Empirical Expression of Phosphorus Solubility in Molten Fe$_{1-y}$Cr$_y$ Given as Functions of Temperature and Phosphorus Activity

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Chemical activity–temperature–composition (a–T–x–y) relationships determined by Knudsen effusion technique were made available for molten Fe–Cr–P system by a group of Russian researchers. Nevertheless, they were not presented in form of solubility $x$ in Fe$_{1-y}$Cr$_y$P$_z$ as explicit functions of phosphorus activity $a_p$ and temperature $T$ for given $y$ and thence they are not readily usable for evaluating $P$ solubility in molten Fe$_{1-y}$Cr$_y$ at arbitrary $T$ under certain $a_p$. In the present work, effort was invested to derive empirical expression for the solubility $x$ in Fe$_{1-y}$Cr$_y$P$_z$ as functions of $T$ and $a_p$ at given $y$ from the reported $a_p$–T–x–y relationships in discrete tabulated format. Such analytical expression of solubility $x$ might allow us to proceed with more profound consideration for atomic interaction and atomic configuration in the molten Fe$_{1-y}$Cr$_y$P$_z$ on the basis of statistical thermodynamics.

KEY WORDS: molten Fe–Cr–P; non-stoichiometry; interstitial compound; phosphorus activity; Knudsen effusion technique.

1. Introduction

Equilibrium composition data for molten (Fe,Cr)P was recently reported by Zaitsev et al.$^{11}$ based on the experiment using Knudsen effusion technique. They measured activities, $a_{Fe}$ of Fe and $a_{Cr}$ of Cr as well as $a_{P}$ of P, over Fe–Cr–P ternary melt with specified compositions as a function of absolute temperature $T$. Thus, the data were not presented in form of explicit analytical expression for $x$ in molten Fe$_{1-y}$Cr$_y$P$_z$ as functions of $a_p$ and $T$ for given $y$. Instead, they are presented in form of discrete set of tabulated parameter values in the publication of Zaitsev et al.$^{11}$ Equilibrium data presented in such discrete format is not readily usable for evaluating the solubility $x$ for given Fe$_{1-y}$Cr$_y$ melt at arbitrary $T$ under certain $a_p$. Therefore, it would be more convenient to present analytical expression for $x$ as explicit functions of $T$ and $a_p$ for specified $y$ in order to take full advantage of the equilibrium solubility data presented for the Fe–Cr–P ternary melt made available by Zaitsev et al.$^{11}$

Purpose of the present work was to derive plausible empirical equations for $x$ in Fe$_{1-y}$Cr$_y$P$_z$ for given $y$ as functions of $a_p$ and $T$ to make the estimation of solubility $x$ easier for Fe$_{1-y}$Cr$_y$P$_z$ of known composition $y$ under specified $T$ at certain $a_p$.

After this first step to establish analytical or numerical $a_p$–T–x relationships for respective $y$ for Fe$_{1-y}$Cr$_y$P$_z$, statistical thermodynamic analysis as the one presented in the earlier work$^{23}$ must be undertaken to check whether the variation pattern of the analytically derived $a_p$–T–x relationships with respect to $y$ might be rationally interpretable in terms of acceptable atom configuration model. For example, available number $\theta$ of interstitial sites for occupation by $P$ atoms per metal atom in molten FeP$_z$ was determined to be 0.5 and reduced $P$ solubility in molten FeZ$_x$P$_z$ ($Z=B$ or C) was demonstrated to be interpreted in terms of reduced number $\theta$ for occupation by $P$ in the molten FeZ$_x$P$_z$. The rate of reduction of $\theta$ per occupation of $Z$ was different depending on whether the another interstitial constituent $Z$ was B or C.$^{21}$

In the case of molten Fe$_{1-y}$Cr$_y$P$_z$, Cr atoms would substitute metal lattice positions of Fe at random. Variation pattern of the $\theta$ parameter with $y$ would reflect the mode of atom clustering around the interstitial site where P atom would reside. If the derived phenomenological expression for $a_p$–T–x relationships for the molten Fe$_{1-y}$Cr$_y$P$_z$ in this work are valid ones, they must be fit in with the rational statistical thermodynamic modelling yielding interpretable $\theta$ vs. $y$ relationships. Anyway, statistical thermodynamic analysis is not within the scope of the present analysis although it must be done later as a separate work using the $a_p$–T–x relationships derived in this work.

For manufacturing of high-quality steel with atom configuration controlled to nano-meter level, analysis of interstitial atom solubilities in terms of statistical thermodynamics rather than with conventional thermodynamics is definitely desirable.
2. Analysis

2.1. Available Equilibrium Phase Relationships for Molten Fe$_1$/H$_{1-\gamma}$Cr$_\gamma$P$_x$

Zaitsev et al.$^{1}$ measured $a_\text{Fe}$, $a_\text{Cr}$ and $a_\text{P}$ using Knudsen effusion technique over Fe–Cr–P ternary melt of specified compositions. As our interest was to derive expressions for $x$ as functions of $a_\text{P}$ and $T$ for given $y$ in molten Fe$_1$/H$_{1-\gamma}$Cr$_\gamma$P$_x$, we reproduce partially the presented data in Table I in Ref. 1 as Table 1 in this article. In the Table 1, the mole fraction expression of the (Fe,Cr)P melt composition was converted to Fe$_1$/H$_{1-\gamma}$Cr$_\gamma$P$_x$ format for convenience of further analysis. As seen in Table 1, the presented data by Zaitsev et al.$^{1}$ might be sub-divided into 15 groups of $(x, y)$ combinations. In Zaitsev et al.'s work,$^{1}$ standard state for the presented chemical activity of the respective elements (Fe, Cr and P) was stated to be the elements in pure molten state.

2.2. Form of Expression for $x$

In the earlier work$^{3}$ on comparative analysis of solubility of H, N and C in Fe, solubilities of H and N (diatomic ideal gas) were demonstrated to be most conveniently represented by expression

$$x = A_x \exp(B \ln T/C/T) \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldOTSIn Fig. 1. In Fig. 2,
the estimated values of the $A$ ($\times$), $B$ ($\times$) and $C$ ($\times$) parameters for the rest of 9 sets with less number of data points are plotted besides those ($A$ ($\times$), $B$ ($\otimes$) and $C$ ($\Box$)) for the major 6 sets of the data. As seen in Fig. 1, the 6 sets with number of the data points greater than 5 were all in the range of $y$ smaller than 0.5. The 9 sets with the number of data points less than 5 are not included in the following consideration due to concern over relatively large margin of error compared with the 6 principal sets with the higher number of data points.

In fact, the estimated parameter values, $A$ ($\times$), $B$ ($\times$) and $C$ ($\times$), for the sets with the less number of data points in the range of $y$ smaller than 0.5 are deviated from those ($A$ ($\times$), $B$ ($\otimes$) and $C$ ($\Box$)) estimated for the sets with the number of the data points greater than 5 whereas those ($A$ ($\times$), $B$ ($\times$) and $C$ ($\times$)) in the range of $y$ greater than 0.5 seem to vary smoothly from those ($A$ ($\times$), $B$ ($\otimes$) and $C$ ($\Box$)) in the range of $y$ smaller than 0.5 as the continuation.

Among the estimated values for the parameters, $A$, $B$ and $C$, from these 6 principal data sets, the $A$ value ($=1.002\times10^4$) for the composition $y=0.274$ (the data set No.V) appeared to be a bit outside the line of the general trend. However, noting that the $A$ parameter is a multiplicative factor to the exponential factor, the observed deviation for $1.000\times10^4$ from the other $A$ values around $1.030\times10^4$ might be considered as still within experimental error margin. The factors, $B$ and $C$, inside the exponential term changed smoothly with $y$.

With the estimated values for $A$, $B$ and $C$, expression for $x$ at $y=0.274$ is given by

$$x (at \ y=0.274) = 1.002\times10^4 a_p \exp\left( -1.41 \ln T \right) + 1.594\times10^4 \frac{1}{T}$$

(3)

Using this expression for $x$, $a_p$ vs. $x$ isotherms are drawn as presented in Fig. 2 in which the 10 data points reported by Zaitsev et al.\textsuperscript{1)} are also plotted. Isothermal curves are drawn between 1 400 K and 1 800 K noting the fact that the experimental data reported by Zaitsev et al.\textsuperscript{1)} were available in the temperature range 1 403–1 821 K. It is noticed in Fig. 2 that all the reported 10 experimental data points fell at adequate locations in the estimated isothermal relationships. The situation was the same for the estimated $a_p$–$x$ relationships for the other $y$ values although not reproduced herein.
2.4. Compatibility of the Present Estimation Results with the Available Information

The derived $a_p$–$T$–$x$ relationships for Fe$_{1-x}$Cr$_x$P$_2$ at $y = 0.274$ look reasonable. However, in order to justify validity of the present derivation method for $x$ estimation formula, derived $x$ formulae at varying $y$ were compared with the available relevant information.

In an earlier publication, Shohoji$^{11}$ derived $p_{P^2}^{1/2}$ vs. $x$ relationships for FeZ$_x$P$_2$ through analyses of experimental data reported by Ban-ya et al.$^{4,5}$ ($p_{P^2}$: partial pressure of diatomic P$_2$ gas and Z: B or C) on the basis of statistical thermodynamics

$$\log p_{P^2} = \left(-12.080+0.005347T\right) + \left(1.860-0.001837\right)x - 2\log[(\theta-x)/x]$$

$$\theta(FeZ_xP_2) = 0.5 - sz$$

where $\theta$ refers to the number of available interstitial sites for occupation by P atoms per metal atom and $x$ the extent of blockage of the interstices per fraction of addition of interstitial element X ($s=0.4$ for B or 0.5 for C).

Figure 3 plots the calculated $p_{P^2}^{1/2}$–$x$ isotherms for molten FeP$_y$ using Eq. (4) with $\theta=0.5$. These relationships were demonstrated to reproduce correctly the experimental equilibrium phase relations reported by Ban-ya et al.$^{4,5}$ In the earlier analysis,$^{3}$ decreased $P$ solubility by increased proportion $z$ of another interstitial constituent Z ($=B$ or C) was taken into account for the representation of $x$ in terms of the decrease in the $\theta$ parameter value (that is, blockage of available interstitial site for occupation by P due to presence of other interstitial atoms Z).

At an intermediate temperature 1 600 K in the range of temperature 1 400–1 800 K over which Zaitsev et al.$^{1}$ investigated the P solubility for the (Fe,Cr) melt, comparison of the $a_p$–$x$ isotherms at varying $y$ was made in Fig. 4. In Fig. 4, the curve for $y=0$ (pure FeP$_y$) was drawn according to Eq. (4) whereas curves for the other $y$ values (Fe$_{1-x}$Cr$_x$P$_2$) were drawn using Eq. (1) with substituted values of constants, $A$, $B$ and $C$, as listed in Table 2. In drawing $a_p$–$x$ isotherm for FeP$_y$ ($y=0$) in Fig. 4, $p_{P^2}$ was converted to $a_p$ using the equilibrium constant expression given in the publication by Ban-ya et al.$^{4,5}$

$$\log(p_{P^2}^{1/2}/a_p) = 2.33 - 6120/T$$

There are a couple of features noticeable in Fig. 4:

(i) When compared at the same $x$, level of $a_p$ for FeP$_y$ ($y=0$) was considerably lower than that for Fe$_{1-x}$Cr$_x$P$_2$.

(ii) At any given $x$, $a_p$ for Fe$_{1-x}$Cr$_x$P$_2$ tended to diminish with increasing $y$ up to $y=0.114$ but then, in the range of $y$ higher than 0.114, that tendency to rise with increasing $y$.

3. Discussion

In a plot as presented in Fig. 4, decreasing $a_p$ at a given $x$ would imply enhanced solubility of P by alteration of concentration of the substitutional alloying constituent Cr to
Fe (that is, the same level of P solubility x is realised by lower \( a_p \)).

Then, the above mentioned feature (i) seems reasonable in a sense that the observed trend reflect correctly the anticipated tendency of P solubility rise by alloying with Cr into Fe but the extent of the observed \( a_p \) shift by the alloying with Cr to Fe appears somewhat excessive (by about three orders of magnitude reduction for \( a_p \) by alloying with Cr corresponding to a level \( y = 0.061 \) to Fe). This considerable shift of the \( a_p - x \) isotherm for \( Fe_{1-x}Cr_yP_x \) from that for FeP, might be genuine but might be the consequence of underestimation of \( a_p \) in the Knudsen effusion technique. In the work of Ban-ya et al.\(^{4,5}\), \( p_{p}\) was carefully measured by transportation method in which diatomic \( P_2 \) gas species being in equilibrium with FeP\(_2\) melt in the reaction tube were extracted out of the reaction chamber by flowing pure Ar carrier gas. Thus, consistency between the \( p_p \) measured by Ban-ya et al.\(^{4,5}\) and the \( a_p \) \((=p_{p}^{1/2})\) determined by Zaitsev et al.\(^{1}\) by Knudsen effusion technique must be carefully reconsidered. Quite probably, some empirical correction factor to calibrate \( p_p \) determined by Knudsen effusion method to fit to \( p_p \) measured by traditional gas equilibrium technique must be introduced. This aspect would deserve serious independent research efforts.

The observed feature (ii) in Fig. 4 is intriguing. Up to \( y = 0.12 \) in \( Fe_{1-x}Cr_yP_x \), \( a_p - x \) isotherm tended to shift towards the lower \( a_p \) side with the increasing \( x \) but then, by further rise of \( y \), \( a_p - x \) isotherm tended to shift towards higher \( a_p \) side with the further increase of \( y \). Such variation pattern of \( a_p - x \) isotherm with respect to \( y \) was observed at other temperatures as presented in Fig. 5. As seen in Fig. 5, at 1800 K, \( a_p - x \) curve for \( y = 0.061 \) and that for \( y = 0.465 \) overlapped accidentally to fall into a single curve.

This feature might look strange at first glance but, with reference to the available atom clustering models for some \( Fe_{1-y}M_yX_y \) systems,\(^{6-12}\) the observed apparently confusing \( y \)-dependence of \( a_p - x \) isotherm shift pattern along \( a_p \) direction must be interpreted in terms of change-over of cluster type surrounding P atom in the interstitial site (probably octahedral interstitial site). In the range of \( y \) smaller than 0.12, Cr-P dipole (or 1Cr/5Fe type cluster) might have formed while, in the range of \( y \) higher than 0.12, 4Cr/2Fe type cluster might have formed with reference to the information gathered by statistical thermodynamic consideration for this type of alloys.\(^{6-12}\) Anyway, to gain more concrete quantitative information, \( a_p - T - x \) relationships estimated in this work for respective \( y \) for \( Fe_{1-y}Cr_yP_x \), must be subjected to detailed statistical thermodynamic analysis. This line of analysis might be made in future as a separate work.

4. Conclusions

Through analysis of experimental data sets for molten \( Fe_{1-y}Cr_yP_x \) presented in form of combinations of (\( a_p \), \( T \)) for fixed combinations of (\( x \), \( y \)) by Zaitsev et al.\(^{1}\) expression for \( x \) as functions of \( a_p \) and \( T \) for respective \( y \) was derived in view of feasibility of more straightforward estimation of \( x \) (specially with further statistical thermodynamic analysis for \( Fe_{1-y}Cr_yP_x \) in mind). Conclusions drawn from the present work are summarised as follows.

(1) The following equation (Eq. (1)) was proved to be acceptable for estimation of \( x \) in \( Fe_{1-y}Cr_yP_x \) at given \( y \).

\[
x = A a_p \exp(B \ln T/C/T)
\]

(2) With the best-fit parameter adjustment procedure, values of constants, \( A \), \( B \) and \( C \), for specified \( y \) values were determined (Table 2).

(3) Estimation results showed that, up to \( y = 0.12 \), Cr alloying enhanced P solubility but, when \( y \) exceeded 0.12, further Cr alloying tended to reduce P solubility in \( Fe_{1-y}Cr_yP_x \).

(4) Compared with the traditional gas equilibrium measurement results, \( p_p \) determined by the Knudsen effusion technique was evaluated to be on the under-estimated side.

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