Kinetics of Carbon- and Oxygen-transfer between CO-CO₂ Mixture and Molten Iron*

By Koin ITO,** Kazuo AMANO*** and Hiroshi SAKAO****

Synopsis

Measurements have been done on the rates of carbon and oxygen transfers between CO-CO₂ mixtures and levitated iron droplets. Supposing that the mass transfer between two phases determines the total reaction rate, the kinetics of this reaction has been considered. Results obtained here are as follows: The form of the reaction in the initial period is different from that in the later period. In the initial, simple absorption of gas takes place independently of the composition of the gas mixture. The rate is controlled by the mass transfer at the melt side. In the later period, decarburization or carburization proceeds and the countercurrent flow of CO and CO₂ in the gas phase controls the total rate. It is concluded that whether iron is melted by the levitation technique or in usual crucibles, there are no essential differences in the mechanism of the reaction, and that one or both of the mass transfers at gas and melt determines the total rate of the reaction according to the experimental conditions such as the flow rate and composition of gas, mass and violence of stirring of melt.

I. Introduction

As the transfer of carbon and oxygen between molten iron and CO-CO₂ mixture is one of the most important processes in steelmaking, so has been studied by many investigators. For example, Tsuchiya *et al.*¹⁾ studied on the kinetics of carbon transfer from CO gas to molten iron and found the activation energy of the reaction to be -19 kcal/mol. Kajiwara *et al.*²⁾ measured the rate of carbon transfer from graphite to molten iron by CO gas as the carbon carrier. Parlee *et al.*,³⁾ Solar and Guthrie,⁴⁾ and King *et al.*⁵⁾ measured the rate of absorption and desorption by means of Sieverts method. They proposed various mechanisms to the absorption and desorption. However, their propositions were not necessarily in good agreement with each other. Moreover, it is thought to be unreasonable that the negative value of the temperature dependence of the overall rate of carburization was caused by the activation energy of the chemical reaction at the interface.^{1,2,6)}

The authors have studied on the kinetics of reactions between molten iron and various gas phases.^{7,8)} There, the mass transfer between molten iron and gas was assumed to be the rate determining step, and the rate of the reaction of every couple was satisfactorily explained. And here, the rates of carbon and oxygen transfers between molten iron and CO-containing gases were measured by using the levitation melting technique and were analyzed by the rate equations derived from the assumption that the mass transfers

between molten iron and gas controlled the overall rate of reaction. Present informations were applied also to analyze the rate of CO absorption by iron melted in the crucible.

II. Experiments

1. Levitation Melting

1. Apparatus

The schematic diagram of the part of the reaction chamber of levitation melting is shown in Fig. 1. The levitation coil was made by winding a copper tube (4 mm O.D.) by 7 turns naturally and by 2 turns reversely. The high frequency generator used was of 350 kHz and its power was 15 kVA. The lower part of the reaction tube was made of a transparent quartz tube (12 mm I.D. and 100 mm length) and was frequently exchanged because it was spoiled by the deposition of iron vapor and of carbon resulted from the thermal decomposition of CO gas. The compositions of cylinder gases used here were as follows.

Ar: Ar > 99.95 %, O₂ < 0.0001 %, N₂ < 0.0005 %, H₂O < 0.005 mg/l

CO: CO > 99.8 %, O₂ < 0.02 %, N₂ < 0.1 %, H₂ < 0.02 %, CO₂ = trace

Fig. 1. Schematic diagram of experimental apparatus.

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** Formerly Faculty of Engineering, Nagoya University. Now at Toyohashi University of Technology, Tempaku-cho, Toyohashi 440.

*** Formerly Graduate School, Nagoya University. Now at Industrial Research Institute, Aichi Pref. Government, Hitotsugi-cho, Kariya 448.

**** Faculty of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464.

CO₂: CO₂=99.994 vol%, H₂O=2.89 wt.ppm, the dew point=-63 °C.

Argon gas was purified by passing through the inert gas purifier, but CO and CO₂ were used from cylinders without purification. Each gas was flown into the reaction chamber through each flowmeter. The temperature of melt was measured by the two color thermometer calibrated at melting points of Ni, Fe and Cr, and its accuracy was ±5 °C. The reaction time was measured by a stop watch and its accuracy was ±0.1 sec.

2. Preparation of Iron Specimen

The apparatus used here was the same as shown in the previous paper.⁷⁾ Electrolytic iron was inductively melted in a magnesia crucible and was deoxidized by H₂-Ar gas mixture sufficiently. Then molten iron was sucked into quartz tubes (5 mm I.D.) and was quickly water-cooled. Iron rods thus obtained were polished and cut to prepare the specimens for the levitation melting. Its weight was 1.35 g, and the oxygen concentration was 0.002 %.

3. Operation

Iron specimen was held by a quartz stand at the center of the coil and argon gas was flown. When the high frequency power was supplied, the specimen was levitated and melted in about 25 sec. The iron droplet was held at the reaction temperature in argon flow (0.5 l/min) for 2 min, and then the atmosphere was changed to CO or CO-CO₂ gas. When a scheduled reaction time passed, the melt was quenched by holding up the water-cooled copper mold with *ca.* 4 mg of aluminum for killing the melt and by cutting off the electric power. The sample was divided into four pieces for the analysis.

2. Crucible Melting

1. Apparatus

The apparatus used was the same as that used to the preparation of specimens for levitation melting with the exception that the CO and CO₂ gas suppliers were added through each flow meters.

2. Operation

After a certain amount of electrolytic iron charged in a magnesia crucible was inductively melted in an argon atmosphere, iron was deoxidized to the scheduled oxygen concentration by blowing H₂-Ar (1:1) for the time estimated from the rate of reduction.⁹⁾ Then the atmosphere was again changed to argon gas for 10 min to remove hydrogen in melt perfectly and to control the temperature. Thereafter, the absorption of CO or CO-CO₂ gas was started by blowing the gas (1 500 cc/min) at 1 600 °C. During the reaction, 3~5 g of molten iron was taken out several times with suitable intervals by a quartz tube to obtain the sample for analysis.

3. Analysis

The concentrations of carbon and oxygen in the sample were measured by the autocoulometry, and their accuracies were ±5 ppm.

III. Experimental Results

1. Levitation Melting

Measurements were done on the absorption of CO gas at the temperature range from 1 800 to 2 100 °C. Concentration changes of carbon and oxygen in melt are shown in Figs. 2 and 3, respectively. In Fig. 2, the oxygen concentration increased within 10 sec from the initial concentration to about 0.06 % and then decreased slowly. On the other hand, the carbon concentration increased as shown in Fig. 3 quickly at the same initial period but the increasing rate of carbon concentration decreased suddenly after the time when the corresponding oxygen concentration began to decrease.

The absorptions of CO-CO₂ mixtures with various partial pressures of CO₂ were measured at 1 825 °C, and the results are shown in Figs. 4 and 5. In every case, the start of reaction retarded by a few seconds. Thereafter, the process of absorption of CO-CO₂ was similar with that of the absorption of CO, with the exception of the cases where the volume fraction of CO₂ was 1.16 and 5 %.

In order to investigate minutely the behavior of the concentration change in the initial period, measure-

Fig. 2. Change of oxygen concentration during the reaction with pure CO at various experimental conditions.

Fig. 3. Change of carbon concentration at the same conditions as shown in Fig. 2.

ments were repeated on the absorption of CO. Here, the reaction time was measured more accurately by the pen recorder. This recorder consisted of a pen bound on an electromagnet and a rotating cylinder. The electric circuit operating the electromagnet was closed by rotating the three-way cock to start the absorption and was cut off by holding the water-cooled mould upto the sampling position. Measurements were done at 1 740, 1 800 and 1 860 °C, and the results are shown in Fig. 6. It is clearly seen that the absorption started at the reaction time $t=2.3$ sec. This time is thought to be the time required for the gas to reach to the surface of the iron droplet.

The weight loss of the iron droplet during the levitation melting caused by the vaporization of iron was about 2 mg/min. Accordingly, the changes of mass and specific area of the droplet during the reaction are thought to be negligibly small.

Fig. 4. Change of carbon concentration during the reaction with various CO-CO₂ mixtures at 1 825 °C.

Fig. 5. Change of oxygen concentration during the reaction shown in Fig. 4.

2. Crucible Melting

Measurements were done at 1 600 °C by using magnesia crucibles of 40 and 30 mm I.D. The mass of iron melt was changed from 400 to 200 g. The results are shown in Fig. 7.

IV. Consideration

Absorption of carbon and oxygen from CO-CO₂ gas mixture into molten iron is thought to proceed by three steps as follows.

- (1) Transfers of CO and CO₂ gas molecules between the bulk of gas flow and the gas-metal interface
- (2) The chemical reactions at the interface
- (3) Transfers of carbon and oxygen between the interface and the bulk of melt

Fig. 6. Change of carbon and oxygen concentrations in the initial period of CO absorption.

Fig. 7. Change of carbon and oxygen concentrations of iron melt in the crucible during CO absorption at 1 600 °C.

The surface chemical reactions in the step (2) are assumed to be always in the equilibrium state because the reaction temperature is sufficiently high. Namely, the reactions

are always in equilibrium at the gas-melt interface. Thus next relations are given.

$$\frac{P_{\text{CO}_2}^s}{P_{\text{CO}}^s n_{\text{O}}^s} = K_1 \dots\dots\dots(4)$$

$$\frac{P_{\text{CO}}^s{}^2}{P_{\text{CO}_2}^s n_{\text{C}}^s} = K_2 \dots\dots\dots(5)$$

$$\frac{P_{\text{CO}}^s}{n_{\text{C}}^s n_{\text{O}}^s} = K_3 \dots\dots\dots(6)$$

where, K_1, K_2, K_3 : equilibrium constants of reactions (1), (2), and (3)

- P : the partial pressure of gas (atm)
- n : the concentration of solute (atom/cm³)
- subscripts: the species of gas or solute
- the values with superscripts s : those at the interface, respectively.

As the results, there forms a boundary layer having the gradient of partial pressure of gas components between the bulk of gas and the gas-melt interface, and this gradient is the cause of the motive force of transfer of gas species in the step (1). On the other hand, there forms another boundary layer having concentration gradients of carbon and oxygen between the interface and the bulk of melt, and the gradients become the motive force of transfers of solute species in the step (3). The rates of mass transfers in the step (1) are represented by

$$\dot{n}_{\text{CO}_2} = \frac{k_g}{RT} (P_{\text{CO}_2} - P_{\text{CO}_2}^s) \dots\dots\dots(7)$$

$$\dot{n}_{\text{CO}} = \frac{k_g}{RT} (P_{\text{CO}} - P_{\text{CO}}^s) \dots\dots\dots(8)$$

where, $\dot{n}$: the rate (mol/cm² sec)
 k_g/RT : the rate constant (mol/cm² atm sec).

The rates of mass transfers in the step (3) are represented by

$$\dot{n}_{\text{C}} = k_{\text{C}}(n_{\text{C}}^s - n_{\text{C}}) \dots\dots\dots(9)$$

$$\dot{n}_{\text{O}} = k_{\text{O}}(n_{\text{O}}^s - n_{\text{O}}) \dots\dots\dots(10)$$

where $k_{\text{C}}, k_{\text{O}}$: the rate constants in cm/sec.

One or both of the rates in steps (1) and (3) are thought to control the rate of the whole reaction.

The relations between the carbon and oxygen concentrations in melt during the reaction by the levitation melting at 1 800 to 1 825 °C are shown in Fig. 8. The curve **CBD** in Fig. 8 is obtained from the equations for the equilibrium between the concentrations of carbon and oxygen in molten iron and CO-CO₂ gas mixtures of total pressure 1 atm¹⁰⁾ by extrapolating to this temperature. The point **A** represents the composition of specimen at the start of the reaction. The gradient of the line **AB** is 4/3 which is

Fig. 8. Change of relations between carbon and oxygen concentrations during reactions at 1 825 °C.

equal to the ratio of the atomic weight of oxygen to that of carbon. The partial pressure of CO₂ equilibrating with the melt represented by the point **B** is evaluated to be about 0.007 atm by using the above mentioned equation for the equilibrium, and the value seems to be in good agreement with the present results. In each series of the present experiments with excepting the series where the volume fraction of CO₂ was 5 %, the relation between the concentrations of carbon and oxygen in the melt moves from **A** to **B** within 7 sec, and then moves from **B** to each equilibrium point on the curve **CBD**. From these observations, it is supposed that the reaction mechanisms before and after the concentration of carbon and oxygen reach to the point **B** are different from each other, or in other words, the principal reaction may take turns.

In the initial period of the reaction, *i.e.*, in the range from **A** to **B** in Fig. 8, it is clear from the gradient of the line **AB** that the oxygen and carbon absorptions proceed at the same molar rates. Accordingly it is seen that the rates of reactions (1) and (2) are the same. As the addition of reaction (1) to reaction (2) gives reaction (3), so only reaction (3) is to be taken into accounts. Namely, it is probable that the whole reaction is the same type as the simple absorption from a pure gas although the gas consists of CO containing CO₂ less than 1 %. Therefore, it is assumed that the components in the bulk of gas may be absorbed in whole. Thus the boundary layer at the gas side of the interface disappears, and the interfacial concentrations of carbon and oxygen in melt become to n_{C}^s and n_{O}^s , respectively, which are represented by point **B** in Fig. 8. Accordingly the rates of absorptions are to be formulated as follows.

$$\dot{n}_{\text{C}} = k_m(n_{\text{C}}^s - n_{\text{C}}) \dots\dots\dots(11)$$

$$\dot{n}_{\text{O}} = k_m(n_{\text{O}}^s - n_{\text{O}}) \dots\dots\dots(11')$$

Because $\dot{n}_{\text{C}} = \dot{n}_{\text{O}}$ in this period, k_{C} and k_{O} are replaced by the same k_m . There is the following relation among the rate of concentration change of solute, dn/dt and its flux, $\dot{n}$,

$\dot{n} = (dn/dt)(V/F) \dots\dots\dots(12)$

where, *V*: the volume of the melt
F: the interfacial area.

Then by integrating Eqs. (11) and (11') and converting the units of concentrations to weight percent, the following relation is obtained.

$$\ln \frac{\%C^{e'} - \%C}{\%C^{e'} - \%C^0} = \ln \frac{\%O^{e'} - \%O}{\%O^{e'} - \%O^0} = - \frac{F}{V} k_m t \dots\dots\dots(13)$$

where, %C⁰, %O⁰: the values at the start of the reaction.

By applying Eq. (13) to data shown in Fig. 6, the relations shown in Fig. 9 are obtained. It is clearly seen that the relations are almost linear. The values of *k_m* at each temperature are estimated from the gradients of these lines as follows:

Temp. (°C)	1 740	1 800	1 860
<i>k_m</i> (cm/sec)	0.094	0.108	0.116

And the temperature dependence is found to be 13 ± 5 kcal/mol. Degassing is the reverse reaction of gas absorption. Present values of *k_m* and its temperature dependence are nearly equal to those found in the study on the kinetics of CO degassing from the iron droplet by argon gas.¹¹⁾

On the nature of *k_m* as well as that of *k_g* at the interface between gas and liquid phases, various theories have been proposed in chemical engineering. For example, *k_m* in the liquid phase is assumed to be *D*/*δ* in the boundary layer theory where *D* is the diffusion constant of solute in the melt and *δ* the thickness of boundary layer,¹²⁾ and to be $\sqrt{2Dv/\pi a}$ in the expression derived by Kaplan and Philbrook¹³⁾ on the basis of the penetration theory where *v* is the velocity of the surface stream of melt and *a* the diameter of the droplet. However, the value of *δ* in the former is unmeasurable at present and is assumed to be 10⁻² to 10⁻³ cm in the experiments of the inductively melted

baths. Though *v* in the latter is measurable indirectly, *v* is estimated to be 1 to 10 cm/sec in the inductively melted baths.¹⁴⁾ The reliabilities of the penetration theory and of the boundary layer theory are much the same. The coefficients of mass transfers found in the previous papers scattered from 0.01 to 0.1 cm/sec at 1 600 °C, and the present values of *k_m* are thought to be located in this range.

After the relation between concentrations of carbon and oxygen in melt arrived at point **B** in Fig. 8, the relation moves from **B** to each equilibrium point along the curve **CBD**, i.e., it is clear that the concentrations change by keeping *n_Cn_O*=constant. Accordingly, the following relation is obtained.

$$\dot{n}_C = - \frac{n_C}{n_O} \dot{n}_O \dots\dots\dots(14)$$

The mass transfer of carbon is caused by reaction (2) and that of oxygen by reaction (1), and the sum of them is equal to that of CO₂ molecule. Thus,

$$\begin{aligned} \dot{n}_{CO_2} &= -\dot{n}_C + \dot{n}_O \\ &= \left(1 + \frac{n_C}{n_O}\right) \dot{n}_O \dots\dots\dots(15) \end{aligned}$$

By introducing Eqs. (7) and (10) into Eq. (15), the following relation is obtained.

$$\alpha(P_{CO_2} - P_{CO}^s) = \left(1 + \frac{n_C}{n_O}\right)(n_O^s - n_O) \dots\dots\dots(16)$$

where,

$$\alpha = \frac{k_g}{k_o RT}$$

P_{CO₂}^s=*K₁P_{CO}^sn_O^s* according to Eq. (4). By introducing this to Eq. (16), *n_O^s* is represented as

$$n_O^s = (\alpha P_{CO_2} + n_C + n_O) / \left(1 + \frac{n_C}{n_O} + \alpha K_1 P_{CO}^s\right) \dots\dots(17)$$

By introducing this *n_O^s* to Eq. (10) the rate equation of oxygen transfer is obtained as follows.

$$\dot{n}_O = \frac{k_g}{RT} \left(\frac{P_{CO_2} n_O - K_1 P_{CO}^s n_O^2}{n_C + n_O + \alpha K_1 P_{CO}^s n_O} \right) \dots\dots\dots(18)$$

Also the rate equation of carbon transfer is written from Eq. (14) as follows.

$$-\dot{n}_C = \frac{k_g}{RT} \left(\frac{P_{CO_2} n_C - K_1 P_{CO}^s n_C n_O}{n_C + n_O + \alpha K_1 P_{CO}^s n_O} \right) \dots\dots\dots(19)$$

Now, the values of *P_{CO}^s* and *P_{CO₂}^s* shall be considered for the cases of the present experiments. At the later period of the absorption from CO-CO₂ containing CO₂ less than 0.7 vol%, namely, during the reaction proceeds from **B** to **C** in Fig. 8, the total pressure *P* (1 atm in the present experiment)=*P_{CO}*+*P_{CO₂}* is approximately equal to *P_{CO}*. And *P_{CO}^s*+*P_{CO₂}^s*=*P*, but because *P_{CO₂}^s* is always less than 0.007 atm, it is possible to assume that *P_{CO}^s* is always approximately equal to *P_{CO}*. *n_O* is replaced by *P_{CO}*/*K₃n_C* according to Eq. (6) because the composition of the bulk of melt is on the curve **BC**. If these approximations are possible, the integration of Eq. (19) gives

Fig. 9. Relation between logarithm of the change of carbon concentration and reaction time by using data shown in Fig. 6.

$$\left(\frac{1}{K_1 P_{CO}} + \alpha + \frac{n_c^0}{P_{CO_2}}\right) \ln \frac{n_c - n_c^0}{n_c^0 - n_c^0} - \left(\frac{1}{K_1 P_{CO}} + \alpha\right) \ln \frac{n_c}{n_c^0} + \frac{1}{P_{CO_2}} (n_c - n_c^0) = \frac{F k_g}{V R T} t \quad \dots\dots\dots(20)$$

The first and second terms of the left hand side of Eq. (20) change remarkably at the low carbon concentration, and the third term changes remarkably at the high carbon concentration. In the case where pure CO gas is used, $P_{CO_2}=0$, and the integration of Eq. (19) gives

$$\left(\frac{1}{K_1 P_{CO}^s} + \alpha\right) \ln \frac{n_c}{n_c^0} + \frac{K_2}{2 P_{CO}^s P_{CO}} (n_c^0 - n_c^0) = \frac{F k_g}{V R T} t \quad \dots\dots\dots(21)$$

At the extent of carbon concentration higher than about 0.1 %, the first term of the left hand side of Eq. (21) becomes to be negligibly small compared with the second term. And so by assuming $P_{CO}^s = P_{CO}$, the following approximation is obtained.

$$(n_c^0 - n_c^0) = \frac{2 P_{CO}^2 F k_g}{K_2 V R T} t \quad \dots\dots\dots(22)$$

By this equation, the relation between carbon concentration and time during the reaction between pure CO gas and the iron droplet shown in Fig. 3 was examined. The results of calculation are shown in Fig. 10. From the gradients of each lines the values of k_g in each series, *e.g.*, at 1 800 °C, are found to be

Gas flow rate (cc/min)	300	573
k_g (cm/sec)	8.1	12

where the mean value of the temperature of the droplet and that of bulk of gas is used as T in Eq. (22), *i.e.*, as the temperature of the gas boundary layer. The temperature dependence of k_g/RT is found to be about 2 kcal/mol.

By the expression derived by Ranz and Marshall from the rate of vaporization of floating droplet,¹⁵⁾ k_g is estimated to be 7.9 cm/sec at 1 800 °C and gas flow

rate 600 cc/min. On the other hand, Baker *et al.*¹⁶⁾ and Distin *et al.*¹⁷⁾ studied on the kinetics of decarburization of iron by the levitation technique and used the expression derived by Steinburger and Treybal¹⁸⁾ which was formulated taking accounts of natural convection caused by the temperature gradient in the gas phase around the molten droplet. By this expression, k_g is estimated to be 12.5 cm/sec under the same conditions. Present results of k_g are in better agreement with those calculated from the latter expression than those from the former.

It is clearly shown in Fig. 3 that the rate of carbon absorption from pure CO gas in the range from point **B** in Fig. 8 to the equilibrium point decreases considerably in accordance with the increase of temperature. That is to say, the temperature dependence of the overall rate constant of CO absorption is found to be -27 ± 4 kcal/mol, and so is undoubtedly negative as well as many investigators reported previously.^{1,2,6)} However, as clearly seen in Eq. (22), the overall rate constant contains the equilibrium constant of reaction (2). Accordingly, the Arrhenius equation in this case becomes

$$k = A e^{-E_A/RT} = A' e^{-(E_A + \Delta H)/RT}$$

Then it is concluded that the apparent temperature dependence of the overall reaction is the sum of that of the rate of gas transfer, *ca.* 2 kcal, and the enthalpy change of the reverse reaction of reaction (2), -34.6 kcal. As the results, it is supposed that the temperature dependence of the overall rate of the reaction is found to be negative as mentioned above.

The changes of carbon and oxygen concentrations in the reactions between CO gas and iron melted in crucibles shown in Fig. 7, proceeded without any refracting point which distinguish the initial period of the reaction and the later, differently from those shown in Figs. 2 to 5. From the results shown in Fig. 7, the relations between carbon and oxygen concentrations in cases where the crucibles of 40 mm I.D. were used are shown in Fig. 11, where the dotted line

Fig. 10. Relation between square of carbon concentration and time during reactions with pure CO gas.

Fig. 11. Change of relations between carbon and oxygen concentrations of iron melt in crucible during CO absorption.

represents the equilibrium relation with $P_{\text{CO}} + P_{\text{CO}_2} = 1$ atm obtained in these series, but this is considerably lower than the recommended values¹⁰⁾ because of the technical difficulty of aluminum-kill at the sampling of melt in this region. In Fig. 11, the marks, ● represent some compositions of melt at arbitrary times, the broken lines are the tangents of the curve at each ●, and the marks ○ are the cross points of the tangents and the dotted line. If the interfacial composition remains at ○, it is obvious that the composition of the bulk of melt changes from ● to ○ along the broken line. Then it is supposed that ○ represents each corresponding interfacial concentrations and $P_{\text{CO}_2}^*$. But because F/V in these cases is very small in comparison with those in levitation melting, it is thought that the rates of concentration changes of carbon and oxygen in the bulk of melt are so slow that $P_{\text{CO}_2}^*$ and the corresponding n_c^* and n_o^* do not keep up the nearly constant value as represented by point B in Fig. 8. Namely, ○ moves to the equilibrium point, i.e., $P_{\text{CO}_2}^* = 0$ along the dotted line. As the results, so soon as the reaction starts, the concentrations of carbon and oxygen in the bulk of melt change gradually in the direction to the moving point of $P_{\text{CO}_2}^*$. It is also clearly seen that the reverse reactions of (1) and (2) take place at different weight varying with the reaction time. The difference of the weights of reactions must be correspondent to the rate of formation of CO_2 at the interface, and so the following equation is given from Eqs. (7), (9) and (10),

$$-\frac{k_g}{RT}P_{\text{CO}_2}^* = k_c(n_c^* - n_c) - k_o(n_o^* - n_o) \quad \dots\dots(23)$$

From the relation shown in Fig. 11 and Eq. (23) by assuming $k_g = 6.4$ cm/sec which is the mean value obtained by the measurements of rate of degassing previously,¹¹⁾ k_c and k_o are estimated to be as follows:

$$k_c = 0.056 \sim 0.045 \text{ cm/sec}$$

$$k_o = 0.050 \sim 0.041 \text{ cm/sec}$$

And these results are thought to be reasonable values in comparison with those obtained previously.

V. Conclusions

On the basis of the results of measurements of the rates of the reaction between $\text{CO}-\text{CO}_2$ gas and iron droplet by the levitation melting, considerations were done on the mechanism of the reaction. Supposing that the mass transfers between two phases determine the rate of total reaction, the following results were obtained.

(1) Type of the reaction in the initial period is

different from that in the later period.

(2) In the initial, a simple gas absorption takes place independently of the composition of gas mixture. The rate of the reaction is controlled by the mass transfer at the melt side.

(3) In the later period, carburization or decarburization proceeds respectively with the composition of gas and the countercurrent flow of CO and CO_2 in the gas phase controls the total rate. The negativity of temperature dependence of the carburization rate of iron melt by CO gas is also explained by the present assumptions.

(4) When iron is melted in usual crucibles, the rates of carburization and oxidation-deoxidation varied continuously. But it is shown that there are no essential differences in the mechanism of the reaction compared with the levitation melting.

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