Statistical Thermodynamics of Sulphur Solution in Molten Iron*

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Synopsis

A sulphur solution in molten iron is analysed by statistical thermodynamics based on the *a priori* assumption of the constant solute-solute interaction at a given temperature. The interaction energy E_{S-Fe} between S and Fe in molten FeS_x is estimated to be about -51 kJ mol^{-1} and E_{S-S} about -9.6 kJ mol^{-1} . The effect of additional interstitial element (C and P) on the solubility of S in molten Fe is also discussed.

I. Introduction

Significant amount of sulphur (S) dissolves into molten iron (Fe). Several studies have been reported on the solubilities of S in molten Fe and its alloys due to the importance in the control of S-content in iron and steel making. These solubility data reported by different researchers have not always been in good accord with each other, however.

Ishii and Fuwa have reported the equilibrium solubilities of S in molten Fe¹⁾ and Fe-alloys²⁾ as functions of temperature T and of the ratio of partial pressures of H_2S gas and H_2 gas, P_{H_2S}/P_{H_2} , in equilibrium with the molten sulphur solution. They have made several efforts to minimize the experimental errors, which might have caused the discrepancies among the earlier measurements. Some of their precautions claimed might be summarized as follows:

(1) Method of heating the sample materials. They have suggested¹⁾ that a resistance furnace should be used but not an induction furnace, in which the gas phase can not be heated up to the temperature of the molten sample and, as a result, the S-concentrations obtained would tend to be systematically lower than the equilibrium values.

(2) Establishment of the equilibrium in the H_2 - H_2S gas mixtures flowing over the molten sample. They confirmed experimentally¹⁾ that, within the flow rates of 100 to 400 ml/min, no deviation from the equilibrium conditions was recognized. Eventually they have used the flow rate of about 200 ml/min for all their measurements.^{1,2)}

(3) Attainment of the equilibrium S-concentrations in the molten samples. In order to confirm this point, the equilibrium was approached from both the higher and the lower initial S-concentrations.^{1,2)} It is judged from these precautions taken by Ishii and Fuwa^{1,2)} that their equilibrium data are highly reliable.

In the present paper the equilibrium solubility data of S in molten Fe reported by Ishii and Fuwa¹⁾ are analysed by statistical thermodynamics based on the *a priori* assumption of the constant solute-solute

interaction within a phase at a given T . Judging from the information³⁾ that iron monosulphide FeS crystallizes into an NiAs-type (B8) structure, Fe and S atoms would distribute over separate sublattices in the condensed phase. Hence, S-solution in molten Fe may be treated as an interstitial solution rather than a substitutional solution. The effect of other interstitial elements (C and P) on the solubility of S in molten Fe²⁾ is also discussed.

The procedure employed for the present analysis is essentially the same as the one employed for the recent analysis of molten FeP_x .⁴⁾ Therefore, the method of analysis is described only briefly in the following.

II. Analysis

1. Method

The following equation is used for the analysis of molten FeS_x :

$$RT \ln \left(\frac{\theta - x}{x} p_s \right) = g + \beta x E_{S-S} \quad \dots\dots\dots (1)$$

where R refers to the gas constant. Fe atoms in molten FeS_x may be assumed to be in the fcc (face centered cubic) arrangement as well as those in molten FeP_x .⁴⁾ Thus, a factor β may be taken as 12. The parameter θ refers to the number of available interstices per Fe atom for the occupation of S atoms in the molten Fe lattice. The value of θ may be chosen so that a linear relation between $\underline{A} \equiv RT \ln \{((\theta - x)/x) p_s\}$ and x is obtained for a given T . This is equivalent to the *a priori* assumption of the constant E_{S-S} within a phase at a given T . A factor g is also an x -independent term in the $\underline{A}$ vs. x plots. The expression for g is as follows:

$$g = K - \mu_s^\circ \quad \dots\dots\dots (2)$$

$$K = 6E_{S-Fe} - RT \ln f_s \quad \dots\dots\dots (3)$$

$$\begin{aligned} \mu_s^\circ &= -RT \ln \left(\frac{(2\pi m_s)^{3/2} (kT)^{5/2}}{h^3} \right) \\ &= -(12.879 + 20.785 \ln T)T, \text{ (J mol}^{-1}\text{)} \quad \dots\dots (4) \end{aligned}$$

where, h : the Planck constant

k : the Boltzmann constant

m_s : the mass of S atom

f_s : the atomic partition function of S in molten Fe.

The experimental results^{1,2)} were summarized in terms of the composition x and the ratio p_{H_2S}/p_{H_2}

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for each T . From given values of $p_{\text{H}_2\text{S}}/p_{\text{H}_2}$ the corresponding pressure p_s (in atm) of monoatomic sulphur gas may be evaluated using the equilibrium constant K_p :

$$p_s = K_p(p_{\text{H}_2\text{S}}/p_{\text{H}_2}) \dots\dots\dots(5)$$

$$\Delta G = -RT \ln K_p = 74\,000 - 26.33T, \text{ (cal/mol)} \dots\dots\dots(6)$$

ΔG given by Eq. (6)^{1,5)} is defined for the reaction:

The total pressure of gas flow was reported to be approximately 1 atm. The experimental results^{1,2)} showed that $p_{\text{H}_2\text{S}}$ is much smaller than p_{H_2} . On the basis of the value of K_p , p_s is smaller than $p_{\text{H}_2\text{S}}$. Thus, eventually $p_s \ll p_{\text{H}_2\text{S}} \ll p_{\text{H}_2} \simeq 1$ atm.

2. Molten FeS_x

The experimental results obtained by Ishii and Fuwa¹⁾ in a resistance furnace are analysed. The values of p_s are estimated by Eq. (5) from the "corrected" values of $p_{\text{H}_2\text{S}}/p_{\text{H}_2}$ summarized in Table 1 in Ref. 1). The "corrected" values of $p_{\text{H}_2\text{S}}/p_{\text{H}_2}$ were obtained by extrapolating the measured values of $p_{\text{H}_2\text{S}}/p_{\text{H}_2}$ at room temperature to the experimental temperature.

For the analysis we must first choose the value of the parameter θ . The plots of Fig. 1 are prepared for this purpose. According to the criteria,⁴⁾ the occurrence of the variation in the solute-solute interaction of the interstitial solid solutions within the same phase at a given T may be appreciated as the consequence of the improper statistical model. Thus, it is evident that the choices of $\theta=0.125$ and $\theta=0.25$ are not recommended for the analysis of molten FeS_x. However, it does not appear to be very clear only from the results in Fig. 1 which value between 0.5 and 1.0 should be taken for the θ -value for the analysis. This ambiguity in determining the θ -value

Fig. 1. $RT \ln \left(\frac{\theta-x}{x} P_s \right)$ vs. x for molten FeS_x at 1873 K with various choices of θ -values.

might be resolved by considering the phase relationships.

Figure 2 shows the phase diagrammes of Fe-P and Fe-S binary systems.³⁾ For the analysis of molten FeP_x, $\theta=0.5$ was chosen.⁴⁾ After Fig. 2, the first complete peak of liquidus in Fe-P binary diagramme appears around Fe₂P, while half peak is recognizable around Fe₃P. This might suggest that the parameter θ is closely related to the metalloid/metal atom ratio of the stable condensed phase in interstitial solutions. Thus, we decided to analyse molten FeS_x with $\theta=1.0$.

Figure 3 shows the plots of Δ vs. x obtained for molten FeS_x with $\theta=1.0$. These results lead to

$$6E_{\text{S-Fe}} = -306.7 \text{ kJ mol}^{-1} \dots\dots\dots(8)$$

$$R \ln f_s = 76.8 \text{ J K}^{-1} \text{ mol}^{-1} \dots\dots\dots(9)$$

These values, respectively, appear to be comparable with the corresponding values for molten FeP_x estimated earlier⁴⁾:

$$6E_{\text{P-Fe}} = -347.1 \text{ kJ mol}^{-1} \dots\dots\dots(10)$$

$$R \ln f_P = 91.5 \text{ J K}^{-1} \text{ mol}^{-1} \dots\dots\dots(11)$$

Considering that S and P are neighbouring elements in the periodic table, these similarities in the param-

Fig. 2. Phase relationships for Fe-X binary systems ($X = \text{P, S}$) after Hansen and Anderko.³⁾

Fig. 3. $RT \ln \left(\frac{1-x}{x} P_s \right)$ vs. x for molten FeS_x.

eters may be reasonable.

The interaction energy E_{S-S} between S atoms in molten Fe is estimated to hold almost constant irrespective of T within the range of 1 773 to 1 873 K ($E_{S-S} = -9.60 \pm 0.03$ kJ mol⁻¹; cf. Fig. 3). In molten Fe, S-S interaction appears to be more attractive than P-P interaction (varying from -1 kJ mol⁻¹ at 1 473 K to -2 kJ mol⁻¹ at 1 773 K⁴⁾). It may be worthwhile noting that, in diatomic molecular state, P-P bond is stronger than S-S bond, judging from the D_{P_2} (≈ 500 kJ mol⁻¹) and the D_{S_2} (≈ 430 kJ mol⁻¹), where D_{X_2} represents the dissociation energy per mol of gaseous X_2 molecule.

The parameter E_{S-S} may be approximately related to the interaction parameter e_S^S defined by Ishii and Fuwa¹⁾ through the following relation:

$$E_{S-S} \approx \frac{2.3026}{12} RT(100e_S^S) = 159.5 T e_S^S, \text{ (J mol}^{-1}\text{)} \quad \dots\dots\dots(12)$$

The value of e_S^S estimated by Ishii and Fuwa¹⁾ at $T=1$ 823 K is -0.048 , which corresponds to $E_{S-S} \approx -14$ kJ mol⁻¹. This value deviates from the present estimation; $E_{S-S} = -9.6$ kJ mol⁻¹. The cause for this discrepancy may be attributable to the definition of K' (cf. Eq. (3) in Ref. 1)):

$$K' = \frac{p_{H_2S}}{p_{H_2} [\% S]} \quad \dots\dots\dots(13)$$

The value of e_S^S was determined as the slope of $\log K'$ vs. $[\% S]$ plots. This relation is, however, merely an approximation valid only for $x \ll 1$.

It may be also worthwhile comparing the present estimation of E_{S-S} with the results reported by Ban-ya and Chipman,⁶⁾ in which the parameters θ_S^S and E_S have been defined. The parameters may be converted to E_{S-S} through the following approximate relation:

$$\begin{aligned} E_{S-S} &\approx \frac{RT}{12} \theta_S^S = 0.6928 T \theta_S^S \\ &= \frac{2.3026}{12} R T E_S = 1.595 T E_S, \text{ (J mol}^{-1}\text{)} \end{aligned} \quad \dots\dots\dots(14)$$

They estimated $E_S = -2.30$ (or $\theta_S^S = -5.3$) from the experimental data at $T=1$ 823 K. They mentioned that this value is in good accord with the one reported earlier by Adachi and Morita.⁷⁾ $E_S = -2.30$ corresponds to $E_{S-S} = -6.7$ kJ mol⁻¹, which also deviates from the present result ($E_{S-S} = -9.6$ kJ mol⁻¹). Ban-ya and Chipman⁶⁾ defined $K'(z)$ as follows:

$$K'(z) = \frac{p_{H_2S}}{p_{H_2}} \cdot \frac{1}{z} \quad \dots\dots\dots(15)$$

$$z = \frac{x}{1-x} \quad \dots\dots\dots(16)$$

Thus, they estimated E_S or θ_S^S from the slope of $\log K'(z)$ vs. z relationship. The expression of $K'(z)$ is comparable with the inside of logarithmic term of the

left-hand side of Eq. (1). Thus, it is evident that E_{S-S} must be estimated from $\log K'(z)$ vs. x relationship rather than $\log K'(z)$ vs. z . The slope of $RT \ln K'(z)$ vs. z would correspond to $12(1-x)E_{S-S}$ rather than $12 E_{S-S}$ itself.

The consideration given above appears to reveal that in some cases the physical meaning of thermodynamic parameters is not very clear-cut. As discussed in the earlier work⁴⁾ statistical thermodynamics may be more appropriate for the analysis of interstitial solutions in a respect that the physical meaning of all the parameters are clear with the standard of energy zero being taken at infinite separation of each component atom at rest.

The enthalpy of solution of $\frac{1}{2}$ mol of S_2 into molten FeS_x , $\Delta H(FeS_x)$, might be given by

$$\Delta H(FeS_x) = 6E_{S-Fe} + 12xE_{S-S} + D_{S_2}/2 \quad \dots\dots\dots(17)$$

Judging from the value of $6E_{S-Fe}$ (cf., Eq. (8)) and D_{S_2} , the term $(6E_{S-Fe} + D_{S_2}/2)$ would contribute approximately -90 kJ mol⁻¹ to $\Delta H(FeS_x)$. At about $x=0.1$ the contribution of $12xE_{S-S}$ would become ca. -10 kJ mol⁻¹. Thus, yields $\Delta H(FeS_{0.1}) \approx -100$ kJ mol⁻¹.

Ishii and Fuwa derived on the basis of thermodynamics the corresponding enthalpy $\Delta H^\theta = -125$ kJ mol⁻¹ (cf., Eq. (11) in Ref. 1)). Ban-ya and Chipman estimated $\Delta H^\theta = -135$ kJ mol⁻¹ (cf., Eq. (18) in Ref. 6)). These thermodynamically estimated values of ΔH^θ do not appear to be in very good accord with the present estimation based on Eq. (17). Ishii and Fuwa¹⁾ defined K' by Eq. (13) and Ban-ya and Chipman⁶⁾ by Eq. (15). The values of ΔH^θ were estimated from those equations. However, those equations were merely approximate ones, as explained earlier in the discussion of E_{S-S} .

3. Molten FeX_yS_x ($X=C, P$)

Ishii and Fuwa²⁾ studied experimentally the effect of third element X on the solubility of S in molten Fe at $T=1$ 823 K. Among the third elements X studied by Ishii and Fuwa²⁾ $X=C$ and P as well as S dissolve interstitially into molten Fe. As discussed earlier⁴⁾ a modified equation

$$\begin{aligned} RT \ln \left(\frac{\theta-x}{x} p_S \right) &= (6E_{S-Fe} + 12yE_{X-S} \\ &\quad - RT \ln f_S - \mu_S^\circ) + 12xE_{S-S} \end{aligned} \quad \dots\dots\dots(18)$$

may be used for the analysis of the ternary phase FeX_yS_x , where X is the interstitial element.

When the experimental results were available for a set of fixed values of y , we might be able to estimate the effect of X on E_{S-Fe} , f_S and E_{S-S} and also be able to evaluate E_{X-S} on the basis of Eq. (18) by choosing the value of θ for each y value so that linear $\underline{A}$ vs. x relationships be obtained. However, the experimental data were only available for the scattered values of y for FeX_yS_x ($X=C, P$) as well as for FeX_yP_x ($X=B, C$).⁴⁾ Thus, such a proper procedure may not be employed for the analysis of molten FeX_yS_x

under consideration.

Eventually the similar approximation as employed for the analysis of molten FeX_yP_x ⁴⁾ is used again for the present analysis; *i.e.*,

- (1) $E_{\text{X-S}}$ in molten FeX_yS_x is negligible,
- (2) $E_{\text{S-S}}$, $E_{\text{S-Fe}}$ and f_{S} in molten FeX_yS_x maintain approximately the same value as in FeS_x .

In this approximation the effect of interstitial alloying element X is simply reduced to the blockage of available interstices for the occupation of S atoms. Thus, the right-hand side of the following relation derived for molten FeS_x at 1 823 K (*cf.*, Fig. 3) is unchanged:

$$\ln\left(\frac{1-x}{x}\right) = -9.147 - 7.58x - \ln p_{\text{S}} \dots\dots\dots(19)$$

but $\theta (=1)$ in the left-hand side of this equation must be replaced by θ which deviates from unity as a function of y . Thus, yields

$$\ln\left(\frac{\theta-x}{x}\right) = -9.147 - 7.58x - \ln p_{\text{S}} \dots\dots\dots(20)$$

It may be more practical to write down this equation in terms of $p_{\text{H}_2\text{S}}/p_{\text{H}_2}$ rather than of p_{S} , since $p_{\text{H}_2\text{S}}/p_{\text{H}_2}$ is the experimentally determined variable. Thus, θ -values for FeX_yS_x at 1 823 K may be estimated as a function of y by the following equation:

$$\theta = x\{1 + \exp(-1.956 - 7.58x - \ln(p_{\text{H}_2\text{S}}/p_{\text{H}_2}))\} \dots\dots\dots(21)$$

The results of the estimation of θ on the basis of this equation are summarized in Fig. 4 for $X=\text{C}$ and P. The reduction of θ from unity in molten FeS_x by the addition of $X(=\text{C}, \text{P})$ appears to be expressed by the form

$$\theta = 1 - sy \dots\dots\dots(22)$$

where s refers to the extent of blockage of the interstices per fraction of addition of X . The value of s for $X=\text{C}$ is 4 and 2.75 for $X=\text{P}$, judged from the results in Fig. 4.

Figure 5 shows the re-constructed $(p_{\text{H}_2\text{S}}/p_{\text{H}_2})$ *vs.* x relationships for FeC_yS_x at 1 823 K on the basis of the equation:

$$\log_{10}(p_{\text{H}_2\text{S}}/p_{\text{H}_2}) = -0.8495 - 3.292x - \log_{10}((\theta-x)/x) \dots\dots\dots(23)$$

This equation is equivalent to Eqs. (20) and (21). The value of θ is determined by Eq. (22) with $s=4$. The experimental results²⁾ for FeC_yS_x are also plotted in Fig. 5 for comparison. The estimated curves appear to be in reasonable accord with the experimental values. Thus, the approximation employed for the present estimation for FeX_yS_x may be justified.

III. Summary

Equilibrium solubility data of S in molten Fe in the range of T between 1 773 and 1 873 K¹⁾ were analysed by statistical thermodynamics based on the

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

Fig. 5. Re-constructed $P_{\text{H}_2\text{S}}/P_{\text{H}_2}$ *vs.* x relationships for molten FeC_yS_x at 1 823 K, together with the experimental results,^{1,2)}

a priori assumption of the constant S-S interaction within a phase at each T .

The $E_{\text{S-Fe}}$ -value was estimated to be about -51 kJ mol^{-1} . The $E_{\text{S-S}}$ value was estimated to be about -9.6 kJ mol^{-1} over the temperature range from 1 773 to 1 873 K.

The following equation may be derived from the present analysis for molten FeX_yS_x

$$\log_{10}(p_{\text{H}_2\text{S}}/p_{\text{H}_2}) = -19.608 + 0.0054T + 16\,175/T + (7.013 - 0.0020T)x - \log_{10}((\theta-x)/x) \dots\dots\dots(24)$$

to express the relationship between the equilibrium solubility x and $(p_{\text{H}_2\text{S}}/p_{\text{H}_2})$ at a given T in a temperature range from 1 750 to 1 900 K. The value of θ for FeS_x is unity, but θ -value for FeX_yS_x might be determined by Eq. (22) with an appropriate value of s for the specific X .

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