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Calculating Models of Mass Action Concentrations for Fe-P and Cr-P Melts and Optimization of Their Thermodynamic Parameters

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Abstract: Based on the phase diagrams, reliable reference experimental data and the coexistence theory of metallic melts structure involving compound formation, calculating models of mass action concentrations for Fe-P and Cr-P melts have been formulated. At the same time, some of their thermodynamic parameters have been optimized. The calculated results not only agree well with the measured values, but also obey the mass action law rigorously, this in turn shows that these models can reflect the structural characteristics of corresponding melts.

Key Words: activity; phase diagram; coexistence theory; mass action concentration

Fe-P and Cr-P binary systems are the fundamental melts of ferrous metallurgy. Metallurgists of the world unremittingly struggle for the reduction of phosphorus content of iron and steel materials, and consistently search for measures to solve the problem of day by day phosphorus content increasing in the scrap of stainless steel. However, until not long ago, we yet know little about the thermodynamic properties of both melts. The published experimental results mostly related only to dilute solutions of phosphorus not only for Fe-P melts [1–4], but also for Cr-P melts [5,6]. So it is difficult to use them as the practical basis to formulate the theoretical model, which obeys the mass action law. Fortunately, in recent years, Russia scholars A.I. Zaitsev, *et al.* [7–9] achieved creative success in the field of studying thermodynamic properties of phosphorus containing metallic melts: choosing pure liquid components as standard states and using Knudsen -cell mass spectrometer, they measured the component activities of Fe-P, Cr-P systems *et al.*, and determined a lot of thermodynamic parameters of different phosphides. These experimental results can be used as reliable practical basis for the formulation of theoretical models. The goal of this paper is just to deduce the calculating models of mass action concentrations for both of the binary systems mentioned above, so as to furnish the theoretical basis for further study.

1 Calculating Models

1.1 Fe-P melts

According to the phase diagram [10], there are FeP, Fe_2P, Fe_3P, FeP_2 and FeP_4 phosphides formed in Fe-P binary melts. As iron and steel melts are iron based materials, the phosphorus content of them is not possible to reach $\Sigma x_P = 0.667–0.8$, so it is reasonable to neglect the presence of FeP_2 and FeP_4 in these melts. Hence, the structural units of these melts can be determined as Fe, P atoms as well as FeP, Fe_2P and Fe_3P molecules. Assuming the composition of the melts as $b=\Sigma x_{Fe}$, $a=\Sigma x_P$; the equilibrium mole fraction of every structural unit expressed by the composition of the melts as $x=x_{Fe}$, $y=x_P$, $z_1=x_{FeP}$, $z_2=x_{Fe_2P}$, $z_3=x_{Fe_3P}$; the mass action concentration of every structural unit after normalization as $N_1=N_{Fe}$, $N_2=N_P$, $N_3=N_{FeP}$, $N_4=N_{Fe_2P}$, $N_5=N_{Fe_3P}$; Σx = sum of all equilibrium mole fractions, then it gives

(1) Chemical equilibria.

$Fe_{(l)} + P_{(l)} = FeP_{(l)}$,

$$K_1=\frac{N_3}{N_1N_2},\quad N_3=K_1N_1N_2,\quad z_1=K_1\frac{xy}{\Sigma x} \tag{1}$$

$\Delta G^\ominus = -81\,025 + 1.4\,T$ (J/mol) [7].

$2Fe_{(l)} + P_{(l)} = Fe_2P_{(l)}$,

$$K_2=\frac{N_4}{N_1^2N_2},\quad N_4=K_2N_1^2N_2,\quad z_2=K_2\frac{x^2y}{(\Sigma x)^2} \tag{2}$$

$\Delta G^\ominus = -145\,990 + 15.6\,T$ (J/mol) [7].

$3\,Fe_{(l)} + P_{(l)} = Fe_3P_{(l)}$,

$$K_3=\frac{N_5}{N_1^3N_2},\quad N_5=K_3N_1^3N_2,\quad z_3=K_3\frac{x^3y}{(\Sigma x)^3} \tag{3}$$

$\Delta G^\ominus = -207\,390 + 53.5\,T$ (J/mol) [7].

(2) Mass balance.

$$N_1+N_2+N_3+N_4+N_5-1=0 \tag{4}$$

$$b=\Sigma x\,(N_1+N_3+2N_4+3N_5)=x+z_1+2z_2+3z_3 \tag{5}$$

$$a=\Sigma x\,(N_2+N_3+N_4+N_5)=y+z_1+z_2+z_3 \tag{6}$$

From equations (5) and (6),

$$aN_1-bN_2+(a-b)N_3+(2a-b)N_4+(3a-b)N_5=0 \tag{7}$$

Equations (4)+(7) gives

$$1-(a+1)N_1-(1-b)N_2=K_1(a-b+1)N_1N_2+K_2(2a-b+1)N_1^2N_2+K_3(3a-b+1)N_1^3N_2 \quad (8)$$

Equations (1)–(8) are the calculating model of mass action concentrations for Fe-P, in which equations (1)–(7) are used for the calculation of the mass action concentrations, while equations (4) and (8) are served for determination of equilibrium constants by regression. However, the correctness of the model can only be verified by the measured activities of the melts.

1.2 Cr-P melts

At present, there are different opinions about the structural units of the phase diagram of Cr-P binary system: the published phosphides of reference [11] are CrP, Cr_2P, Cr_3P and CrP_2; the presence of seven phosphides CrP, $Cr_{12}P_7$, Cr_2P, Cr_3P, Cr_2P_3, CrP_2 and CrP_4 is considered by reference [12]; while A.I. Zaitsev, *et al.* [8] presented four phosphides CrP, Cr_2P, Cr_3P and Cr_3P_2 in their thermodynamic calculation. Comparison of three opinions by calculation shows that the latter agrees better with practice than the other two. However, when it was used in Fe-Cr-P ternary melts [13], it happened that at $\Sigma x_P>0.3$, N_P would be much greater than a_P. From this it is seen that at high phosphorus content, the neglect of the presence of CrP_2 is unreasonable. Thus the structural units of Cr-P binary melts can be determined as Cr, P atoms as well as CrP, Cr_2P, Cr_3P, Cr_3P_2 and CrP_2 molecules. Putting the composition of the melts as $b=\Sigma x_{Cr}$, $a=\Sigma x_P$; the equilibrium mole fraction of every structural unit expressed by the composition of the melts as $x=x_{Cr}$, $y=x_P$, $z_1=x_{CrP}$, $z_2=x_{Cr_2P}$, $z_3=x_{Cr_3P}$, $z_4=x_{Cr_3P_2}$, $z_5=x_{CrP_2}$; the mass action concentration of every structural unit after normalization as $N_1=N_{Cr}$, $N_2=N_P$, $N_3=N_{CrP}$, $N_4=N_{Cr_2P}$, $N_5=N_{Cr_3P}$, $N_6=N_{Cr_3P_2}$, $N_7=N_{CrP_2}$; Σx = sum of all equilibrium mole fractions, then it gives

(1) Chemical equilibria.

$Cr_{(l)} + P_{(l)} = CrP_{(l)}$,

$$K_1=\frac{N_3}{N_1N_2},\quad N_3=K_1N_1N_2,\quad z_1=K_1\frac{xy}{\Sigma x} \quad (9)$$

$\Delta G^\ominus = -103\,560+1.2T$ (J/mol) [8].

$2\,Cr_{(l)} + P_{(l)} = Cr_2P_{(l)}$,

$$K_2=\frac{N_4}{N_1^2N_2},\quad N_4=K_2N_1^2N_2,\quad z_2=K_2\frac{x^2y}{(\Sigma x)^2} \quad (10)$$

$\Delta G^\ominus = -150\,607+34.2\,T$ (J/mol) [8].

$3Cr_{(l)} + P_{(l)} = Cr_3P_{(l)}$,

$$K_3=\frac{N_5}{N_1^3N_2},\quad N_5=K_3N_1^3N_2,\quad z_3=K_3\frac{x^3y}{(\Sigma x)^3} \quad (11)$$

$\Delta G^\ominus = -229\,587-53.6\,T$ (J/mol) [8].

$3Cr_{(l)} + 2P_{(l)} = Cr_3P_{2(l)}$,

$$K_4=\frac{N_6}{N_1^3N_2^2},\quad N_6=K_4N_1^3N_2^2,\quad z_4=K_4\frac{x^3y^2}{(\Sigma x)^4} \quad (12)$$

$\Delta G^\ominus = -261\,070+0.4\,T$ (J/mol) [8].

$Cr_{(l)} + 2P_{(l)} = CrP_{2(l)}$,

$$K_5=\frac{N_7}{N_1N_2^2},\quad N_7=K_5N_1N_2^2,\quad z_5=K_5\frac{xy^2}{(\Sigma x)^2} \quad (13)$$

$\Delta G^\ominus = -479\,274.51+165.778\,T$ (J/mol) [13].

$\Delta G^\ominus_{CrP_2}$ in equation (13) is an optimized thermodynamic parameter obtained during the formulation of the calculating model of mass action concentrations for ternary Fe-Cr-P melts [13].

(2) Mass balance.

$$N_1+N_2+N_3+N_4+N_5+N_6+N_7-1=0 \quad (14)$$

$$b=\Sigma x(N_1+N_3+2N_4+3N_5+3N_6+N_7)=x+z_1+2z_2+3z_3+3z_4+z_5 \quad (15)$$

$$a=\Sigma x(N_2+N_3+N_4+N_5+2N_6+2N_7)=y+z_1+z_2+z_3+2z_4+2z_5 \quad (16)$$

From equations (15) and (16),

$$aN_1-bN_2+(a-b)N_3+(2a-b)N_4+(3a-b)N_5+(3a-2b)N_6+(a-2b)N_7=0 \quad (17)$$

Equations (14)+(17) gives:

$$1-(a+1)N_1-(1-b)N_2=K_1(a-b+1)N_1N_2+K_2(2a-b+1)N_1^2N_2+K_3(3a-b+1)N_1^3N_2+K_4(3a-2b+1)N_1^3N_2^2+(a-2b+1)N_1N_2^2 \quad (18)$$

Aforementioned equations (9)–(18) are the calculating model of mass action concentrations for Cr-P melts, in which equations (9)–(17) are used to calculate the mass action concentrations, while equations (14) and (18) are applied for the determination of equilibrium constants by regression.

2 Calculated Results and Discussions

2.1 Fe-P melts

In the course of the calculation by equations (1)–(7), it was found that compared with a_{Fe} and a_P respectively N_{Fe} and N_P still have obvious error, *i.e.* N_{Fe} and N_P are respectively smaller than a_{Fe} and a_P: $R_{Fe.average}(=a_{Fe}/N_{Fe})=1.044\,084$, $R_{P.average}(=a_P/N_P)=1.067\,87$. In order to correct the erroneous situation, the optimization of $K_{Fe\text{-}P}$ was performed, putting

$$K_{FeP}=10^{[(207390-53.5T)/4.575/4.1868\,T]}/C.$$

Changing C from 1 to 3 and observing the variation of R_{Fe} and R_P, it was found that when $C=1.798\,341$, $R_{Fe.average}=0.998\,449\,3$, $R_{P.average}=1.025\,267$, *i.e.* N_{Fe} and N_P are respectively in good agreement with a_{Fe} and a_P, in this case

$\Delta G^{\ominus} = -207\,390 + 58.382\,T$ (J/mol).

This figure is very close to that published later by A. I. Zaitsev, *et al.* [9] as $\Delta G^{\ominus} = -207\,390 + 58.5\,T$ (J/mol), which can also make $R_{\mathrm{Fe,average}} = 0.997\,584\,5$, $R_{\mathrm{P,average}} = 1.024\,658$. Hence for binary systems, using both of them will give accurate calculation of mass action concentrations. How ever, when they were used to the Fe-Cr-P ternary melts, the former made the correlation coefficient $r = 0.801\,37$ for the relationship between $\lg K_{\mathrm{FeCrP}}$ and $1/T$, while the latter got $r = 0.786\,33$. Therefore, seeing the situation as a whole, the former is superior to the latter. By means of equations (1)–(7) and the optimized $\Delta G^{\ominus}_{\mathrm{Fe,P}}$, calculated N_{Fe} and N_{P} are compared respectively with a_{Fe} and a_{P} at different temperatures and compositions of the melts (in **table 1**). It can be seen that the calculated and measured values are in good agreement, showing that the deduced model can reflect the structural reality of Fe-P melts. In order to have an overview of these melts, the variations of the mass action concentrations of different structural units with Σx_{P} for the melts at 1 773 K are given in **figure 1**.

2.2 Cr-P melts

Using equations (9)–(17), the calculated N_{Cr} and N_{P} are compared respectively with a_{Cr} and a_{P} at different temperatures and compositions of the melts (in **table 2**). It is seen that the agreement between the calculated and measured values are well, this in turn shows that the aforementioned model can reflect the structural characteristics of Cr-P melts. The variations of the mass action concentrations of all structural units with compositions of Cr-P melts at 1 773 K are illustrated in **figure 2**.

3 Conclusions

(1) According to the phase diagrams, reliable measured activities and thermodynamic parameters from reference sources as well as the coexistence theory of metallic melts structure involving compound formation, the calculating models of mass action concentrations for Fe-P and Cr-P melts have been formulated. The calculated results agree well with practice, showing these models can reflect the structural reality of corresponding melts.

(2) The optimized thermodynamic parameter $\Delta G^{\ominus} = -207\,390 + 58.382\,T$ (J/mol) not only makes the calculated results agree with practice, but also renders the relationship between K_{FeCrP} and $1/T$ more reasonable, so

Table 1 Comparison of calculated N_{Fe} and N_{P} with measured a_{Fe} and a_{P} respectively at different temperatures and compositions of the melts

Σx_{P}	T/K	N_{Fe}	a_{Fe}	N_{P}	a_{P}
0.015	1 790	0.984 488 4	0.989	$4.039\,648\times10^{-6}$	3.97×10^{-6}
0.030	1 772	0.967 874 9	0.973	$7.797\,246\times10^{-6}$	7.82×10^{-6}
0.101	1 775	0.870 554 8	0.865	$4.034\,881\times10^{-5}$	4.03×10^{-5}
0.101	1 723	0.870 001 9	0.873	$2.940\,323\times10^{-5}$	4.89×10^{-5}
0.101	1 695	0.879 685 1	0.880	$2.455\,374\times10^{-5}$	2.47×10^{-5}
0.101	1 601	0.868 507 7	0.862	$1.266\,355\times10^{-5}$	1.25×10^{-5}
0.150	1 711	0.776 767 2	0.778	$5.995\,781\times10^{-5}$	6.06×10^{-5}
0.150	1 406	0.763 543 7	0.764	$5.346\,938\times10^{-6}$	5.35×10^{-6}
0.200	1 770	0.654 407 4	0.656	$1.926\,813\times10^{-4}$	1.87×10^{-4}
0.200	1 669	0.646 849 9	0.638	$1.071\,090\times10^{-4}$	1.11×10^{-4}
0.200	1 525	0.633 249 2	0.627	$3.944\,751\times10^{-5}$	4.01×10^{-5}
0.200	1 437	0.622 661 7	0.623	$1.902\,697\times10^{-5}$	1.92×10^{-5}
0.240	1 757	0.525 363 5	0.517	$3.876\,418\times10^{-4}$	3.86×10^{-5}
0.240	1 624	0.507 009 3	0.505	$1.853\,500\times10^{-4}$	1.76×10^{-4}
0.240	1 449	0.474 251 0	0.472	$5.568\,930\times10^{-5}$	5.54×10^{-5}
0.270	1 768	0.414 757 2	0.414	$8.218\,189\times10^{-4}$	8.17×10^{-4}
0.270	1 729	0.407 901 0	0.399	$6.873\,943\times10^{-4}$	6.79×10^{-4}
0.270	1 591	0.380 085 9	0.383	$3.390\,104\times10^{-4}$	3.37×10^{-4}
0.300	1 773	0.297 809 7	0.303	$1.934\,716\times10^{-3}$	1.95×10^{-3}
0.300	1 709	0.283 477 0	0.285	$1.518\,739\times10^{-3}$	1.50×10^{-3}
0.300	1 640	0.266 830 0	0.265	$1.146\,936\times10^{-3}$	1.12×10^{-3}
0.320	1 677	0.201 431 3	0.200	$2.691\,464\times10^{-3}$	2.72×10^{-3}
0.320	1 649	0.194 381 3	0.195	$2.454\,937\times10^{-3}$	2.45×10^{-3}

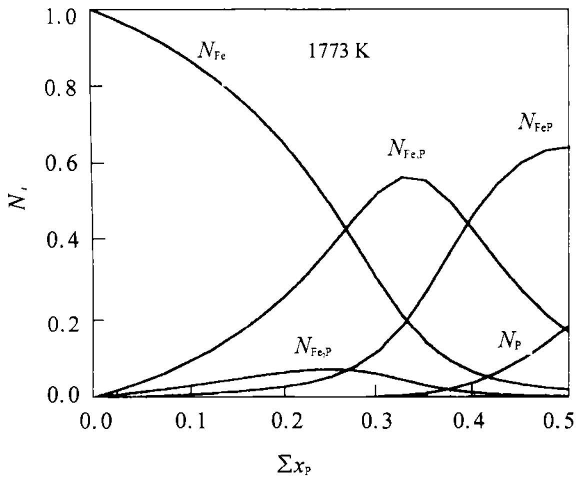

Figure 1 Change of the mass action concentrations of different structural units in Fe-P melts with Σx_P at 1 773 K

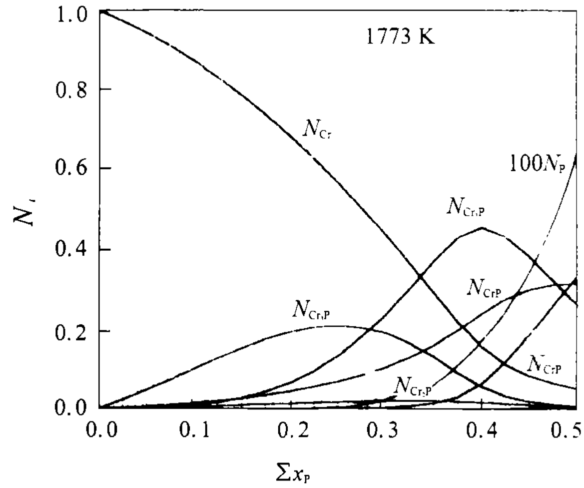

Figure 2 Change of the mass action concentrations of different structural units in Cr-P melts with Σx_P at 1 773 K

Table 2 Comparison of calculated N_{Cr} and N_P with measured a_{Cr} and a_P respectively at different temperatures and compositions of the melts

Σx_P	T / K	N_{Cr}	a_{Cr}	N_P	a_P
0.130	1 814	0.826 843 7	0.833	$3.353\,331\times10^{-5}$	3.28×10^{-5}
0.130	1 780	0.823 0700	0.821	$2.708\,547\times10^{-5}$	2.73×10^{-5}
0.153	1 810	0.785 662 1	0.785	$4.447\,868\times10^{-5}$	4.51×10^{-5}
0.153	1 775	0.780 097 3	0.778	$3.615\,496\times10^{-5}$	3.61×10^{-5}
0.153	1 741	0.774 5000	0.766	$2.918\,134\times10^{-5}$	2.89×10^{-5}
0.153	1 708	0.768 954 2	0.770	$2.337\,978\times10^{-5}$	2.37×10^{-5}
0.153	1 664	0.761 530 9	0.759	$1.699\,172\times10^{-5}$	1.66×10^{-5}
0.175	1 812	0.744 221 4	0.745	$5.942\,771\times10^{-5}$	6.02×10^{-5}
0.175	1 782	0.738 015 1	0.729	$5.042\,093\times10^{-5}$	4.98×10^{-5}
0.175	1 738	0.728 364 5	0.729	$3.900\,815\times10^{-5}$	3.90×10^{-5}
0.175	1 706	0.721 002 3	0.718	$3.194\,396\times10^{-5}$	3.14×10^{-5}
0.195	1 815	0.704 591 6	0.710	$7.712\,140\times10^{-5}$	7.64×10^{-5}
0.195	1 790	0.698 3960	0.705	$6.790\,816\times10^{-5}$	6.80×10^{-5}
0.195	1 743	0.685 897 1	0.681	$5.274\,114\times10^{-5}$	4.05×10^{-5}
0.250	1 819	0.583 321 2	0.578	$1.527\,061\times10^{-4}$	1.55×10^{-4}

it is an ideal thermodynamic parameter.

(3) At high content of phosphorus, the consideration of the presence of CrP_2 in the calculating model is favorable to obtain good agreement between the calculated and measured values.

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