# Thermodynamics of Phosphorus and Silicon Solutions in Manganese Based Melts

V.Ya.Dashevskii, V.I.Kashin and N.P.Lyakishev

A.A.Baikov Institute of Metallurgy, Russian Academy of Science, Moscow, Russia

The study of Mn-P and Mn-Si systems is of great importance to develop and improve on dephosphorization processes in manganese based melts, production of silicomanganese, and silicothermic process to produce refined manganese ferroalloys. Published data on manganese activity in Mn-P [1-4] and Mn-Si [5-8] melts are contradictory. It results in a lack of reliable information on phosphorus and silicon activity in these melts, which is obtained through integrating the Gibbs-Dugem equation with the knowledge of manganese activity.

Up-to-date method to obtain the reliable information on thermodynamic properties of melts is a co-ordinated description of different solution characteristics measured (activities, heat of mixing) and parameters of the corresponding phase diagram.

The description performed of thermodynamic properties of the Mn-P and Mn-Si systems is based on the theory of associated solutions [9], which is applicable for ones with a strong interparticle interaction [10]. This approximation supposes an existence of complexes or associates of $A_mB_k$-type and A and B monomers in dynamic equilibrium

$$mA + kB = A_mB_k, \qquad (1)$$

$$K = \frac{\psi_{A_mB_k} X_{A_mB_k}}{(\psi_A X_A)^m (\psi_B X_B)^k}, \qquad (2)$$

where $X_A$, $X_B$, $X_{AmBk}$ - mole portions of components in associated solution; $\psi_A$, $\psi_B$, $\psi_{AmBk}$ - activity coefficients.

According to [9]

$$a_1 = \gamma_1 N_1 = \psi_A X_A, \qquad (3)$$

$$a_2 = \gamma_2 N_2 = \psi_B X_B, \qquad (4)$$

$$X_A = N_1 - [m - (m + k - 1) N_1] X_{AmBk}, \qquad (5)$$

$$X_B = N_2 - [k - (m + k - 1) N_2] X_{AmBk}, \qquad (6)$$

where $a_1$ and $a_2$ - activities; $\gamma_1$ and $\gamma_2$ - activity coefficients of components 1(A) and 2(B), respectively; $N_1$ and $N_2$ - mole portions.

Calculations were carried out according to the model of quasi-associated solutions [11]. In so doing:

$$K = \frac{X_{A_mB_k}}{(X_A)^m (X_B)^k}, \quad \psi_{A_mB_k} = \psi_A^m \psi_B^k, \qquad (7)$$

$$RT \ln \psi_A = N_2^2 \left[ \Phi_{12}(1 - 2N_1) + 2\Phi_{21} N_1 \right], \qquad (8)$$

$$RT \ln \psi_B = N_1^2 \left[ 2\Phi_{12} N_2 + \Phi_{21}(1 - 2N_2) \right], \qquad (9)$$

$$\Delta H = N_1 N_2 (\Phi_{12} N_2 + \Phi_{21} N_1) + \frac{X_{A_mB_k} RT \, d\ln K / dT}{[1 + (m + k - 1)] X_{A_mB_k}}, \qquad (10)$$

where $\Phi_{12}$, $\Phi_{21}$ - model parameters.

Mn-P system thermodynamic properties were calculated basing on information about the phase diagram [12] and enthalpy of manganese-phosphorus mixing [13]. Manganese activity on the "$Mn_2P$ solid phosphide - melt" phase equilibrium line for $N_P$ = 0.331 - 0.411 (phosphorus content) was estimated as follows:

$$a_{Mn} = p_{Mn} / p^o_{Mn}, \qquad (11)$$

where $p_{Mn}$ - manganese vapor pressure above $Mn_2P$ phosphide, calculated according to mass-spectrometric data on thermal stability of Mn-P compounds [14],

$$\lg p_{Mn} = -16278/T + 9.702; \qquad (12)$$

$p^o_{Mn}$ - vapor pressure above pure liquid manganese [15] Mn

$$\lg p^o_{Mn} = -14520/T - 3.02 \lg T + 19.24. \qquad (13)$$

Manganese activity on the "solid manganese - melt" phase equilibrium line for $N_P$ = 0.035 - 0.133 was calculated by Wagner formula [16]:

$$RT \ln a_{Mn} = \Delta G_{mel}, \qquad (14)$$

taking into account thermodynamic properties of pure manganese [15].

Manganese activities obtained for liquidus line of the phase diagram together with data on heat of phosphorus solution in manganese (Table 1) were taken as an initial experimental information to use the quasi-ideal associated solution model [11].

Table 1. Manganese Activity on Liquidus Line of Phase Diagram and Enthalpy of Mixing for Mn-P Melts

| T, K | $N_{Mn}$ | $a_{Mn}$ | T, K | $N_{Mn}$ | $a_{Mn}$ |
|---|---|---|---|---|---|
| 1440 | 0.589 | 0.060/0.051* | 1588 | 0.9903 | 2.043/2.151** |
| 1467 | 0.598 | 0.067/0.060 | 1588 | 0.9916 | 1.742/1.876 |
| 1478 | 0.599 | 0.070/0.062 | 1588 | 0.9927 | 1.651/1.633 |
| 1529 | 0.616 | 0.085/0.082 | 1588 | 0.9939 | 1.270/1.366 |
| 1575 | 0.641 | 0.100/0.110 | 1588 | 0.9948 | 1.080/1.160 |
| 1600 | 0.669 | 0.110/0.144 | 1588 | 0.9957 | 0.921/0.951 |
| 1233 | 0.867 | 0.737/0.582 | | | |
| 1300 | 0.896 | 0.811/0.713 | | | |
| 1384 | 0.932 | 0.892/0.852 | | | |
| 1488 | 0.965 | 0.946/0.942 | | | |

* Numerator - calculation on data of [12, 14, 15], denominator - calculation by the model.

**Numerator - experimental data [13], denominator - calculation by the model.

Complexes of $Mn_3P$ and $Mn_2P$ types were assumed for Mn-P system. The calculations allowed us to conclude that Mn-P melts might be preferably characterized by $Mn_3P$ clusters. The following model parameters were obtained:

$$\Phi_{P,Mn} = -100.2 \text{ kJ/mole}; \ln K = 16500/T - 8.145.$$

Using these parameters, thermodynamic characteristics of Mn-P melts were calculated (Figs.1-3). As shown, the Mn-P liquid solutions are characterized by the significant negative deviation from ideality. The quasi-ideal associated solution model allows us to write the following expression for phosphorus activity coefficient providing that infinite diluting:

$$\ln\gamma_P^o = \Phi_{P,Mn}/(RT) - \ln(K + 1). \quad (15)$$

Considering $\Phi_{P,Mn}$ and $\ln K$ we obtain

$$\ln \gamma_P^o = -12051/T - \ln[\exp(16500/T - 8.145) + 1], \quad (16)$$

whence $\gamma_P^o = 5.50 \cdot 10^{-5}$ at 1600 K. Table 2 shows obtained as compared with published data.

Table 2. Phosphorus Activity Coefficient at Infinite Dilution

| $\gamma_P^o$ | Source |
|---|---|
| $5.50 \cdot 10^{-5}$ | Present study |
| $5.21 \cdot 10^{-7}$ | [1] |
| $3.63 \cdot 10^{-10}$ | [3] |
| $3.40 \cdot 10^{-3}$ | [4] |
| $3.12 \cdot 10^{-5}$ | [17] |
| $1.40 \cdot 10^{-3}$ | [18] |
| $3.28 \cdot 10^{-6}$ | [19] |

Our value of $\gamma_P^o$ is close to published data [17], where thermodynamic characteristics of Mn-P melts were calculated on phase diagram using a polynomial parameterization of thermodynamic functions of mixing: $\Delta G$, $\Delta H$, $\Delta S$, and assuming that $\Delta H$ and $\Delta S$ are independent on temperature. The use of the polynomial method to approximate the temperature and concentration dependencies of thermodynamic functions is limited because of an ambiguous determination of parameters based on experimental information. It especially displays when thermodynamic properties of melts are calculated through phase diagrams [20]. Apparently, it resulted in the fact that values of a $_{Mn}$ [17] corresponding to data of [2] are close to our $\gamma_P^o$. It is obviously, that our concentration dependence of $a_{Mn}$, being located between the data of [2] and [3] (Fig.1), is better corresponding to the value of $\gamma_P^o$ in order of value.

Rather good agreement of $\gamma_P^o$ obtained with value calculated by us according to formula of I.S.Kulikov [19] should be noticed

$$R \ln \gamma_B^o = \Delta H_{298}^o (1/T - 4.5 \cdot 10^{-5}). \quad (17)$$

Considering $\Delta H_{298}^o(\text{MnP}) = -181$ kJ/mole [21], the formula (17) results in $\gamma_P^o = 3.28 \cdot 10^{-6}$. Value of in [18] should be considered as a too high one. I.B.Baratashvili [18] used partial enthalpy of solution of liquid phosphorus in liquid manganese $\Delta H_P^o = -147$ kJ/mole obtained in [13] on calculating by the quasi-regular solution model. However, if well-known equation for subregular solution is used

$$RT \ln \gamma_P^o = H_P^o, \quad (18)$$

then we can result in $\gamma_P^o = 1.59 \cdot 10^{-5}$ for 1600 K.

Values of enthalpy of mixing for dilute phosphorus solution in manganese [13] are in a good agreement with the quasi-ideal associated solution model (see Table 1). Comparatively high absolute values obtained for enthalpy of mixing, Gibbs energy and excessive energy are attributed to the strong interaction between atoms of manganese and phosphorus in melt. This confirms an appropriateness of he theory of associated solutions to describe thermodynamics of the system. Negative entropy of mixing confirms a tendency for Mn-P alloys to be ordered in liquid state.

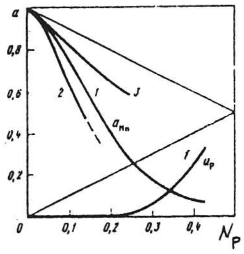

Fig. 1. Manganese and phoshorus activity in Mn-P melts: 1 - 1600 K, calculation; 2 - 1573 K [3]; 3 - 1593 K [2]

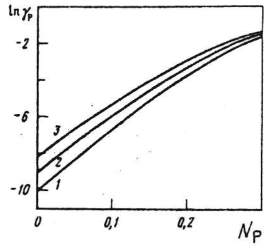

Fig. 2. Dependence of phosphorus activity coefficient on concentration in Mn-P melts T,K: 1-1573; 2-1673; 3-1773

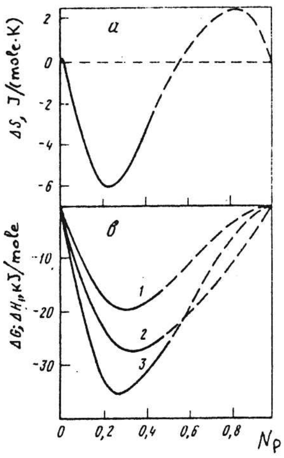

Fig. 3. Integral thermodynamic functions for Mn-P melts at 1573 K: a - $\Delta$S; b: 1 - $\Delta G^{exp}$; 2-$\Delta$G; 3 - $\Delta$H

Thermodynamic characteristics of Mn-Si system were estimated through co-ordinating of data on manganese activity with results of the calorimetric examination of the system [22]. The Mn-Si melts are characterized by a tendency to ordering within the composition range of the phase diagram [23] corresponding to $Mn_5Si_3$ [6-8] or MnSi [5,6] compounds which are congruently melting. Therefore, our calculations were performed by two ways - both for $Mn_5Si_3$ complex and MnSi one.

Calorimetric results [22] (Table 3) are in a satisfactory agreement only with data of [7], which shows that the "siliconactivity coefficient - silicon content" relationship obtained through integrating the Gibbs-Dugem equation for experimental manganese activity is in a good agreement with the phase diagram. Published data [7, 22] were used as an original experimental information to process results by the quasi-ideal associated solution model [11]. Calculations performed allowed us to

Table 3. Enthalpy of Mixing for Mn-Si Melts at 1743 K

| $N_{Mn}$ | $-\Delta H$, kJ/mole |  | $N_{Mn}$ | $-\Delta H$, kJ/mole |  |
|---|---|---|---|---|---|
|  | experiment [22] | model |  | experiment [22] | model |
| 0.1 | 10.467 | 9.477 | 0.6 | 36.425 | 41.647 |
| 0.2 | 19.468 | 19.363 | 0.7 | 28.679 | 35.695 |
| 0.3 | 27.842 | 29.140 | 0.8 | 19.887 | 27.113 |
| 0.4 | 35.587 | 37.787 | 0.9 | 10.676 | 15.267 |
| 0.5 | 39.146 | 42.966 |  |  |  |

conclude that Mn-Si melts may be preferably characterized by clusters of MnSi type. The following model parameters were found:

$$\Phi_{Mn,Si} = -29.38 \text{ kJ/mole}; \quad \Phi_{Si,Mn} = -109.8 \text{ kJ/mole};$$

$$\ln K = 7693.6/T - 1.242.$$

Basing on parameters obtained, thermodynamic characteristics of Mn-Si melts were estimated (Figs. 4, 5). These data shows rather strong negative deviation from ideality for Mn-Si liquid solutions. Comparatively high absolute values of enthalpy and Gibbs energy of mixing indicate that there is a strong interaction between manganese and silicon atoms in melt. The equation for the dependence of silicon activity coefficient on temperature in Mn-Si melts was obtained for infinite diluting with the use of Eq. (15):

$$\ln \gamma^{o}_{Si} = -13206/T - \ln [\exp(7693.6/T - 1.242) + 1], \qquad (19)$$

whence $\gamma^{o}_{Si} = 7.2 \cdot 10^{-6}$ at 1600 K.

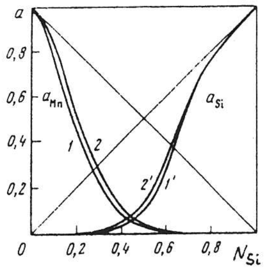

Fig. 4. Manganese and silicon activity in Mn-P melts: T, K: 1 - 1673; 2 - 1873

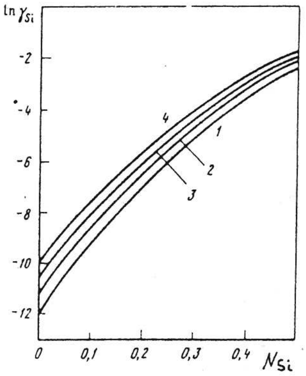

Fig. 5. Dependence of silicon activity coefficient on concentration in Mn-P melts: T, K: 1 - 1573; 2 - 1673; 3 - 1773; 4 - 1873

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