Statistical Thermodynamic Analysis of Phosphorus Solubility in Molten Iron*

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Synopsis

Appreciable amount of phosphorus dissolves interstitially into molten iron. A statistical thermodynamic analysis, based on a *a priori* assumption of constant solute-solute interaction at a given temperature T , is applied to molten FeP_x . The interaction energy, $E_{\text{P-Fe}}$, between P and Fe in molten FeP_x obtained by the analysis is about -58 kJ mol^{-1} in the range of 1 473 to 1 773 K. The interaction energy, $E_{\text{P-P}}$, between P atoms in molten FeP_x is estimated to be weak and attractive (varying from $\sim -1 \text{ kJ mol}^{-1}$ at 1 473 K to $\sim -2 \text{ kJ mol}^{-1}$ at 1 773 K). Analysis is also made for some ternary molten FeX_yP_x , where X is another interstitial element (X=C, B).

I. Introduction

Appreciable amount of phosphorus (P) dissolves interstitially into molten iron (Fe). Recently, Ban-ya *et al.*¹⁾ measured the phosphorus partial pressure p_{P_2} in equilibrium with molten FeP_x ($x < 0.42$) by the transportation method in the temperature range of 1 473 to 1 773 K. Further, Ban-ya *et al.*²⁾ reported the equilibrium p_{P_2} - x relationships for the ternary Fe-X-P systems (X=B, C, Si, Al) at 1 673 K. They analysed the experimental p_{P_2} - T - x relationships on the basis of conventional thermodynamics. However, the experimental data in the composition range of $x > 1/3$ were not used for their analysis, because a kink appeared around the composition of Fe_3P in the plot of the apparent equilibrium constant $\log K'_1(Z)$ against Y_{P} (x in the present notation) (*cf.*, Eq. (19) and Fig. 5 in Ref. 1)). According to the results of the recent statistical thermodynamic analyses of several interstitial solid solutions MX_x ,³⁻¹²⁾ this type of kink or discontinuity of the plots may be avoided by properly choosing the number θ of the available interstices for occupation by the interstitial atom X per host metal atom M. The choice of the value of parameter θ may be made so that the linear

$$\Delta \equiv RT \ln \left(\frac{\theta - x}{x} p_{\text{X}_2}^{1/2} \right) \text{ vs. } x$$

relationship yields at a given temperature. This is to satisfy a *a priori* assumption of constant solute-solute interaction at a given temperature.

The purpose of the present study is to analyse the available p_{P_2} - T - x relationships reported by Ban-ya *et al.*^{1,2)} in terms of statistical thermodynamics, rather than the conventional thermodynamics, on the basis of a *a priori* assumption of constant P-P interaction at a given temperature in molten FeP_x and FeX_yP_x (X=B, C).

II. Method of Analysis

As has been employed commonly in the recent analyses³⁻¹²⁾ for interstitial solid solutions, the fundamental equation:

$$RT \ln \left(\frac{\theta - x}{x} p_{\text{P}_2}^{1/2} \right) = g + \beta x E_{\text{P-P}} \quad \dots\dots\dots (1)$$

is used for the present analysis of molten FeP_x , where, R refers to the gas constant and p_{P_2} the phosphorus partial pressure (in atm). In molten FeP_x , Fe atoms may be assumed to be in the close packed arrangement (fcc; face centred cubic).^{1,2)} Then, the parameter β in Eq. (1) is equal to 12 and x -independent factor g may be expressed as

$$g = K - \mu_{\text{P}}^{\circ} \quad \dots\dots\dots (2)$$

$$K = 6E_{\text{P-Fe}} - RT \ln f_{\text{P}} \quad \dots\dots\dots (3)$$

where, f_{P} : the atomic partition function of P in molten FeP_x

μ_{P}° : the chemical potential of the gaseous phosphorus with the reference state being taken as the gaseous phosphorus atom at rest.

The expression for μ_{P}° may be given as

$$\mu_{\text{P}}^{\circ} = RT C(T) - D_{\text{P}_2}/2 \quad \dots\dots\dots (4)$$

$$C(T) = -\frac{1}{2} \ln \left(\frac{(4\pi m_{\text{P}})^{3/2} k^{5/2}}{2h^3} \frac{T^{7/2}}{\theta_r} \right) + \frac{\theta_v}{4T} + \frac{1}{2} \ln (1 - \exp(-\theta_v/T)) \quad \dots\dots\dots (5)$$

where, h : the Planck constant

k : the Boltzmann constant

m_{P} : the mass of P atom

θ_v ($= 1\,123 \text{ K}$), θ_r ($= 0.436 \text{ K}$): the characteristic temperatures for vibration and rotation, respectively, of P_2 molecule

D_{P_2} : the dissociation energy per mole of P_2 molecule (*e.g.*, Ref. 13)).

In the following, a brief explanation will be given to the reason why a *a priori* assumption of constant solute-solute interaction at a given temperature is employed. It has been a common practice in the analysis of interstitial solutions (*e.g.*, Refs. 8, 9, 13-19)) to take the value of parameter θ to be equal to the total number θ_0 of the relevant interstices per metal atom. Then, the estimated interaction energy, E_{ij} , between component atoms, i and j , in MX_x were found to

* Manuscript received on June 25, 1985; accepted in the final form on October 11, 1985. © 1986 ISIJ

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hold constant. These results had been appreciated as rational and acceptable. However, in the analysis of hypostoichiometric chromium subnitride Cr_2N , an apparent anomaly was observed³⁾; *i.e.*, with $\theta=1$ (which corresponds to the random distribution of N atoms over all the available O-sites (octahedral interstices) in hcp (hexagonal close packed) Cr-lattice), the value of $E_{\text{N-N}}$ varies with N-content at a given temperature. This unexpected variation of $E_{\text{N-N}}$ with N-concentration was found to be avoided by the choice of $\theta=0.5$.³⁾ This value of θ suggests that only half of the total O-sites would provide as available sites for the occupation by N atoms. This model appears to be compatible with the X-ray diffraction observation²⁰⁾ showing the ordered distribution of N atoms over the O-sites in hcp Cr-lattice. Further analyses of miscellaneous interstitial solutions on the basis of the assumption of constant $E_{\text{X-X}}$ at a given temperature led to the following conclusions⁴⁻¹⁰⁾:

(1) Similar atomic partition function f_{X} as well as the similar interaction energy term $E_{\text{X-M}}$ is derived for the metals belonging to the same group in the periodic table, which appears to be realistic, judging from the similarity of the electronic structure of the metals of same group.

(2) The value of parameter θ is estimated to be close to the maximum solubility limit x' of $\text{MX}_{x'}$ ($\theta > x'$).

These results seem to support the employment of *a priori* assumption of constant $E_{\text{X-X}}$ at a given temperature. Without this assumption, the statistical thermodynamic analysis of interstitial solution may become too much arbitrary; *e.g.*, $E_{\text{H-H}}$ in YH_x may be estimated to be either positive (repulsive) or negative (attractive) depending on the choice of θ .²¹⁾ There is no justification to choose some value of θ based simply on the crystal structure being considered.

III. Results and Discussion

1. Molten FeP_x

In order to determine the value of the parameter θ

Fig. 1. Effect of the choice of parameter θ on $RT \ln \left(\frac{\theta-x}{x} p_{\text{P}_2}^{1/2} \right)$ vs. x plots for molten FeP_x at 1 673 K.

Fig. 2. $RT \ln \left(\frac{0.5-x}{x} p_{\text{P}_2}^{1/2} \right)$ vs. x plots for molten FeP_x .

for FeP_x , Δ vs. x plots are prepared using the experimental p_{P_2} - x relationship at 1 673 K¹⁾ with various choices of θ -values, as shown in Fig. 1. As is clear from Eq. (1), the slope of Δ vs. x plots is proportional to $E_{\text{P-P}}$. Judging from the results summarized in Fig. 1, the choice of $\theta=0.5$ appears to satisfy *a priori* assumption of constant $E_{\text{P-P}}$ at a given temperature. Thus, $\theta=0.5$ is employed for the analysis of molten FeP_x . This choice of θ -value may imply that half the number of total O-sites in "molten fcc lattice" of Fe is subjected to the occupation by P atoms alternately.

Figure 2 shows the plots of Δ vs. x for molten FeP_x with $\theta=0.5$. From these plots, the value of $\beta E_{\text{P-P}}$ and K may be derived as a function of temperature (*cf.*, Fig. 3). Interaction between P atoms in molten FeP_x appears to be attractive and slightly dependent on temperature (varying from ~ -1 kJ mol⁻¹ at 1 473 K to ~ -2 kJ mol⁻¹ at 1 773 K). From the K - T relationship summarized in Fig. 3, the following parameters may be estimated, when $E_{\text{P-Fe}}$ and f_{P} are assumed to be independent of temperature:

$$6E_{\text{P-Fe}} = -347.1 \text{ kJ mol}^{-1} \dots\dots\dots(6)$$

$$R \ln f_{\text{P}} = 91.5 \text{ J K}^{-1} \text{ mol}^{-1} \dots\dots\dots(7)$$

The atomic partition function f_{P} is in fact a function which is dependent on temperature. However, as discussed in the earlier work (*cf.*, Appendix in Ref. 8)), this approximation would not cause very serious error in the estimation of $E_{\text{P-Fe}}$ over a temperature range of a few hundred Kelvin.

2. Molten FeX_yP_x ($\text{X}=\text{B}, \text{C}$)

Ban-ya *et al.*²⁾ reported that Si and Al form substitutional solutions with molten Fe but that B and C dissolve interstitially into molten Fe. In the following, analysis of the p_{P_2} - x relationships for FeX_yP_x ($\text{X}=\text{B}, \text{C}$) at 1 673 K²⁾ is given.

For the analysis of FeX_yP_x , a modified version of Eq. (1) must be used; *i.e.*,

Fig. 3. Values of $\beta E_{\text{P-P}}$ and K for molten FeP_x as a function of T .

$$RT \ln \left(\frac{\theta-x}{x} p_{P_2}^{1/2} \right) = (6E_{P-Fe} + 12yE_{X-P} - RT \ln f_P - \mu_P^0) + 12xE_{P-P} \dots\dots\dots(8)$$

This modification is resulted from the alteration of the lattice energy E of FeX_yP_x from that of FeP_x :

$$E(FeX_yP_x) = 6n_{Fe}E_{Fe-Fe} + 6n_XE_{X-Fe} + 6n_PE_{P-Fe} + 6 \frac{n_X^2}{n_{Fe}} E_{X-X} + 12 \frac{n_X n_P}{n_{Fe}} E_{X-P} + 6 \frac{n_P^2}{n_{Fe}} E_{P-P} \dots\dots\dots(9)$$

where, n_i ($i=Fe, X, P$) refers to the number of component atom i in molten FeX_yP_x . Interstitial elements, B and C, as well as P are supposed to occupy the O-sites in molten Fe-lattice.

The number W of configuration of interstitial atoms in molten FeX_yP_x may be given as

$$W(FeX_yP_x) = \frac{(\theta' n_{Fe})!}{(\theta' n_{Fe} - n_X)! n_X!} \frac{(\theta n_{Fe})!}{(\theta n_{Fe} - n_P)! n_P!} \dots\dots\dots(10)$$

instead of

$$W(FeP_x) = \frac{(\theta n_{Fe})!}{(\theta n_{Fe} - n_P)! n_P!} \dots\dots\dots(11)$$

where, the parameter θ' refers to the number of available interstices for X atoms per Fe atom. This alteration of $W(FeX_yP_x)$ from $W(FeP_x)$ does not affect the apparent functional form of the left-hand side of the equilibrium formula (cf. Eqs. (1) and (8)). However the parameter θ in FeX_yP_x does not possess the same value as that in FeP_x , but may deviate from 0.5 as a function of $y=n_X/n_{Fe}$ due to the blockage of the interstitial sites by X atoms.

If it is assumed that E_{X-P} is negligible and that E_{P-P} , E_{P-Fe} and f_P in FeX_yP_x are not affected by the addition of X and maintain approximately the same value as in FeP_x , Eq. (8) for FeX_yP_x may be reduced to the same form as Eq. (1) with only the value of the parameter θ deviating from 0.5. In this approximation, the effect of the addition of interstitial element X is simply reduced to the blockage of the available interstices.

Equilibrium relation for FeP_x at 1 673 K may be expressed as follows (cf., Fig. 2):

$$\ln \left(\frac{\theta-x}{x} p_{P_2}^{1/2} \right) = -3.514 - 1.44x \dots\dots\dots(12)$$

with $\theta=0.5$. From the above mentioned approximation for FeX_yP_x , the value of θ as a function of y may be estimated from the following equation:

$$\theta = x \left(1 + \exp \left(-3.514 - 1.44x - \frac{1}{2} \ln p_{P_2} \right) \right) \dots\dots\dots(13)$$

The results of this estimation for $X=B$ and C are summarized in Fig. 4. It appears that C blocks the interstices more extensively than B per fraction of

addition, provided that the approximation is valid.

The analysis for the substitutional addition $Fe_{1-z}X_zP_x$ ($X=Si, Al$)²⁾ was not made, since the alteration of the electronic structure of the host metal lattice $Fe_{1-z}X_z$ from pure Fe may cause quite significant changes in E_{P-P} and the atomic partition function f_P and, further, even the explicit functional form for K may be altered to

$$K(Fe_{1-z}X_zP_x) = 6(1-z)E_{P-Fe} + 6zE_{P-X} - RT \ln f_P \dots\dots\dots(14)$$

in place of Eq. (3).

3. Re-construction of p_{P_2} - T - x Relationships

Using the parameters estimated from this analysis, p_{P_2} - T - x relationships may be re-constructed for FeP_x and for FeX_yP_x . Equations may be as follows:

$$\log_{10} p_{P_2} = -2.698 - 1.38x - 2 \log_{10} ((\theta-x)/x), \quad 1\,773\,K \dots\dots\dots(15)$$

$$\log_{10} p_{P_2} = -3.052 - 1.25x - 2 \log_{10} ((\theta-x)/x), \quad 1\,673\,K \dots\dots\dots(16)$$

$$\log_{10} p_{P_2} = -3.610 - 0.95x - 2 \log_{10} ((\theta-x)/x), \quad 1\,573\,K \dots\dots\dots(17)$$

$$\log_{10} p_{P_2} = -4.292 - 0.87x - 2 \log_{10} ((\theta-x)/x), \quad 1\,473\,K \dots\dots\dots(18)$$

For FeP_x , the re-construction of p_{P_2} - T - x relationships may be made with $\theta=0.5$. The results are summarized in Fig. 5, together with the experimental results¹⁾ for the sake of comparison. The agreement between the estimated and the experimental values appears to be reasonable.

Figure 6 shows the results for estimation of the p_{P_2} - x relationships for FeC_yP_x at 1 673 K with the choice of θ -values based on the results given in Fig. 4; i.e.,

$$\theta(FeC_yP_x) = 0.5 - 1.25y \dots\dots\dots(19)$$

The experimental results²⁾ appear to be in reasonable accord with the estimation; for example, points 6 ($y=0.052$) and 7 ($y=0.051$) are on the estimated curve for $FeC_{0.05}P_x$.

4. Comparison with the Thermodynamic Analysis

Ban-ya *et al.* derived thermodynamically the value of -117.2 kJ mol⁻¹ for the enthalpy ΔH^θ of P solution in molten Fe (cf., Eq. (40) in Ref. 1)). On the other hand, the following expression may be given for the enthalpy ΔH in terms of the parameters appearing in the present analysis:

$$\Delta H = 6E_{P-Fe} + 12xE_{P-P} + D_{P_2}/2 \dots\dots\dots(20)$$

Value of $6E_{P-Fe}$ is given by Eq. (6) and the value of D_{P_2} is about 248 kJ mol⁻¹.¹³⁾ Thus, the contribution of the sum $(6E_{P-Fe} + D_{P_2}/2)$ to ΔH is estimated to be about -100 kJ mol⁻¹. The order of magnitude of E_{P-P} is rather small; e.g., the term, $12xE_{P-P}$, would give a contribution of no more than -5 kJ mol⁻¹ to ΔH at the composition of $x=0.2$. Thus, the discrepancy between ΔH^θ estimated by Ban-ya *et al.*¹⁾ and

Fig. 4. Estimated values of θ for molten FeX_yP_x as a function of y ($X=\text{B}, \text{C}$).

Fig. 5. Estimated $\log_{10} p_{\text{P}_2}^{1/2}$ vs. x relationships for molten FeP_x compared with the experimental data.¹⁾

Fig. 6. Estimated $\log_{10} p_{\text{P}_2}^{1/2}$ vs. x relationships for molten FeC_yP_x compared with the experimental data.²⁾

ΔH estimated in the present work is *ca.* 10 kJ mol⁻¹. This discrepancy does not appear to be very serious, considering that, in the present analysis, by taking $\theta=0.5$, the experimental p_{P_2} - T - x data from all the composition range ($x<0.42$) reported by Ban-ya *et al.*¹⁾ were used, while in their own analysis, the data for $x>1/3$ were discarded.

One of the advantages of statistical thermodynamics relative to the conventional thermodynamics is that all the parameters appearing in the equations have clear physical meanings with the reference state of energy zero being taken at the infinite separation of each component atom at rest, while thermodynamics usually gives the relative values, which are entirely dependent on the choice of arbitrary reference state.

IV. Summary

Experimental p_{P_2} - T - x relationships reported by Ban-ya *et al.* for molten FeP_x ¹⁾ and molten FeX_yP_x ($X=\text{B}, \text{C}$)²⁾ were analysed by statistical thermodynamics on the basis of a *a priori* assumption of constant $E_{\text{P-P}}$ at a given temperature. This *a priori* assumption may be met by properly choosing the parameter θ . While the p_{P_2} - T - x data for the composition range of $x>1/3$ were not involved for the thermodynamic analysis of FeP_x ¹⁾ the experimental data for all the composition range ($x<0.42$) were used in the present statistical thermodynamic analysis.

The value of $E_{\text{P-Fe}}$ was estimated to be about -58 kJ mol⁻¹ (*cf.*, Eq. (6)). Interaction between P atoms in molten Fe was estimated to be weak and attractive (varying from ~ -1 kJ mol⁻¹ at 1473 K to ~ -2 kJ mol⁻¹ at 1773 K).

The following generalized formula may be used for the estimation of the p_{P_2} - T - x relationships for FeP_x and FeX_yP_x (*cf.*, Eqs. (15)~(18)):

$$\begin{aligned} \log_{10} p_{\text{P}_2} = & (-12.080 + 0.00534 T) \\ & + (1.86 - 0.00183 T)x \\ & - 2 \log_{10} ((\theta - x)/x) \dots\dots\dots(21) \end{aligned}$$

The value of θ for FeP_x may be taken as 0.5. The value of θ for FeX_yP_x may be given by

$$\theta(\text{FeX}_y\text{P}_x) = 0.5 - sy \dots\dots\dots(22)$$

where, s refers to the extent of blockage of the interstices per fraction of addition of interstitial element X (*e.g.*, $s=0.4$ for B and $s=1.25$ for C (*cf.*, Fig. 4)). If the element X alters significantly the values of $E_{\text{P-P}}$, $E_{\text{P-Fe}}$ and f_{P} in FeX_yP_x from those in FeP_x , this approximation would not be valid.

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