_0 \rho ([O] - [O]_\infty)}{1600 \Delta l} \frac{\text{atoms}}{\text{cm}^2 \text{ sec}} \end{aligned} \quad (2.3)$$

In these equations D_c and D_o are the diffusion

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coefficients for $\underline{C}$ and $\underline{O}$, Δl represents boundary layer thickness, $[\underline{C}]_{\Omega}$ and $[\underline{O}]_{\Omega}$ respectively are weight per cents of $\underline{C}$ and $\underline{O}$ on the surface. Of course, an important relation

$$J_c = J_o = J \quad (2.4)$$

must hold always, in order to realize the stoichiometric chemical reaction and to reach chemical equilibrium on the gas-metal interface. This relation has also been adopted in their kinetic study of C-O evolution by Parlee, Seagle and Schuhmann⁷⁾.

III. Nucleation of CO Bubbles

The problem of CO bubble formation in liquid iron belongs to a sort of phase transformation. Then this process can be treated by means of some method like Volmer-Becker-Döring's theory⁸⁾⁹⁾.

In the case of carbon oxidation the free energy change (per molecule)

$$\Delta G_{co} = -\frac{RT}{N_o} l_n \frac{P_{co}}{[\underline{C}][\underline{O}]K_{co}} \quad (3.1)$$

must have a negative value. In equation (3.1), K_{co} is the equilibrium constant for the reaction

and P_{co} is the partial pressure of CO in the bulk gas phase. However, equation (3.1) needs a correction due to surface effect if the size of the gas bubble follows progressive processes:

where n means the number of CO molecules in the bubble. Hence, the free energy for forming a bubble containing n molecules from the dissolved carbon and oxygen in liquid iron is given by

$$\Delta G_n = n\Delta G_{co} + \sigma S_n \quad (3.4)$$

where σ is the surface energy of liquid iron per unit area, and S_n is the surface area of the bubble. The first term in equation (3.4) has a negative value, while the second is positive. Then, ΔG_n must pass through a maximum, at $n=n^*$. In other words, the worth of sub-microscopic bubbles of CO should be permitted to begin after the number of molecules overcomes this critical number n^* . The critical size of the present gas bubble, r^* , may be evaluated approximately as follows. The relation between the pressure of the bubble and the number of the molecules in the bubble may be described by

$$\left(P + \frac{2\sigma}{r}\right) \frac{4}{3}\pi r^3 = \frac{nRT}{N_o} \quad (3.5)$$

where r is the radius of the gas bubble, and P is the pressure of the atmosphere plus the ferrostatic pressure. Putting $S_n = 4\pi r^2$, one obtains

$$r^* = \left(-\frac{2RT}{N_o \Delta G_{co}} - \frac{4}{3}\right) \frac{\sigma}{P} \quad (3.6)$$

from equation (3.5) and

$$(\partial \Delta G_n / \partial r)_{r=r^*} = 0 \quad (3.7)$$

Using $[\underline{O}]_{ce}$, which is defined by

$$[\underline{O}]_{ce} = \frac{K_{co}}{[\underline{C}]} \quad (3.8)$$

one has

$$r^* = \left[\frac{2}{l_n([\underline{O}]/[\underline{O}]_{ce})} - \frac{4}{3} \right] \frac{\sigma}{P} \quad (3.9)$$

The free energy change of critical size of the gas bubble is given by

$$\Delta G^* = 4\pi\sigma r^{*2} \left[1 - \frac{\frac{4\sigma}{r^*} + 2P}{\frac{4\sigma}{r^*} + 3P} \right] \quad (3.10)$$

Inserting, $r^* \cong 10^{-3}$ cm and $\sigma \cong 1500$ dyne/cm into (3.10), one will find that ΔG^* is extremely large. Consequently, the actual origin of bubble formation should exist in another place, where easier processes prevail in terms of energy. These places may be contact surfaces between porous solids and liquids, e.g., the surfaces of furnace bottoms, brick walls, limestone, ore materials and scrap metals, etc.

IV. The Motion of CO Bubbles

As has been discussed by many investigators, the favorable place of origin for bubble formation would be in the solid-liquid interfaces⁶⁾. The holes of the solid surface may not be entirely filled under the influence of high surface tension of liquid metals, thus creating small gas pockets. These tiny gaseous spaces on the interfaces facilitate continuous bubble formation. If the holes or cavities are assumed to be a cylinder with radius d , favorable condition for bubble nucleation is that $d > r^*$. This is because of the impossibility of formation of smaller bubbles due to the existence of a large amount of Gibbs free energy change for nucleation of gas bubbles with radius r^* as shown in the preceding section.

The motion of gas bubbles in liquid iron may be described by the Stokes-Navier equation. If the viscosity of liquid iron denoted by η were large enough (i.e. small Reynolds number), the famous Stokes law

$$F_{RS} = 6\pi\eta rv \quad (4.1)$$

could be used to express the frictional force of a sphere having radius r and velocity v in liquids. The buoyancy of the gas bubble must be balanced by this frictional force. Thus,

$$v = \frac{2}{9} \frac{g}{\eta} \rho r^2 \quad (4.2)$$

Using $\rho \cong 7$, $\eta \cong 2 \times 10^{-2}$ poise, one obtains $v \cong 700$ m/second for radius of bubble, 1 cm. This figure leads to $R^* \cong 10^5$ in equation (2.2). Therefore, Newton's equation should be used in place of equation (4.1). That is roughly

$$F = \pi r^2 \rho v^2 \quad (4.3)$$

Thus, one obtains

$$v = \left(\frac{4}{3} r g \right)^{\frac{1}{2}} \quad (4.4)$$

Then, the velocity of gas bubbles with a radius of 1 cm is less than 40 cm/sec. This figure in liquid irons is concordant with the above discussion in section 2, in which the large Reynolds number results in the formation of the boundary interface layer.

As stressed by Darken⁵⁾ and Larsen⁶⁾, the size of the gas bubble in the open hearth is supposed to have a dimension of about 1 cm. Consequently, the present discussion may be a reasonable explanation for the phenomena concerning the gas bubbles in liquid iron.

V. Rate of Carbon-Oxygen Reaction in the Open Hearth

This problem has been extensively discussed by Darken³⁾⁵⁾. Here, a modified consideration is presented from a similar point of view. As shown in equation (2.4), the flow of carbon and oxygen from a bulk liquid to the surface being in chemical equilibrium must have the same number of respective atoms. Thus, one obtains

$$-\frac{d[C]}{dt} = \frac{3}{4} D_o \frac{[O] - [O]_{\Omega e}}{l \Delta l} \frac{S_g}{S_m} \quad (5.1)$$

$$-\frac{d[C]}{dt} = D_c \frac{[C] - [C]_{\Omega e}}{l \Delta l} \frac{S_g}{S_m} \quad (5.2)$$

where l is the depth of the liquid metals, S_g is the surface area between gas and metal, and S_m is that between slag and metal. $[O]_{\Omega e}$ and $[C]_{\Omega e}$ satisfy the relation

$$[C]_{\Omega e} [O]_{\Omega e} = K_{co\Omega} \quad (5.3)$$

From equations (5.1) and (5.2)

$$\frac{[C] - [C]_{\Omega e}}{[C] - [O]_{\Omega e}} = \frac{3}{4} \frac{D_o}{D_c} = \frac{1}{A} \quad (5.4)$$

Substituting equation (5.3) into (5.4), and putting $[O] \ll [C]$ A , one has

$$[O]_{\Omega e} = \frac{K_{co\Omega}}{[C] - [O]/A} \quad (5.5)$$

Using the limiting value of $[O]_{\Omega e}$ at $[O] \rightarrow 0$, equation (5.1) becomes the same equation as the one given by Darken, that is

$$-\frac{d[C]}{dt} = \frac{3}{4} D_o \frac{[O] - [O]_{ce}}{l \Delta l} \frac{S_g}{S_m} \quad (5.6)$$

The difference between the present equation (5.1) and Darken's equation (5.6) is shown by the following factor:

$$[O] - [O]_{\Omega e} \cong ([O] - [C]_{ce}) - \frac{K_{co}[O]}{[C]^2 A} \quad (5.7)$$

The second term on the right hand side represents the difference of concentration between that in Darken's equation and in the present theory. If $[O]$ is extremely smaller than $[C]$, the second term is unnecessary. However, the second term may be effective with a decrease of carbon concentration. In other words, the rate of carbon oxidation $-d[C]/dt$ becomes slower with advancement of the reaction, since $[O] - [O]_{\Omega e} < [C] - [C]_{\Omega e}$. This prediction is in agreement with some observations, showing a slow rate in high oxygen region¹⁰⁾.

VI. Measurement of Carbon Oxidation in Liquid Iron by Means of Oxygen Blowing

1. Experimental Method

It is interesting to study the rate of carbon-oxygen gas reaction in relation to the above mentioned mechanism. This procedure has been popular as a subsidiary technique in the open hearth process.

The experimental method for this problem is as follows. An alumina Tammann tube is charged with Fe-C alloy containing about 4% carbon weighing 40 g and set in a gas tight silica tube. When the alloy has been molten by induction heating, a mixture of nitrogen and oxygen gas, which is adjusted concerning its molar ratio, is induced in the depth of 5~8 mm into the liquid alloy through a high alumina blowing pipe (I.D. 6 mm). The amount of gas mixture entering into the liquid alloy is checked by a flow meter. CO gas generated due to carbon oxidation is measured by being converted into CO₂ through CuO maintained at 350~400°C and by being absorbed in soda lime by means of the ordinary combustion method.

2. Experimental Results

The rates of the present reaction measured at various flow rates of the gas mixture whose partial pressure of oxygen is equal to 150 mm Hg are represented in Fig. 1, in which carbon dioxide produced by carbon oxidation is plotted against the flow rate of the gas mixture. It is readily seen that the oxygen supplied is completely consumed in the cases of all flow rates. Therefore, it may

Fig. 1. Yield of carbon dioxide per minute as a function of rate of gas flow at 150 mm Hg of O₂ pressure and 1550°C (Straight line represents the complete consumption of O₂.)

be emphasized that the rate of the chemical reaction which may occur on the interface between the liquid iron and the gas phase is sufficiently rapid to be settled by a supply of reacting species.

The rates against the variations in oxygen pressure are shown in Table 1 and the degree of decarbonization versus oxygen pressure is represented in Fig. 2. The full line, the best curve through the points over the range of oxygen pressure less than 300 mm Hg, shows a relation of perfect consumption of oxygen supplied for carbon oxidation, while the dotted line, valid for oxygen pressure higher than 300 mm Hg, represents the constant rate of carbon oxidation independent of oxygen pressure. This is probably due to the fact that the rate-determining factor exists in a sluggishness of transfer of reactants (i.e. carbon) towards the surface where chemical equilibrium may occur.

3. Interpretation of the Present Data

In view of the points indicated in the preceding section, the following assumptions could reasonably be made to explain the experimental results:

i) When the amount of oxygen supply is very small, the rate of the reaction is determined by the

Table 1. Effect of partial pressure of oxygen gas on carbon oxidation

Partial pressure of O ₂ (mmHg)	Flow rate (cc/min)	CO ₂ produced per minute (gr/min)	Efficiency of carbon oxidation* (%)
25	60	0.009	124
50	60	0.018	120
50	150	0.036	98
75	55	0.020	101
150	60	0.045	102
150	60	0.046	104
300	60	0.088	100
300	60	0.086	97
380	60	0.106	97
380	60	0.087	79
450	60	0.097	74
450	60	0.091	69
600	60	0.106	62
600	60	0.106	60
600	60	0.237	48

* Efficiency of carbon oxidation is defined as twice the moles of carbon monoxide divided by the moles of oxygen supplied.

Fig. 2. Yield of CO₂ per minute as a function of partial pressure of O₂, with fixed flow rate, 60 cc/min, at 1550°C

rate of the oxygen supplied. (100% efficiency).

ii) When the amount of oxygen supply is too large, the rate of the reaction is determined by the flow of carbon through the boundary layer (diffusion film) near the bubbles. (less than 100% efficiency). For this case we have equation (6.2) from the discussion of the diffusion film theory.

$$-\frac{d[C]}{dt} = \frac{D_c S_{gm}}{V} \frac{[C] - [C]_\Omega}{\Delta l} \quad (6.2)$$

where V is the volume of liquid iron, and S_{gm} is the surface area of gas bubbles in contact with liquid iron. Integrating equation (6.2) from time t_i to t , the amount of carbon atoms removed from liquid iron to a single bubble is evaluated by

$$\xi = \frac{\rho V}{1200} ([C]_i - [C]_\Omega) \left\{ 1 - \exp \left[-\frac{D_c S_{gm} (t - t_i)}{V \Delta l} \right] \right\} \quad (6.3)$$

where $[C]_i$ is the initial concentration of carbon and ξ is expressed in terms of the number of gram atoms of carbon. Considering $D_c \cong 1 \times 10^{-4}$ cm²/sec, $\Delta l \cong 0.01$ cm and $V \cong 6$ cc, (6.3) becomes

$$\xi = \frac{\rho D_c S_{gm}}{1200 \Delta l} (t - t_i) \{ [C]_i - [C]_\Omega \} \quad (6.4)$$

as long as $S_{gm} (t - t_i) \ll 10^3$ cm²/sec. For a single gas bubble, emerged from the blowing tube, which reacts with carbon in liquid iron equation (6.4) may be reasonable, because the bubble is very short in life and small in surface area due to its shallow depth and its narrow outlet. The total amount of carbon taken away from liquid iron is

$$\Xi = \sum_n \xi_n \cong \frac{\rho n}{1200} \cdot \frac{D_c S_{gm} (t - t_o)}{\Delta l} \left\{ \frac{[C]_{1i} + [C]_{ni}}{2} - [C]_\Omega \right\} \quad (6.5)$$

where ξ_n means the amount of carbon for the n th bubble and $[C]_{ni}$ is the initial concentration in the n th bubble. S_{gm} and the life of a single bubble ($t - t_o$) are assumed to be common to every bubble. Furthermore,

$$\sum_n [C]_n = n \frac{[C]_{1i} + [C]_{ni}}{2} \quad (6.6)$$

Thus, numerical evaluation of equation (6.5) gives approximately

$$\Xi \cong 1 \times 10^{-2} S_{gm} (t - t_i) \quad (6.7)$$

in units of mole/min. It is supposed that the order of magnitude of $S_{gm} (t - t_i)$ might be 10^{-1} in the present experiment. This value ($\Xi \cong 1 \times 10^{-3}$) is in rough agreement with observed values in the region of oxygen pressure higher than 380 mm Hg, since 3×10^{-3} (mole/min) corresponds to yield in Fig. 2. The proposed mechanism from the diffusion film theory may be qualitatively reasonable for an explanation of the present experimental result.

Finally it is to be noted that in present experiment a side reaction such as

can occur simultaneously with (6.1). The effects of such refractory-metal reactions may correspond to the 120% efficiency of the reaction (6.1) in Table 1, according to the preliminary experimental data in this laboratory.

VII. Summary

The reaction of carbon oxidation in liquid iron,

should be rapid in true terms of homogeneous chemical reaction. This can be confirmed by the fact that

is very rapid in the present experiments, as well as by the theoretical reason of the absolute reaction rate theory. The most reasonable view for the rate-determining step of the above reaction may be obtained from the "diffusion film theory". Then, the thickness of the diffusion layer is briefly discussed in terms of the Reynolds number of liquid iron. The origin and growth of CO gaseous bubble are explained from the point of view of the "theory of heterogeneous phase transformation" and the "theory of diffusion film". It is to be noted that the effect of viscosity is limited to the narrow region near the boundary interfaces between heterophases but leads to an apparently slow chemical reaction owing to the retarding transport of materials.

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