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Statistico-Thermodynamical Studies on Fundamental Reactions concerning Steel-Making. VI

On the Configuration of Fe-O Molten Slag and its Interaction with Gaseous Oxygen*

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Synopsis

The iron and oxygen atom-ratio of Fe-O melts is continuously variable by the change of oxygen pressure in the gaseous phase. It is very reasonable that we suppose Fe-O melts are constructed by ionic components Fe^{++} , Fe^{+++} and O^{--} , thanks to the previous results on Fe-O solid-solution phases (ref. previous Reports II and IV) and the electro-conductivity of melts. We assume the following configurational model for Fe-O molten system: (1) Oxygen ions O^{--} are arranged on the face-centered cubic lattice (nearly close-packed), because they are very large compared with iron ions. (2) Fe^{++} ions are distributed on the tetrahedral and octahedral interstitial lattice points of the oxygen-ion lattice. (3) If any tetrahedral lattice point is occupied by a iron ion, its nearest octahedral lattice points are vacant, and it is the same for the nearest neighbors of octahedral iron ions. (4) Positive holes are randomly distributed on Fe^{++} ions, and thus Fe^{+++} ions are formed. Using the above model the partition function of the Fe-O molten slag was formulated by the statistical thermodynamic method, and the equilibrium relation between the slag composition and the pressure of oxygen in gas phase was calculated. These theoretical results are in good agreement with the measured values of Darken and Gurry (1946) in the wide range of pressure, 10^{-10} to 1 atm of O_2 , and temperature 1400° to 1600°C .

I. Introduction

By measurement of the electromotive force, electric conductivity, viscosity and others, the thermodynamical and physical properties of molten slag have been gradually clarified, but we have not yet any consistent theory to interpret many properties concerning molten slags.

It has been proved that the assumptions, under which the Fe-O system in the solid state consists of iron ions, oxygen ions, lattice defects and electron deficits, and change in the relative amount of these quantities takes place accompanied by oxidation or reduction, are more effective for elucidation of thermodynamical properties for wüstite,⁽¹⁾ magnetite⁽²⁾ and hematite phases. Accordingly, we are now

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- (1) S. Takeuchi and K. Igaki, *Journal of the Japan Institute of Metals* **B14**(1950) 23; *Sci. Rep. RITU* **A4**(1953) 164 [Report II].
- (2) S. Takeuchi and K. Furukawa, *Journal of the Japan Institute of Metals* **19**(1954) 165; *Sci. Rep. RITU* **A12**(1960) 120 [Report IV].

proceeding to the study of slags in molten phases from similar view points. In this paper the Fe-O system in the molten state is taken up as the simplest of fundamental slag systems, and establishing a configurational model of iron and oxygen ions based on the results of our foregoing studies on the iron oxide phases and the known physical properties of such slags, the change of partial oxygen pressure against the change of composition in molten system is computed by statistico-thermodynamical treatment of such a model. Then these computed values are compared with the experimental values for discussing the adequacy of our model. We have the valuable data measured by Darken and Gurry⁽³⁾ ranging over the oxygen pressure of 10^{-10} to 1 atmosphere and temperatures of 1,400° to 1,600°C which are available for comparison.

II. Configuration of Fe-O slags in molten state

We have few studies on the configuration of the molten state of ionic crystals. We know that three phases of iron oxides, wüstite, magnetite and hematite have a typical ionic character, and are the solid solutions of wide ranges of oxygen ion concentrations. Therefore, we can assume that these are in the form of ionic bonds, not essentially different from the ionic crystal state, in their molten states having atom ratio widely varying from O/Fe=1.02 to 1.36, and such ionic nature can be proved from the measurement of electric conductivity in the molten state.⁽⁴⁾

These considerations lead to the inference that the force acting between the ions is a Coulomb force, so that the similar relation of negative ions located around positive ions as in solids is maintained in the molten state, and since such a force is effective to a far larger distance than in the case of other chemical bonding, a sort of regular arrangement like in a crystal is retained in a molten state too. This can be also inferred in that the fusion entropy is equal approximately to the increase of entropy produced by the volume expansion on melting.

It has been generally considered from the stand-point of the free volume theory of liquid that the atomic configurations in liquids can be physically supposed to be similar to that of solids. This theory is based on the assumption of the intuitive model in which the molecules (atoms) are distributed at appropriate lattice points and every one of the atoms is in gas-like thermal motion in the cell of the mean intermolecular force field produced between its neighbouring molecules.⁽⁵⁾ The partition function derived by such a model has been proved to correspond to the first approximation for the theoretically precise partition function.⁽⁶⁾ It is particularly powerful in interpreting the properties of melts of high density in the temperature range of not much higher than the melting point. Accordingly, we

(3) L.S. Darken and R.W. Gurry, *J. Am. Chem. Soc.* **68** (1946) 798.

(4) M.J. Simnad and G. Derge, *J. Chem. Phys.* **21** (1953) 933; J. O'M. Bockris, J.A. Kitchener, S. Ignatowicz and J.W. Tomlinson, *Trans. Far. Soc.* **48** (1952) 75; J. O'M. Bockris and H. Inouye, *J. Chem. Phys.* **20** (1952) 192.

(5) J.E. Lennard-Jones and A.F. Devonshire, *Proc. Roy. Soc.* **A169** (1939) 317.

(6) J.G. Kirkwood, *J. Chem. Phys.* **18**(1950) 380; J.E. Mayer and G. Careri, *J. Chem. Phys.* **20** (1952) 1001.

will introduce the free volume theory into our theoretical studies of the molten slag.

The exact structure of such melts can only be suggested by the x-ray diffraction analysis of molten state of slag, but we could not find the available data.

It has been known that wüstite, magnetite and hematite in solid phases consist of the NaCl type, the Spinel type and the Corundum type crystals respectively, in which the oxygen ions are all arranged in the close-packed types. The oxygen ions in wüstite and magnetite are close-packed in the face-centered cubic lattice and in hematite close-packed in the hexagonal lattice, and the small positive ions Fe^{++} and Fe^{+++} are arranged in the interstitial positions between the lattice of oxygen ions, that is, all of the Fe^{++} and Fe^{+++} ions are in the octahedral lattice points in the case of wüstite and hematite respectively, and all of the Fe^{++} ions and half of the Fe^{+++} ions in octahedral and the rest of the Fe^{+++} ions in tetrahedral lattice points in magnetite as shown in Table 1. It, therefore, seems reasonable to

Table 1.

	Wüstite	Magnetite	Hematite
Crys. struc	NaCl type	Inversed spinel type	Corundum type
Configuration of O^{--} ion	Cubic close packed	Cubic close packed	Hexagonal close packed
Configuration of Fe ion	Fe^{++} octahedral	Fe^{++} $Fe^{+++} \times \frac{1}{2}$) octahedral $Fe^{+++} \times \frac{1}{2}$ tetrahedral	Fe^{+++} octahedral

suppose that in the molten state also the oxygen ions are nearly as dense as close-packed, but as the distance between the oxygen ions is increased a little on melting, the positive ions may be in motion more freely than in the case of the solid. And then it may be supposed that the positive ions occupy the tetrahedral and then it may be supposed that the positive ions occupy the tetrahedral and octahedral interstices in an appropriate ratio different from the case of the solid. However, it would be very reasonable, to set down here a restricting condition that, if an iron ion Fe^{++} or Fe^{+++} occupies one of the tetrahedral lattice points, no other iron ion can enter into the nearest neighbouring octahedral lattice points due to the extreme proximity and the mutual repulsion acting at such a short distance. The same is applied to an iron ion occupying one of the octahedral lattice points. Next, as long as the atom ratio Fe/O is equal to 1, all the iron ions are Fe^{++} ions, but with the rise in oxygen concentration, electron deficits are created, that is, some of the Fe^{++} ions turn into Fe^{+++} ions, to keep the electric charge in balance.

From the above consideration we can assume the structural model of Fe-O molten system as follows:

1) The oxygen ions, O^{--} , in the molten Fe-O slag are located all in the close-packed type, forming the face-centered cubic lattice.

2) The positive ions, Fe^{++} , occupy some of the tetrahedral interstices (called lattice I) and of the octahedral interstices (called lattice II) of the oxygen lattice.

3) When one of the positive ions occupies a site of lattice I, its nearest neighbouring sites, which belong to lattice II, can not be simultaneously occupied by iron ions, and vice versa.

4) When the concentration of oxygen rises beyond that of the stoichiometric composition FeO, positive holes are formed, distributing statistically among the Fe^{++} ions and such a Fe^{++} ion turns into the Fe^{+++} ion. Lattice I is of simple cubic type with the edge length of its cube half as large as that of the face-centered cubic lattice consisted of O^{--} , and lattice II is a face-centered cubic type equivalent to the O^{--} lattice. In other words, O^{--} ions and sites of lattice II are alternately placed at the body centered positions of cubic lattice I.

III. Partition function of Fe-O molten system

From the model described above, the free energy of the Fe-O molten system is obtained if the partition function can be computed.

If the molten slag in consideration is composed of N_0 O^{--} ions, N_2 Fe^{++} ions and N_3 Fe^{+++} ions, the total partition function may be written formally as follows:

$$\Gamma_M = q_0^{N_0} \cdot q_2^{N_2} \cdot q_3^{N_3} \cdot \int \dots \int G(N_2, N_3) \exp \left[-E(N_2, N_3, N_0)/kT \right] \cdot \prod_{i=1}^N dv_i, \quad (1)$$

where $\prod_{i=0}^N$ denotes the product of volume elements of N_0 O^{--} ions, N_2 Fe^{++} ions; and q_0 , q_2 and q_3 are the functions depending only upon the temperature respectively, and written by

$$q_i = \sigma \cdot (2\pi m_i kT/h^2)^{3/2} \cdot j_i \quad (i=0, 2 \text{ and } 3) \quad (2)$$

m_i : mass of ion i

k : Boltzmann's constant

h : Planck's constant

and σ represents a physical quantity related with the so-called communal entropy⁽⁶⁾⁽⁷⁾ of liquid, and this quantity can not be precisely calculated theoretically, but known to be approximately 1 at high density of liquid and to take the value of e at low density. j_i , ($i=0, 2$ and 3), denotes the partition function for the internal degrees of freedom of ion and $G(N_2, N_3)$ the number of distinguishable configurations with N_2 Fe^{++} and N_3 Fe^{+++} ions among the sites of lattices I and II.

Since N_0 oxygen ions are arranged in a type of face-centered cubic lattice, the lattice sites in the lattices I and II should be $2N_0$ and N_0 respectively and all the iron ions $N_f = N_2 + N_3$ are distributed among these lattice points. If all of the iron ions were arranged simply at random among the sites of lattices I and II, $\frac{2}{3} N_f$ of iron ions would occupy the lattice I and $\frac{1}{3} N_f$ the lattice II. But the number of iron ions occupying the sites of lattice I (or II) would differ from $\frac{2}{3} N_f$ (or $\frac{1}{3} N_f$) because the arrangement must be controlled by the condition 3) described in paragraph II. If an iron ion Fe^{++} or Fe^{+++} occupies a site of lattice I, its

(7) J.S. Rowlinson and C.F. Curtiss; J. Chem. Phys. **19** (1951) 1519; J. de Boer, Proc. Roy. Soc. **A215** (1952) 4.

nearest neighbouring sites of the lattice II can not be occupied by any iron ion, and vice versa. We, therefore, must take this condition into the calculation of the number of distinct configurations.

Let pN_f iron ions occupy the lattice I and $(1-p)N_f$ the lattice II, and N_{ff} be the number of pairs of nearest neighbouring iron ions of which one iron ion occupies a site of the lattice I (or lattice II) and another ion a site of the lattice II (or lattice I) adjacent to the former site, and N_{fv} and N_{vv} denote for the numbers of pairs of an iron ion and a vacancy and of two vacancies in the nearest neighbour to each other respectively, then we have

$$\left. \begin{aligned} N_{ff} &= zpN_f\eta_f^f \\ N_{vf} &= z(2N_0 - pN_f)\eta_f^v \\ N_{fv} &= zpN_f(1 - \eta_f^f) \\ N_{vv} &= z(2N_0 - pN_f)(1 - \eta_f^v) \end{aligned} \right\} \quad (3)$$

where z denotes the number of sites in the lattice II adjacent to a site of the lattice I, and it can be considered to be equal to 4. η_f^f is the probability of a site of the lattice II closest to any iron ion in the lattice I being occupied by an iron ion, η_f^v the probability of a site of the lattice II closest to any vacancy site of the lattice I being occupied by an iron ion, η_v^f the probability of a site of the lattice II closest to any iron ion in the lattice I being unoccupied by iron ion, and η_v^v that of existence of the pair of vacant sites adjacent to each other. The probability η_f^v can be replaced by a term of η_f^f from the following relation ;

$$\begin{aligned} N_{ff} + N_{vf} &= 2z(1-p)N_f \\ \therefore \eta_f^v &= \frac{2z(1-p)N_f - zpN_f\eta_f^f}{z(2N_0 - pN_f)} = \frac{2(1-p)N_f - pN_f\eta_f^f}{(2N_0 - pN_f)} \end{aligned} \quad (4)$$

The required number of configurations $G(N_2, N_3)$ can be obtained approximately by taking $\eta_f^f = 0$ in the number of configurations $G(N_2, N_3, N_{ff})$ to a given values of N_2 , N_3 and N_{ff} (and so of N_{fv} , N_{vf} and N_{vv}). In the limit of random distribution we note that such a number of configurations $G(N_2, N_3, N_{ff})$ must be given by following formula ;

$$G_0 = \sum_{N_{ff}} G(N_2, N_3, N_{ff}) = \frac{(2N_0)!}{(pN_f)!(2N_0 - pN_f)!} \cdot \frac{N_0!}{[(1-p)N_f]! [N_0 - (1-p)N_f]!} \cdot \frac{N_f!}{N_2! N_3!}, \quad (5)$$

This sum is indeed the total number of ways we may distribute N_2 Fe⁺⁺ ions and N_3 Fe⁺⁺⁺ ions on $2N_0$ and N_0 sites in the lattices I and II. If we could assume that the number of configurations of pairs on the sites of lattices I and II may be calculated as if the various types of pairs did not interfere with one another, we would have

$$g(\eta_f^f) = \frac{(2zN_0)!}{N_{ff}! N_{fv}! N_{vf}! N_{vv}!} \cdot \frac{N_f!}{N_2! N_3!} \quad (6)$$

Formula (6) certainly overestimates the number of configurations because different pairs do interfere with one another and therefore $\sum_{\eta_f^f} g(\eta_f^f)$ does not completely agree with G_0 in (5), which is the number of distinguishable configurations in the case of the random distribution of iron ions. So we can correct this error by multiplying (6) by a factor $h(N_2, N_3)$ independent of N_{ff} in such a way that the total number of configurations is correctly given by (5)⁽⁸⁾. Using this procedure we have from (6)

$$G(N_2, N_3, N_{ff}) = h(N_2, N_3) \cdot g(\eta_f^f) \quad (7)$$

The factor $h(N_2, N_3)$ can be determined by

$$G_0 = \sum_{N_{ff}} G(N_2, N_3, N_{ff}) = h(N_2, N_3) \cdot \sum_{\eta_f^f} g(\eta_f^f) \quad .$$

The value of sum $\sum_{\eta_f^f} g(\eta_f^f)$ can be replaced by the maximum term in the summation without being accompanied by a serious error, and the maximum term can be determined by taking the value, say $\bar{\eta}_f^f$, of η_f^f satisfying the equation

$$\frac{\partial \log g(\eta_f^f)}{\partial \eta_f^f} = 0,$$

from which we have

$$\bar{\eta}_f^f = \frac{(1-p)N_f}{N_0} \quad (8)$$

Now the value of $\bar{\eta}_f^f$ which maximizes $g(\eta_f^f)$ is undoubtedly the one corresponding to the complete disorder. We have merely to substitute $\bar{\eta}_f^f$ into $g(\eta_f^f)$ to obtain a formula for $\sum g(\eta_f^f)$.

$$h(N_2, N_3) = \frac{G_0(p, N_2, N_3)}{\sum g(\eta_f^f)} = \frac{G_0(p, N_2, N_3)}{g(\bar{\eta}_f^f)},$$

and then we have

$$G(N_2, N_3, N_{ff}) = G_0(N_2, N_3, p) \cdot \frac{g(\eta_f^f)}{g(\bar{\eta}_f^f)} \quad (9)$$

The required formula for the correct number of configurations can be deduced from (9) by taking $\eta_f^f = 0$ and we have

(8) R.H. Fowler and E.A. Guggenheim: "Statistical Thermodynamics" (1939) Chap. 13.

$$\begin{aligned}
 G(N_2, N_3, p) = & \frac{[2N_0]!}{[pN_f]![2N_0 - pN_f]!} \cdot \frac{[N_0]!}{[(1-p)N_f]![N_0 - (1-p)N_f]!} \cdot \frac{[N_f]!}{[N_2]![N_3]!} \\
 & \times \frac{[zp(1-p)\frac{N_f^2}{N_0}]![z p N_f \{1 - \frac{(1-p)N_f}{N_0}\}]![z\{2(1-p)N_f - p(1-p)\frac{N_f^2}{N_0}\}]!}{[z p N_f]![z 2(1-p)N_f]!} \\
 & \frac{[z\{2N_0 - pN_f\} - 2(1-p)N_f + p(1-p)\frac{N_f^2}{N_0}]!}{[z\{(2N_0 - pN_f) - 2(1-p)N_f\}]!} . \quad (10)
 \end{aligned}$$

The parameter p included in this formula (10) can be estimated from the condition that the free energy of the molten state should take a minimum value for a certain value of p .

Next, we will discuss the energy of the molten state. Since the ions in molten state are presumed to be in motion over a rather wide extent around their mean positions, the potential energy of each ion should be considered as composed of the potential energy $E_i(o)$ at its mean position and the energy change $E_i(r) - E_i(o)$ due to its displacement from its mean position over a distance r , we have then

$$E = \sum_i E_i(o) + \sum_i \{E_i(r) - E_i(o)\}, \quad (11)$$

where \sum_i means the sum for all the ions O^{--} , Fe^{+++} and Fe^{+++} . Now, if the potential energy of the Fe^{++} and Fe^{+++} ions in lattice I to the surrounding ions are denoted by U_2^I , U_3^I , that of the Fe^{++} and Fe^{+++} ions in lattice II by U_2^{II} , U_3^{II} , and the potential energy of O^{--} ion by U_0 , then we have

$$E(o) = pN_2 \cdot U_2^I + (1-p)N_2 \cdot U_2^{II} + pN_3 U_3^I + (1-p)N_3 U_3^{II} + N_0 U_0. \quad (12)$$

We must now consider on the difference of energies U^I and U^{II} of Fe ions occupying sites of lattices I and II. It has been assumed in the paragraph II that the Fe ions are able to distribute themselves at random on the sites of lattices I and II under the restriction which any others of the Fe ions cannot occupy every nearest neighbouring sites to a site occupied by any one Fe ion. This means that the energy of any Fe ion in the lattice I cannot be much different from that of the same kind of Fe ion in lattice II. And since it is considered that in the molten state the thermal motion may be larger than in the solid state and the field of force may be well equalized around the sites in lattices I and II occupied by the same kind of Fe ion, we can put as follows,

$$U = U^I = U^{II}. \quad (13)$$

And also as it is known that in an ionic crystal, lattice energy is not much different in an inversed as well as a normal spinel, in the molten state the assumption (13) may be considered as a good approximation.

We can have a simplified formula of energy from (13) and (12),

$$E(o) = N_2 U_2 + N_3 U_3 + N_0 U_0 \quad (14)$$

Similarly we can know easily that the sum $\sum \{E_i(r) - E_i(o)\}$ is also independent

of p . Accordingly, the integration in (1) can be performed independent of the configurations of iron ions from the above consideration, we have then

$$\int \cdots \int G\{N_2, N_3, N_0\} \exp\{-E(N_2, N_3, p)/kT\} \Pi dv_i \\ = v_0^{N_0} \cdot v_2^{N_2} \cdot v_3^{N_3} \cdot G(N_2, N_3, p) \exp\{-E(o)/kT\}, \quad (15)$$

where v_i denotes the free volume around an ion and it is written as

$$v_i = \int_{\text{cell}} \exp\{-[\bar{E}_i(r) - E_i(o)]/kT\} dr. \quad (16)$$

Thus, the total partition function Γ_M in (1) can be written as follows;

$$\Gamma_M(T) = (q_0 v_0)^{N_0} \cdot (q_2 v_2)^{N_2} \cdot (q_3 v_3)^{N_3} \cdot G(N_2, N_3, p) \exp\{-E(o)/kT\}, \quad (17)$$

where $G(N_2, N_3, p)$ and $E(o)$ are given by (10) and (14) respectively.

The free energy of Fe-O system in molten state is calculated from the partition function:

$$\begin{aligned} F_M &= -kT \log \Gamma_M \\ &= E(o) - kT(N_0 \log q_0 v_0 + N_2 \log q_2 v_2 + N_3 \log q_3 v_3) \\ &\quad - kT[2N_0 \log 2 + 3N_0 \log N_0 - pN_f \cdot \log pN_f - (2N_0 - pN_f) \cdot \log(2N_0 - pN_f) \\ &\quad - \{(1-p)N_f\} \log\{(1-p)N_f\} - \{N_0 - (1-p)N_f\} \log\{N_0 - (1-p)N_f\} + N_f \cdot \log N_f \\ &\quad - N_2 \log N_2 - N_3 \log N_3] \\ &\quad - zkT \left[p(1-p) \frac{N_f^2}{N_0} \log p(1-p) \frac{N_f^2}{N_0} + pN_f \left\{ 1 - \frac{(1-p)N_f}{N_0} \right\} \log pN_f \left\{ 1 - \frac{(1-p)N_f}{N_0} \right\} \right. \\ &\quad \left. + \left\{ 2(1-p)N_f - p(1-p) \frac{N_f^2}{N_0} \right\} \log \left\{ 2(1-p)N_f - p(1-p) \frac{N_f^2}{N_0} \right\} \right. \\ &\quad \left. + \left\{ (2N_0 - pN_f) - 2(1-p)N_f + p(1-p) \frac{N_f^2}{N_0} \right\} \log \left\{ (2N_0 - pN_f) - 2(1-p)N_f + p(1-p) \frac{N_f^2}{N_0} \right\} \right. \\ &\quad \left. - pN_f \log pN_f - 2(1-p)N_f \cdot \log 2(1-p)N_f \right. \\ &\quad \left. - \left\{ (2N_0 - pN_f) - 2(1-p)N_f \right\} \cdot \log \left\{ (2N_0 - pN_f) - 2(1-p)N_f \right\} \right]. \quad (18) \end{aligned}$$

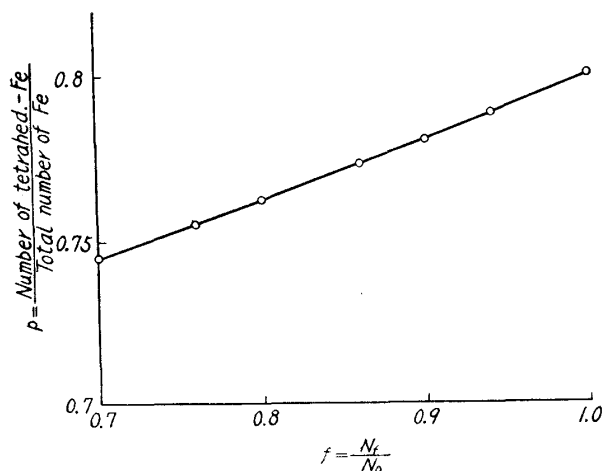


Fig. 1. Variation of the parameter p with composition of liquid iron-oxide.

The parameter p denoting the ratio of iron ions in the lattices I and II can be determined from the thermodynamical condition that the free energy F_M must have a minimum value in respect to p , and so p can be obtained as the root satisfying the following equation,

$$\frac{\partial F_M}{\partial p} = 0.$$

If we carry out the computation of the above equation, we obtain

$$2(1-p) \left\{ 1 - (2-p) \frac{N_f}{2N_0} + 2p(1-p) \left(\frac{N_f}{2N_0} \right)^2 \right\} = p \left\{ 1 - (2-p) \frac{N_f}{2N_0} \right\} \left(\left(1 - p \frac{N_f}{2N_0} \right) \right). \quad (19)$$

The value of p calculated from (19) graphically is dependent of the ratio N_f/N_0 as shown in Fig. 1 and increases with the decrease of oxygen content becoming 0.8 at $\frac{N_f}{N_0} = 1$, the stoichiometric composition of FeO.

IV. Calculation of oxygen pressure in the equilibrium Fe-O system in molten state

The partition function of gaseous oxygen is written as follows:

$$\Gamma_g = \frac{1}{n_{O_2}!} \cdot \{f_{O_2} \cdot \exp[-\chi_{O_2}/kT]\}^{n_{O_2}} \quad (20)$$

where χ_{O_2} and f_{O_2} denote the dissociation energy and the partition function of oxygen molecules respectively, n_{O_2} number of oxygen molecules in the gaseous phase.

The free energy of gaseous phase of oxygen is given by

$$F_g = -kT \log \Gamma_g = n_{O_2} \cdot \chi_{O_2} + n_{O_2} \cdot kT [\log n_{O_2} - \log f_{O_2} - 1]. \quad (21)$$

When the gaseous phase and the molten phase are in equilibrium at given temperature, the total free energy of the system must have a minimum value. It follows, then, at the given temperature,

$$\delta F_g + \delta F_M = 0. \quad (22)$$

And we have the following relations between the concentration variables;

$$\begin{aligned} N_2 + N_3 &= N_f = \text{constant}, \\ 2n_{O_2} + N_0 &= \text{constant}, \\ 2N_2 + 3N_3 &= 2N_0, \end{aligned}$$

where the first equation denotes the fact that the total number of iron ions is kept in a given constant value during the reaction between the gaseous phase and molten slag, in the second equation the total number of oxygen atoms in the two phases is held in the constant value, and in the third equation the positive electric charges of iron ions in the molten slag are balanced by the negative charges of oxygen ions. Consequently we have

$$\left. \begin{aligned} \delta N_2 + \delta N_3 &= \delta N_f = 0, \\ 2\delta n_{O_2} + \delta N_0 &= 0, \\ 2\delta N_2 + 3\delta N_3 &= 2\delta N_0. \end{aligned} \right\} \quad (23)$$

The equilibrium relation between the molten and gaseous phases can be deduced from (22) and (23) as follows:

$$\left(\frac{\partial F_M}{\partial N_2} \right)_{N_3, N_0} - \left(\frac{\partial F_M}{\partial N_3} \right)_{N_2, N_0} = \frac{1}{2} \left(\frac{\partial F_M}{\partial N_0} \right)_{N_2, N_3} - \frac{1}{4} \left(\frac{\partial F_g}{\partial n_{O_2}} \right). \quad (24)$$

Calculating the left-hand side and the first term of the right-hand side of (24) from (18) we have

$$\frac{1}{kT} \left[\left(\frac{\partial F_M}{\partial N_2} \right) - \left(\frac{\partial F_M}{\partial N_3} \right) \right] = \log \frac{q_3 v_3}{q_2 v_2} \cdot e^{\frac{1}{kT}(U_2 - U_3)} - \log \frac{N_3}{N_2}, \quad (25)$$

and

$$\begin{aligned} \frac{1}{2} \frac{1}{kT} \left(\frac{\partial F_M}{\partial N_0} \right) &= \frac{1}{2} \frac{U_0}{kT} - \frac{1}{2} \log q_0 v_0 \\ &- \frac{1}{2} \left[\log \frac{N_0}{N_0 - (1-p)N_f} \cdot \left(\frac{2N_0}{2N_0 - pN_f} \right)^2 \cdot \left\{ \frac{(2N_0 - pN_f) - 2(1-p)N_f + p(1-p)\frac{N_f^2}{N_0}}{(2N_0 - pN_f) - 2(1-p)N_f} \right\}^{2z} \right] \end{aligned} \quad (26)$$

Consequently we have

$$\begin{aligned} \frac{1}{kT} \frac{\partial F_g}{\partial n_{O_2}} &= \frac{2}{kT} \left(\frac{\partial F_M}{\partial N_0} \right) - \frac{4}{kT} \left[\left(\frac{\partial F_M}{\partial N_2} \right) - \left(\frac{\partial F_M}{\partial N_3} \right) \right] \\ &= \log \left(\frac{q_2 v_2}{q_3 v_3} \right)^4 \cdot \left(\frac{1}{q_0 v_0} \right)^2 \cdot \exp \left[\{ 2U_0 - 4(U_2 - U_3) \} / kT \right] \\ &+ \log \left(\frac{N_3}{N_2} \right)^4 \cdot \left(\frac{N_0 - (1-p)N_f}{N_0} \right)^2 \cdot \left(\frac{2N_0 - pN_f}{2N_0} \right)^4 \cdot \left\{ \frac{(2N_0 - pN_f) - 2(1-p)N_f}{(2N_0 - pN_f) - 2(1-p)N_f + p(1-p)\frac{N_f^2}{N_0}} \right\}^{4z} \end{aligned} \quad (27)$$

The second term of the right-hand side of (24) is obtained from (21),

$$\frac{1}{kT} \cdot \frac{\partial F_g}{\partial n_{O_2}} = \log \frac{n_{O_2}}{f_{O_2} \cdot \exp[-\chi_{O_2}/kT]} \quad (28)$$

If we write (27) in the term of absolute activity of oxygen it follows,

$$\begin{aligned} \lambda_{O_2} &= \exp \left(\frac{1}{kT} \cdot \frac{\partial F_g}{\partial n_{O_2}} \right) = f_{O_2} \cdot \exp[-\chi_{O_2}/kT] \\ &= \alpha(T) \cdot Y(N_0, N_f, p), \end{aligned} \quad (29)$$

where

$$\begin{aligned} Y(N_0, N_f, p) &= \left(\frac{N_3}{N_2} \right)^4 \cdot \left\{ \frac{\left\{ 2 \left(1 - \frac{N_f}{N_0} \right) + p \frac{N_f}{N_0} \right\}^8}{\left\{ \left(1 - \frac{N_f}{N_0} \right) + p \frac{N_f}{N_0} \right\}^7 \left\{ 1 - \frac{p}{2} \frac{N_f}{N_0} \right\}^6} \right\}^{z/2} \\ \alpha(T) &= \frac{1}{2^{16}} \left(\frac{q_2 v_2}{q_3 v_3} \right)^4 \cdot \left(\frac{1}{q_0 v_0} \right)^2 \cdot \exp \left[\{ 2U_0 - 4(U_2 - U_3) \} / kT \right] \end{aligned} \quad (30)$$

In the above calculation, we are dealing with only the change of Fe^{+++} ion concentration in the molten slag accompanied by oxidation, and the state containing no Fe^{+++} ion, that is, the state of the stoichiometric composition FeO is taken as the standard one. Therefore, we must subtract the value of the absolute activity of oxygen $\beta(T)$ for the composition FeO from λ_{O_2} . Then the (29) is rewritten as follows:

$$\lambda_{O_2} = Y \cdot \alpha(T) + \beta(T). \quad (31)$$

Substituting (29) into the left-hand side of (31), we obtain

$$n_{O_2} = [Y \cdot \alpha(T) + \beta(T)] \{ f_{O_2} \cdot \exp[-\chi_{O_2}/kT] \} \quad (32)$$

If we take

$$P_{O_2} \cdot v = n_{O_2} \cdot kT$$

under the assumption of gaseous oxygen being a ideal gas, the partial pressure of oxygen P_{O_2} can be expressed by

$$P_{O_2} = \alpha'(T) \cdot Y - \beta'(T) \quad (33)$$

or

$$\log[P_{O_2} - \beta'(T)] = \log Y + \log \alpha'(T) \quad (33')$$

where $Y, \alpha'(T)$ and $\beta'(T)$ denote respectively

$$\left. \begin{aligned} z=4, \quad \frac{N_3}{N_0} = x, \quad \frac{N_2}{N_0} = y, \quad \frac{N_2 + N_3}{N_0} = \frac{N_f}{N_0} = f, \\ Y = \left(\frac{x}{y}\right)^4 \left[\frac{\{2(1-f) + pf\}^8}{(1 - \frac{pf}{2})^6 \{(1-f) + pf\}^7} \right]^2, \\ \alpha'(T) = \alpha(T) \frac{f_{O_2} \cdot \exp[-\chi_{O_2}/kT]}{v/kT} \end{aligned} \right\} \quad (34)$$

and

$$\beta'(T) = \beta(T) \frac{f_{O_2} \cdot \exp[-\chi_{O_2}/kT]}{v/kT}$$

If m_{O_2} , A_{O_2} , θ_{O_2} and ε_{O_2} are the mass, the moment of inertia of rotation, the characteristic temperature of vibration and the weight at the lowest electronic state of oxygen molecule respectively, and ρ_0 denotes the weight of nuclear spin of oxygen atom, we obtain

$$\frac{f_{O_2}}{v/kT} = \left(\frac{2\pi m_{O_2} \cdot kT}{h^2}\right)^{3/2} \cdot \frac{8\pi^2 \cdot A_{O_2} \cdot kT}{h^2} \cdot kT \{1 - \exp(-\theta_{O_2}/T)\}^{-1} \cdot \varepsilon_{O_2} \cdot \rho_0^2 \quad (35)$$

As $\alpha'(T)$ and $\beta'(T)$ are functions of temperature, and Y a function of concentration given by (34), we can determine theoretically the dependence of the equilibrium oxygen pressure on the concentration and temperature from (33) or (33').

V. Comparison with experimental values

The oxygen pressures in equilibrium with the molten slag of the Fe-O system have been measured by Darken and Gurry. They have obtained the experimental values over the ranges of 10^{-10} to 1 atmospheric pressure of oxygen, of atomic ratio of oxygen to iron of 1.02 to 1.38 and of temperature of 1,400°C to 1,600°C. These measured values are known to be of the highest dependability among similar experiments.

The function Y in (33) or $\log Y$ in (33') can be calculated for any composition from (34) with p 's values given by (19) or Fig. 1. Since the other terms are functions depending on temperature only, $\alpha'(T)$ can be determined as the inclination of a plot of the experimental P_{O_2} at a given temperature against Y calculated from (24) and then $\beta'(T)$ can be obtained as the value of P_{O_2} by a extrapolation of the above plot. As the value of $f_{O_2} \cdot \exp(-\chi_{O_2}/kT)/v/kT$ can be calculated theoretically, so $\alpha(T)$ can be estimated from $\alpha'(T)$ determined by means of the above method. Each set of $\beta'(T)$ and $\alpha(T)$ at temperatures of 1,400°, 1,500° and 1,600°C obtained respectively are shown in Table 2.

Table 2.

	1600°C	1500°C	1400°C
$\beta'(T)(\text{atm.})$	9.47×10^{-9}	1.131×10^{-9}	0.1297×10^{-9}
$\log_e [f_{\text{O}_2} \cdot \frac{kT}{v} \cdot \exp(-\chi_{\text{O}_2}/kT)]$ (theoretical calculation)	59.27	60.83	62.63
$\log_e \alpha(T)$	-73.77	-77.64	-81.85

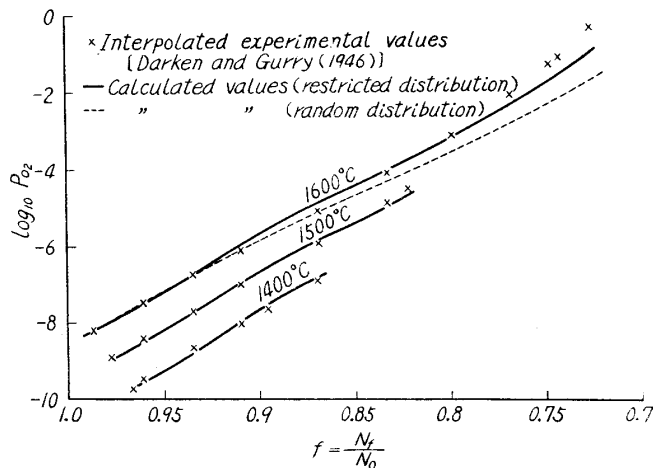


Fig. 2. Relations between partial pressures of oxygen in atmosphere and compositions of the molten Fe-O.

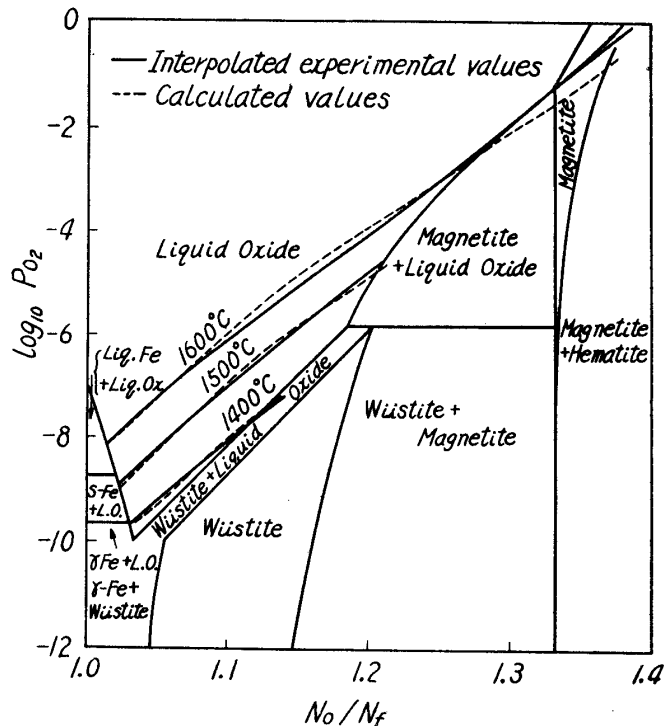


Fig. 3. Relations between partial pressures of oxygen in atmosphere in equilibrium with the molten iron-oxide and the phase diagram [from DARKEN and GURRY (1946)].

The values of partial pressure of oxygen calculated from the formula (33) using the values of $\alpha(T)$, $\beta'(T)$ etc. in Table 2 are plotted against the compositions of molten slag in Figs. 2 and 3 together with the measured values by Darken and Gurry. Our calculated results are in good agreement with the experimental values as seen from Fig. 2. The observed values over such wide ranges of compositions and oxygen pressures cannot explain by calculation under assumptions that the iron ions are randomly distributed at the sites of the tetrahedral and the octahedral interlattices or that the iron ions occupy the sites of octahedral lattice and the tetrahedral lattice points are not taken into account. We believe that the possibility of expressing the required relations so admirably by a single formula containing only a few parameters, in spite of a wide range of measurements, may suggest the correctness of the model of molten phase and the statistico-thermodynamical method we have adopted in this paper.

Generally speaking, liquids may be roughly classified into van der Waals liquids, metallic liquids and ionic liquids. At present, research on ionic liquids seems to be least advanced. The cause of this lag is considered to lie, beside the experimental difficulties, in the anticipated difficulty in theoretical treatment due to the distant action of the interionic force. But we believe our study has demonstrated that in the molten state the thermal motion is intensified so that the fields of forces acting on the ions become considerably equalized, and therefore simple approximated treatment is made possible.

Summary

A model upon the ionic configuration in the molten state of Fe-O system, one of the fundamental slags in steel-making, was deduced from the results of our previous studies on the solid state of wüstite and magnetite, and it is assumed that O^{2-} ions of larger ionic radius are arranged in the form of the close-packed lattice, iron ions are distributed on the tetrahedral and octahedral interstitial sites of the oxygen ion lattice under a special restriction, and oxidation is accompanied by the formation of F^{+++} ions from F^{++} ions.

The partial pressures of oxygen in equilibrium with such model of liquid slag are calculated by the statistico-thermodynamical method based on the free-volume theory of liquid and our results by these procedures are capable of reproducing the experimental values with good approximation over a wide range of compositions, pressures and temperatures.