Note

Reassessment of $\underline{\text{C}}+\underline{\text{O}}=\text{CO}(\text{g})$ Equilibration

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1. Introduction

The reaction between carbon and oxygen in molten iron is one of the most fundamental reactions in the iron- and steelmaking process, and many experiments have been carried out and the results are well summarized by Kawai and Mori.¹⁾ However, the close investigation on the interaction parameters shows very interesting factor. The values of interaction parameter between carbon and oxygen in weight percent standard state, $\varepsilon_{\text{C}}^{\text{O}}$, determined in the earlier studies^{2–6)} are in range from -0.4 to -0.6 , while the values from relatively later studies^{7–9)} are in range from -0.3 to even $+0.1$.

The interaction parameter between carbon and oxygen $\varepsilon_{\text{C}}^{\text{O}}$ was mostly determined from the equilibration between CO/CO_2 gas mixture and molten $\text{Fe}-\text{C}$ metal contained in CaO , MgO , Al_2O_3 or graphite crucible. In certain cases, a reaction furnace was designed to carry out the equilibration under high pressure up to 80 atm. However, several difficulties of the experiments have been pointed out: (i) precise control and analysis of CO/CO_2 ratio in gas due to very low CO_2 level, (ii) evolution of CO gas during the solidification of samples after equilibration and consequent addition of Al to prevent this oxygen loss, (iii) possible contamination of oxygen due to the adsorption of oxygen to graphitic specimens, (iv) very sluggish reaction between $\text{Fe}-\text{C}$ melt and CO/CO_2 gas especially at high C concentration.

In the present study, several representative experimental studies will be critically reviewed again, and the thermodynamics of the $\text{Fe}-\text{C}-\text{O}$ system will be reassessed based on more recent thermodynamic description of the $\text{Fe}-\text{C}$ system.

2. Thermodynamics

Carbon and oxygen can react together to produce CO gas:

The standard state of C and O_2 can be changed to the infinite dilution (Henrian) standard state using the following relationships:

$$\underline{\text{C}}_{\text{Henrian}} = \text{C}(\text{s}), \quad \Delta G_2^\circ = -RT \ln \gamma_{\text{C}}^\circ \quad (2)$$

$$\underline{\text{O}}_{\text{Henrian}} = 1/2 \text{O}_2(\text{g}), \quad \Delta G_3^\circ = -RT \ln \gamma_{\text{O}}^\circ \quad (3)$$

where γ_i° is the Henrian activity coefficient of i element. Then, the combination of reactions (1) to (3) can produce the well known reactions:

2.1. Classical Wagner Interaction Parameter Formalism

Using the Classical Wagner Interaction Parameter Formalism (CWIPF),¹¹⁾ the Gibbs energy of reaction (4) can be expanded:

$$\begin{aligned} \Delta G_4^\circ &= \Delta G_1^\circ - RT(\ln \gamma_{\text{C}}^\circ + \ln \gamma_{\text{O}}^\circ) = -RT \ln(P_{\text{CO}}/a_{\text{C}}/a_{\text{O}}) \\ &= -RT \ln P_{\text{CO}} + RT \ln f_{\text{C}} + \ln x_{\text{C}} + \ln f_{\text{O}} + \ln x_{\text{O}} \quad (5) \end{aligned}$$

where f_{C} and f_{O} are the activity coefficients of C and O relative to the infinite dilution standard state given by:

$$\ln f_{\text{C}} = \varepsilon_{\text{C}}^{\text{C}} x_{\text{C}} + \varepsilon_{\text{C}}^{\text{O}} x_{\text{O}} + \cdots \quad (6)$$

$$\ln f_{\text{O}} = \varepsilon_{\text{O}}^{\text{O}} x_{\text{O}} + \varepsilon_{\text{O}}^{\text{C}} x_{\text{C}} + \cdots \quad (7)$$

where the ε coefficients are called first-order interaction parameters. Second or higher order interaction parameters can be included too. Note that $\varepsilon_{\text{C}}^{\text{C}} = \varepsilon_{\text{O}}^{\text{O}}$. These interaction parameters can be determined from the experimental data of the $\text{Fe}-\text{C}$ ($\varepsilon_{\text{C}}^{\text{C}}$), $\text{Fe}-\text{O}$ ($\varepsilon_{\text{O}}^{\text{O}}$), and $\text{Fe}-\text{C}-\text{O}$ ($\varepsilon_{\text{C}}^{\text{O}}$, $\varepsilon_{\text{O}}^{\text{C}}$) system.

In general, the molar Gibbs energy of the $\text{Fe}-\text{M}-\text{O}$ system, G , can be described by the CWIPF as follow:

$$\begin{aligned} G &= (x_{\text{Fe}} g_{\text{Fe}}^\circ + x_{\text{M}} g_{\text{M}}^\circ + x_{\text{O}} g_{\text{O}}^\circ) \\ &+ RT(x_{\text{Fe}} \ln x_{\text{Fe}} + x_{\text{M}} \ln x_{\text{M}} + x_{\text{O}} \ln x_{\text{O}}) \\ &+ RT(x_{\text{Fe}} \ln \gamma_{\text{Fe}} + x_{\text{M}} \ln \gamma_{\text{M}} + x_{\text{O}} \ln \gamma_{\text{O}}) \quad (8) \end{aligned}$$

where g_i° is the molar Gibbs energy of the i element in the Raoultian standard state, $\gamma_{\text{Fe}} = 1$, and γ_{M} and γ_{O} are activity coefficients. When the standard states of M and O are changed to their infinite dilution standard states,

$$\begin{aligned} G &= (x_{\text{Fe}} g_{\text{Fe}}^\circ + x_{\text{M}} g_{\text{M}}^\circ + x_{\text{O}} g_{\text{O}}^\circ) \\ &+ RT(x_{\text{Fe}} \ln x_{\text{Fe}} + x_{\text{M}} \ln x_{\text{M}} + x_{\text{O}} \ln x_{\text{O}}) \\ &+ RT(x_{\text{Fe}} \ln f_{\text{Fe}} + x_{\text{M}} \ln f_{\text{M}} + x_{\text{O}} \ln f_{\text{O}}) \quad (9) \end{aligned}$$

where $g_i^\circ (=g_i^\circ + RT \ln \gamma_i^\circ)$ is the molar Gibbs energy of i element in its infinite dilution (Henrian) standard state, $f_{\text{Fe}} = 1$, and f_{M} and f_{O} are activity coefficients relative to the infinite dilution standard state.

The CWIPF can accurately reproduce the measured deoxidation equilibria over a limited range of temperature and composition. However, the resultant equations extrapolate very poorly outside this range.

2.2. Unified Interaction Parameter Formalism

The CWIPF is very simple and useful for dilute solution, but it has been frequently misunderstood or misapplied to higher concentration range. The formalism obeys the Gibbs–Duhem equation only in the limit of infinite dilution. However, in the case of the $\text{Fe}-\text{C}-\text{O}$ system, $[\text{C}]$ interested for iron-making can reach up to carbon saturation, $\sim 5.0 \text{ wt\% C}$ at 1600°C ($x_{\text{C}} \sim 0.21$). The limit of the CWIPF can be overcome by the Unified Interaction Parameter Formalism (UIPF) by Pelton.¹²⁾ The equation of the UIPF can be exactly reduced to the original CWIPF at the infinite dilute solution. Thus, the UIPF used in the present study is a more general solution model covering to higher concentration range.

If only the first- and second-order interaction parameters are considered, the activity coefficient in Eqs. (6) and (7) for the $\text{Fe}-\text{M}-\text{C}$ system can be expanded by the UIPF as follows:

$$\ln f_{\text{M}} = \sum_{N=\text{M},\text{O}} \varepsilon_{\text{MN}} x_{\text{N}} + \sum_{N,\text{L}=\text{M},\text{O}} \varepsilon_{\text{MNL}} x_{\text{N}} x_{\text{L}} + \ln f_{\text{Fe}} \quad (10)$$

$$\ln f_{\text{O}} = \sum_{N=\text{M},\text{O}} \varepsilon_{\text{ON}} x_{\text{N}} + \sum_{N,\text{L}=\text{M},\text{O}} \varepsilon_{\text{ONL}} x_{\text{N}} x_{\text{L}} + \ln f_{\text{Fe}} \quad (11)$$

$$\ln f_{\text{Fe}} = -\frac{1}{2} \sum_{i,j=\text{M},\text{O}} \varepsilon_{ij} x_i x_j - \frac{2}{3} \sum_{i,j,k=\text{M},\text{O}} \varepsilon_{ijk} x_i x_j x_k \quad (12)$$

ε_{ij} is the first-order interaction parameter (identical to ε_i^j) between i and j solute elements, and $\varepsilon_{ij} = \varepsilon_{ji}$. ε_{ijk} is the second-order interaction parameter between i , j , k elements (identical to ε_i^{jk}), and $\varepsilon_{ijk} = \varepsilon_{ikj} = \varepsilon_{jik} = \varepsilon_{kji} = \varepsilon_{kij}$. When x_{M} and x_{O} approach to zero, $\ln f_{\text{Fe}}$ becomes diminished faster and the equations become equivalent to the CWIPF. General equations for the UIPF can be found elsewhere.¹²⁾

3. Evaluation of Fe–C–O Equilibrium

3.1. Review of Experimental Data

Several key experiments for the Fe–C–O system were critically reviewed in the present study.

The experimental data of Ban-Ya and Matoba³⁾ were mainly used for the thermodynamics of the Fe–C–O system in JSPS evaluation.¹⁾ Ban-Ya and Matoba equilibrated the Fe–C melts contained in CaO or MgO crucible with various CO/CO₂ gas mixtures. After equilibration, the samples were not directly quenched, but the power of an induction furnace was turned off and the crucibles were lowered to cool the samples as soon as possible. In order to prevent gas evolution from the melts containing [wt% C]<0.3% during solidification, about 0.5% Al was added 15 s before switching off the power. The melts containing [wt% C]>0.4% were thoroughly solidified without adding Al. The oxygen contents in samples were analyzed by the vacuum fusion method. As mentioned by Ban-Ya and Matoba, the intention to approach to equilibration state from both higher [C] side and lower [C] side was not always satisfactory for high carbon containing melts. Very small amount of CO₂ gas was mixed with CO for high carbon containing melts. For example, CO₂/CO ratios for the equilibration with liquid Fe containing 2 wt% [C] were less than 5×10^{-4} , which is difficult to control.

El-Kaddah and Robertson⁹⁾ used a high pressure levitation cell to minimize both carbon deposition changing the CO/CO₂ gas composition and effect of thermal diffusion in gas mixture. Gas pressures of CO/CO₂ mixtures were increased up to 80 atm in the temperature range from 1550 to 1750°C. Oxygen analysis was carried out by the vacuum fusion method. Specimens containing [wt% C]<2.0 at 1750°C showed CO evolution during solidification, but no evolution of CO was observed for the samples containing at [wt% C]>2.0. Thus, about 0.05% Al was added to the Fe–C melts containing [wt% C]<2.0 20 s before quenching the samples.

Schenck *et al.*⁴⁾ used a sealed graphite crucible. About 100–200 g of Fe–C alloy was added in the crucible with 1–2 g of solid Fe₂O₃ for oxygen source. Then, CO gas was generated by the reaction of Fe₂O₃ and [C] (or graphite crucible) at 1600°C. Although CO gas pressure could build up easily in a sealed crucible, total pressure of gas was not measured in their experiments. For example, 1 g of Fe₂O₃ can produce 2.9 L of CO gas at 1 atm and 1600°C. If the empty volume of a crucible is assumed to be 0.05 L, 1 g of Fe₂O₃ can generate total gas pressure of about 57 atm at 1600°C. Of course, oxygen solubility at given carbon content can be increased with total pressure of CO gas in a sealed crucible. Therefore, it should be noted that the experimental conditions of Schenck *et al.* were not well defined, and the results seem to be less reliable to use in the evaluation of the C–O equilibration.

Fisher and Janke⁶⁾ performed the C–O equilibration for the Fe–C melt containing $0.01 < [\text{wt}\% \text{ C}] \leq \text{carbon saturation}$ at 1600°C and 1 atm. CaO, MgO or graphite crucible was used. The experiments were carried out with decarburization route. Oxygen activity was also measured by an emf technique. They obtained very scattered results of oxygen content and activity in high carbon concentration range.

Marshall and Chipman²⁾ observed CO bubbling or blowholes in the quenched Fe–C samples containing $0.02 < [\text{wt}\% \text{ C}] < 2.0$ at 20 atm gas pressure. So they intentionally added small amount of Al before quenching process to keep the oxygen in liquid Fe–C. Later, Fuwa and Chipman⁷⁾ examined this system more carefully and reported the possibility of substantial errors in oxygen content of the previous experiments including their own experiment using Al addition.

As [Al] decreases the activity of oxygen significantly, it may increase the equilibrium oxygen content in liquid Fe–C. Thus, they performed the experiments at [wt% C]>2.0 where no Al addition was required. In addition, they found that oxygen or water vapor could be easily adsorbed on the porous graphitic surface of the Fe–C specimen. According to their experiment, the carbon-saturated specimen placed under vacuum immediately after preparation or analyzed immediately after experiment contained about 3 wt ppm oxygen. On the other hand, the samples treated as normal procedure contained oxygen up to 20 wt ppm. Based on this result, they claimed the most of samples in the previous studies might be contaminated and have excess oxygen. For example, Fuwa and Chipman⁷⁾ reported the equilibrium oxygen content at [wt% C]=2.0 is about 7 wt ppm at 1540°C under 1 atm CO atmosphere, while Ban-Ya and Matoba³⁾ reported about 20–30 wt ppm at the same condition.

Matsumoto⁸⁾ conducted the experiment at [C]>1 wt% without Al addition under 1, 4, 8 and 16 atm CO gas pressures at 1500°C and found consistent results with Fuwa and Chipman.⁷⁾ In particular, Matsumoto used both electrolytic iron with carbon and Fe–C alloy premelted in a vacuum furnace as starting Fe–C metal materials. Oxygen contents approached from higher oxygen content side (in case of the electrolytic iron with carbon) were the same as those approached from lower oxygen content side (in case of the premelted Fe–C) within experimental error limits. In this way, he confirmed the equilibration of his experiments. Oxygen content was analyzed by the vacuum fusion method.

Several studies including Marshall and Chipman²⁾ and El-Kaddah and Robertson⁹⁾ under normal pressure and higher gas pressure (up to 80 atm) claimed that CO bubbles were evolved from the Fe–C samples during the solidification at [wt% C]<2.0. However, it is strange why this phenomenon was not observed by Ban-Ya and Matoba³⁾ at $0.4 < [\text{wt}\% \text{ C}] < 2.0$ under 1 atm gas pressure.

The reported interaction parameters between carbon and oxygen (e_{O}^{C}) are quite different in the above experimental studies: $e_{\text{O}}^{\text{C}} = -0.42$ by Ban-Ya and Matoba,³⁾ $e_{\text{O}}^{\text{C}} = -0.13$ by Fuwa and Chipman,⁷⁾ $e_{\text{O}}^{\text{C}} = 0.075$ by El-Kaddah and Robertson,⁹⁾ and $e_{\text{O}}^{\text{C}} = 0.05$ by Matsumoto.⁸⁾ Moreover, the Henrian activity coefficient of C ($\gamma_{\text{C}}^{\text{H}}$) and self interaction parameter of carbon (e_{C}^{C}) used in the above studies are also different.

3.2. Activity of Carbon in Liquid Fe–C

Gustafson¹³⁾ performed critical evaluation and optimization of all thermodynamic and phase diagram data of the Fe–C system and presented the optimized Gibbs energy functions for all solid (FCC, BCC, Fe₃C and C) and liquid phases. The phase diagram of the Fe–C system is experimentally well determined and the experimental data are quite consistent with each other. In the case of activity of carbon for solid FCC and BCC solutions, the experimental data are consistent with each other. However, the activity of carbon of liquid phase is somewhat scattered at [wt% C]>1.0. Since the phase diagram is the representation of the Gibbs energy functions of all phases with temperature, the phase diagram information can constrain the Gibbs energy function of liquid phase (activity of carbon in liquid solution). In this way, the inconsistency of the activity data in liquid phase was resolved by Gustafson. The thermodynamic assessment of Gustafson is widely used by the Calphad community (for example, it is used for the commercial steel database of FactSage¹⁴⁾ and Thermocalc¹⁵⁾). In the present study, the Henrian activity coefficient and interaction parameters of C for liquid Fe–C were taken from the optimized model parameters of Gustafson, as listed in Table 1.

Table 1. Optimized Henrian activity coefficients and interaction parameters for the Fe–C–O system.

Fe–C system	
$C(s) = \underline{C}^{13)}$	
$\ln r_C^0 = 11578.5/T - 7.6137$	
$\varepsilon_{CC} = -64492.2/T + 0.6693$	
$\varepsilon_{CCC} = 536652.4/T - 229.467$	
$\varepsilon_{CCCC} = -396615.2/T + 152.978$	
Fe–O system	
$1/2O_2(g) = \underline{O}^{1,17)}$	
$\ln r_O^0 = -15280.0/T + 3.50$	
$\varepsilon_{OO} = -115309.0/T + 50.791$	
Fe–C–O system	
$C(s) + 1/2O_2(g) = CO(g): \Delta G_1^0 = -114959 - 85.668T^{10)}$	
$\varepsilon_{CO} = \varepsilon_{OC} = 0$ ($e_C^O = e_O^C = 0$): this study	

Figure 1 shows the activity of carbon calculated from Gustafson¹³⁾ along with experimental data. Both Ban-Ya and Matoba³⁾ and El-Kaddah and Robertson⁹⁾ determined the activity of carbon from the equilibration of the Fe–C melts with CO/CO₂ gas mixtures: $\underline{C} + CO_2(g) = 2CO(g)$. However, as can be seen in Fig. 1, the experimental results are quite different each other. The discrepancy may result from very sluggish equilibration between the Fe–C melt and CO/CO₂ gas mixture. Normally more than 10 h were required to achieve equilibration at high C concentration, and Ban-Ya and Matoba also mentioned that the results were not always satisfactory even after such a long equilibration time. In comparison with the optimized results of Gustafson,¹³⁾ the experimental data are in good agreement with the calculated curves at [wt% C] < 1.0. The deviation of Ban-Ya and Matoba becomes quite significant at [wt% C] > 1.0. The results of El-Kaddah and Robertson are lower than the calculations, but the deviation is less significant. This implies that both experimental data might have some error at [wt% C] > 1.0. In the case of Ban-Ya and Matoba, the error at high carbon concentration region might be induced also by the difficulty of very low CO₂ control (less than 0.1 volume %) in CO/CO₂ gas mixtures. In the case of El-Kaddah and Robertson, the CO₂ was controlled between 0.8 vol% and 8.7 vol%.

3.3. Activity of Oxygen in Liquid Fe–O

The Henrian activity coefficient and interaction parameters of O in the Fe–O liquid are relatively well known and the experimental data are more consistent each other. The parameters used in the present study are listed in Table 1, which are taken from recent study.^{1,14)}

3.4. Interaction between Carbon and Oxygen in Liquid Fe–C–O

Figure 2 shows the relationship between [C] and [O] in liquid Fe–C–O in equilibration with CO gas. In the experiments,^{2–9)} temperatures were varied from 1540 to 1750°C and total gas pressures were also varied from 1 to 80 atm. In principle, the equilibrium oxygen content in liquid Fe–C phase is increased with increasing temperature and pressure at the given carbon content.

Deoxidation curves of liquid Fe–C–O in Fig. 2 are calculated using the FactSage¹⁴⁾ thermochemical software with the UIPF¹²⁾ model and thermodynamic data in Table 1. It should be noted that the interaction parameter between carbon and oxygen is determined to be zero in the calculations. That is, $\varepsilon_O^C = \varepsilon_C^O$ ($e_O^C = e_C^O$) = 0. The calculated curves are not straight but slightly declining with the increase of

Fig. 1. Activity of carbon in liquid Fe–C phase relative to solid standard state. The curves are calculated using the optimized Gibbs energy functions for liquid Fe–C by Gustafson.¹³⁾

Fig. 2. Equilibrium [C] and [O] contents in liquid Fe–C–O in equilibration with CO gas at various temperatures and pressures. Curves are calculated using the interaction parameters $e_C^O = e_O^C = 0$.

[C] because of the self interaction parameters of carbon itself.

The calculated curves are in good agreement with the experimental data of Fuwa and Chipman⁷⁾ and Matsumoto⁸⁾ at [wt% C] > 1.0 and total pressure up to 8 atm. Experimental data of El-Kaddah and Robertson⁹⁾ at 40 atm total pressure are slightly lower than the calculated curves but they are in fair agreement within experimental error limit. The experimental data of Marshall and Chipman²⁾ up to 20 atm pressure are also in good agreement with calculated curves up to [wt% C] < 1.0.

In the case of Schenck *et al.*,⁴⁾ as discussed above in the Sec. 3.1, the experimental gas pressures were not well defined in their experiments due to the usage of a sealed crucible. If the empty volume of a sealed crucible is assumed to be 0.05 L, 1 g Fe₂O₃ would generate total gas pressure of about 57 atm at 1600°C. In this condition, the oxygen content at carbon saturation will be calculated to be log[wt% O] = −2.26 in the present study, which is close to the maximum value of their experimental data. In the case of 0.5 g of Fe₂O₃ in 0.05 L sealed crucible, the pressure would be about 28 atm at 1600°C and the calculated log[wt% O] = −2.56 at carbon saturation, which is close to their lowest experimental data. Big scatter of oxygen contents (from 40 to 85 ppm) at carbon saturation also raises doubts about their experimental results.

Large discrepancy between the present calculations and the experimental data of Ban-Ya and Matoba are found.³⁾ The experimental data are consistently slightly higher than calculated curves below [wt% C] < 0.5. Then, the oxygen content begins to deviate positively from calculations at [wt% C] > 0.5. It is hard to explain this deviation clearly. However, it is interesting to see that the activity of carbon

in Fig. 1 is also seriously deviated from optimal curves at $[\text{wt}\% \text{C}] > 1.0$. The results of Schenck and Hinze⁵⁾ are similar to Ban-Ya and Matoba. The results of Fisher and Janke⁶⁾ are also quite scattered at high carbon concentration (experimental data are scattered within dashed line boundary in Fig. 2). However, the minimum oxygen contents at the given carbon content are in good agreement with calculated curves at $[\text{wt}\% \text{C}] < 1.0$. Similar to the results of Ban-Ya and Matoba,³⁾ the experimental data begin to deviate positively at $[\text{wt}\% \text{C}] > 1.0$.

Fuwa and Chipman⁷⁾ reported the possible contamination of oxygen in the Fe–C sample at high carbon content. They reported that Fe–C metal sample can be easily contaminated by the atmosphere and about 20 wtppm excess oxygen can be adsorbed in the metallic sample after experiment. Similar results were also reported by Kusnetsov *et al.*¹⁶⁾ This means that the experimental results with lower $[\text{O}]$ seem to be more accurate than the higher $[\text{O}]$. If this error is considered for the results of Ban-Ya and Matoba,³⁾ for example, their results can be in good agreement with the present calculations too.

Recently the author presented the associate model¹⁷⁾ to accurately describe the deoxidation phenomena of molten iron by many deoxidizing elements including Ca, Mg, Ba, Al, Ti, Mn, Si, *etc.* In the case of C, no associates (CO or C_2O) are required. The evaluated thermodynamic data in Table 1 is incorporated to the FACT FeLq database¹⁴⁾ for the complex thermodynamic calculations between molten steel and slag/inclusion/refractory/gas.

4. Conclusions

Several key experimental studies on the Fe–C–O system

were critically reviewed and the interaction parameter between oxygen and carbon (e_{O}^{C}) is reassessed in the present study. Based on the optimized thermodynamic functions of carbon in the Fe–C system, it is suggested that $e_{\text{O}}^{\text{C}} = e_{\text{C}}^{\text{O}}$ ($e_{\text{O}}^{\text{C}} = e_{\text{C}}^{\text{O}} = 0.0$) can reproduce the reliable experimental data for the Fe–C–O system at iron- and steel-making conditions.

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