CALCULATING MODELS OF MASS ACTION CONCENTRATIONS FOR MATTES (Cu_2S-FeS-SnS) INVOLVING EUTECTIC

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ABSTRACT

Based on the the facts that cations and anions of molten salts and binary basic oxide solid solutions don't separate from each other as well as that the electric conductivities of mattes are greater than that of salts and basic oxide solid solutions, calculating models of mass action concentrations for binary and ternary mattes involving eutectic have been formulated according to the same principle that cations and anions of mattes also don't separate from each other. Calculated results agree well with measured values, this in turn shows that the calculating models can reflect the structural characteristics of the mattes concerned.

1. INTRODUCTION

Mattes are important intermediate products in the extraction of copper, nickel and lead from their concentrates. A large number of research works has been done in the technology of extraction. However, a little is known about the thermodynamical properties of mattes, especially about the activities of mattes. It had been shown that cations and anions of molten salts as well as binary basic oxide solid solutions don't separate from each other on account of their great electric conductivities, hence being short of dielectric medium, so as to reduce the strong attractive forces between cations and anions[1,2]. For this reason, the mass action concentrations of molten salts and basic oxide solid solutions can be calculated by the same calculating models of mass action concentrations for corresponding metallic melts (involving compound, peritectic, solid solution, eutectic and so on)[3—6]. The electric conductivities[7] of FeS and Cu_2S at 1500℃ are respectively 1500 and 150 Ω^{-1} cm^{-1}. The electric conductivity[8] of 100% Cu_2S is 100 $\Omega^{-1}cm^{-1}$, that of 25%Cu_2S and 75%FeS melts equals 930 Ω^{-1} cm^{-1}. In both cases, electronic conductivity plays greater role, and their electric conductivities are greater than that of molten salts and basic oxide solid solutions ($<0.1\sim20$ $\Omega^{-1}cm^{-1}$). In case of absence of electric field, it is difficult to say, that there would be any dielectric medium, being able to reduce the attractive forces between cations and anions of mattes and make them separate from each other. So it is reasonable to suppose, that the mass action concentrations of mattes can also be calculated by the same models for corresponding metallic melts. The goal of this paper is just to realize the supposition.

2. CALCULATING MODELS

2.1 Binary mattes involving eutectic

According to the structure of binary metallic melts involving eutectic[6], the following assumptions can be drawn for the structure of binary mattes involving eutectic[9,10].

(1) Within molten mattes, eutectic structure is still retained to different degree. So mattes are practically composed of two solutions.

(2) There are intermediate compound (or short range order chemical cluster) formation within mattes, which plays role of reducing the mass action concentrations of molten mattes and can dissolve in both solutions.

(3) Chemical reactions between the two solutions obey the mass action law.

As binary mattes Cu_2S—FeS, Cu_2S—SnS and FeS—SnS exhibit symmetrical deviations of activity, which indicates the formation of AB — form intermediate compound (short range order chemical cluster). So taking FeS—SnS melts for example, it can be assumed that they consist of SnS, FeS and intermediate compound $FeSnS_2$, and form two solutions FeS+$FeSnS_2$ and SnS+$FeSnS_2$.

Putting $b=\sum n_{FeS}$, $a=\sum n_{SnS}$, $x=n_{FeS}$, $y=n_{SnS}$, $z=n_{FeSnS_2}$, $N_1=N_{FeS}$, $N_2=N_{SnS}$, $N_3=N_{FeSnS_2}$ ($\sum n$ represents mole number calculated from results of chemical analysis; N_i are the mass action concentrations, i. e. equilibirum mole fractions), then it gives chemical equilibrium:

$$(Fe^{2+}S^{2-})+(Sn^{2+}S^{2-})=(FeSnS_2) \qquad K=N_3/N_1N_2,\ N_3=KN_1N_2 \tag{1}$$

and mass balance:

$$b=x+z, \quad a=y+z \tag{2}$$
$$N_1=x/b, \quad N_2=y/a \tag{3}$$

Substituting Eqs. (3) into Eqs. (2) then

$$N_1+KN_1N_2/b=1,\ N_2+KN_1N_2/a=1 \tag{4}$$

from Eqs. (4)

$$\left.\begin{aligned} &N_1+N_2+KN_1N_2(1/a+1/b)=2\\ &K=ab(2-N_1-N_2)/(a+b)/N_1N_2\end{aligned}\right] \tag{5}$$

Equation (5) is used for calculation of equilibrium constant at given measured activities ($N_1=a_1$, $N_2=a_2$).

Furtheremore from Eqs. (4)

$$N_1+KN_1N_2/b=N_2+KN_1N_2/a \tag{6}$$

and from Eqs. (2)

$$y=a-b+x,\ N_2=y/a=1-b(1-N_1)/a \tag{7}$$

Substtitution of Eqs. (7) into Eq. (6) gives.

$$\left.\begin{aligned} &bKN_1^2+[(a-b)K+ab]N_1-ab=0\\ &N_1=\{-[(a-b)K+ab]\\ &\quad+[((a-b)K+ab)^2+4ab^2K]^{1/2}\}/2bK\end{aligned}\right] \tag{8}$$

Eqs. (3), (5), (7) and (8) are the calculating models of mass action concentrations for binary mattes involving eutectic.

2. 2 Ternary mattes involving eutectic

As mattes $FeS-Cu_2S-SnS$ consist of three binary mattes involving eutectic, so they are practically composed of three solutions: $FeS+Cu_2FeS_2+FeSnS_2$, $Cu_2S+Cu_2FeS_2+Cu_2SnS_2$ and $SnS+Cu_2SnS_2+FeSnS_2$.

Putting $a=\sum n_{FeS}$, $b=\sum n_{Cu_2S}$, $c=\sum n_{SnS}$, $x=n_{FeS}$, $y=n_{Cu_2S}$, $z=n_{SnS}$, $u=n_{Cu_2FeS_2}$, $v=n_{FeSnS_2}$, $w=n_{Cu_2SnS_2}$, $N_1=N_{FeS}$, $N_2=N_{Cu_2S}$, $N_3=N_{SnS}$, $N_4=N_{Cu_2FeS_2}$, $N_5=N_{FeSnS_2}$, $N_6=N_{Cu_2SnS_2}$, then it gives chemical equilibria:

$$(Fe^{2+}S^{2-})+(Cu_2^{2+}S^{2-})=(Cu_2FeS_2) \qquad K_1=N_4/N_1N_2,\ N_4=K_1N_1N_2 \tag{9}$$

$$(Fe^{2+}S^{2-})+(Sn^{2+}S^{2-})=(FeSnS_2) \qquad K_2=N_5/N_1N_3,\ N_5=K_2N_1N_3 \tag{10}$$

$$(Cu_2^{2+}S\,2-)+(Sn^{2+}S^{2-})=(Cu_2SnS_2) \qquad K_3=N_6/N_2N_3,\ N_6=K_3N_2N_3 \tag{11}$$

and mass balance:

$$a=x+u+v$$
$$N_1+(K_1N_1N_2+K_2N_1N_3)/a=1 \tag{12}$$

$$b=y+u+w$$
$$N_2+(K_1N_1N_2+K_3N_2N_3)/b=1 \tag{13}$$

$$c=z+v+w$$
$$N_3+(K_2N_1N_3+K_3N_2N_3)/c=1 \tag{14}$$

(12)+(13)+(14) gives

$$abc(3-N_1-N_2-N_3)=c(a+b)K_1N_1N_2+b(a+c)K_2N_1N_3+a(b+c)K_3N_2N_3 \tag{15}$$

Equations (12), (13), (14) and (15) are the calculating model of mass action concentrations for ternary mattes involving eutectic, in which Eq. (15) is used for calculating equilibrium constants by regression method.

Of course, the correctness of calculating models can only be verified by measured activities.

3. CALCULATED RESULTS

3. 1 Binary mattes involving eutectic

By use of measured activities from literatures[11-13]and Eq. (5) the calculated equilibrium constants of intermediate compound formation for three binary mattes Cu_2S-FeS, Cu_2S-SnS and FeS-SnS are shown in Tab. I. It can be seen from the table, that the equilibrium con-

stants of intermediate compound formation for three binary mattes are fairly constant, this confirms that the aforementioned chemical reactions rigorously obey the mass action law.

Tab. I Equilibrium constants of intermediate compound formation for several binary mattes

x_a	Cu_2S-FeS	Cu_2S—SnS			FeS—SnS	
	1473K	1323K	1423K	1473K	1073K	1273K
0.1	2.48889		2.711250	2.385890	0.586006	0.630062
0.2	2.65770		2.366240	2.193640	0.589670	0.652993
0.3	2.45355	2.718526	2.238551	2.050773	0.609078	0.694103
0.4	2.34056	2.632597	2.148001	1.974899	0.609682	0.677350
0.5	2.30202	2.631792	2.179931	1.931574	0.606936	0.695900
0.6	2.32168	2.632597	2.150057	1.962188	0.614236	0.686473
0.7	2.41082	2.718526	2.328261	2.028680	0.626900	0.678414
0.8	2.49768		2.507800	2.102087	0.618159	0.674795
0.9	2.77851		2.637931	2.228260	0.601236	0.679302
Kaver	2.58349	2.666808	2.363252	2.095332	0.606878	0.674377
$\triangle G°$, J/mol	−11630	−10795	−10181	−9064	4458	4172

The relationship of equilibrium constant and temperature of Cu_2SnS_2 compound formation for mattes Cu_2S—SnS is

$$\log K = -1298.56/T - 10.565 \qquad (16)$$

Its standard free energy of formation is

$$\triangle G°_{1323-1473K} = -24873.4 + 10.5657T, \text{ J/mol } (r = 0.9770117) \qquad (17)$$

The relationship of equilibrium constant and temperature of $FeSnS_2$ compound formation for mattes FeS—SnS is

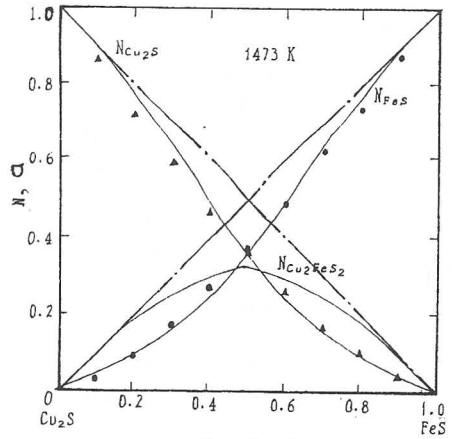

Fig. 1 Comparison of calculated mass action concentrations with measured activities for Cu_2S—FeS mattes at 1473K

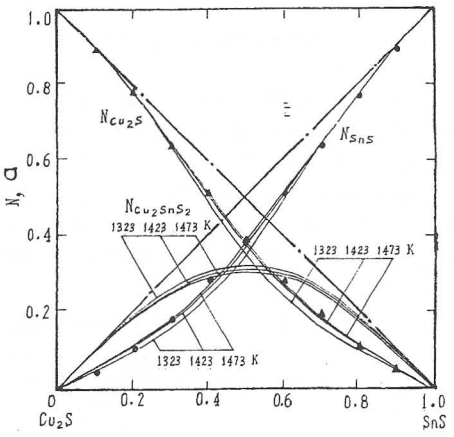

Fig. 2 Comparison of calculated mass action concentrations with measured activities for Cu_2S—SnS mattes

$$\log K = -312.8/T + 0.074627 \qquad (18)$$

Its standard free energy of formation is

$$\triangle G°_{1073-1273K} = 5991.56 - 1.4295T, \text{ J/mol } (r = 1.000) \qquad (19)$$

The calculated mass action concentrations by Eqs. (1), (7) and (8) are compared with measured activities as shown in Fig. 1, Fig. 2 and Fig. 3. It is seen from the figures, that irrespective as to whether positive or negative deviations relative to Raoult's law,

the agreement between calculated and measured values is fairly good, this in turn shows that the calculating model can reflect the structural characteristics of three binary mattes.

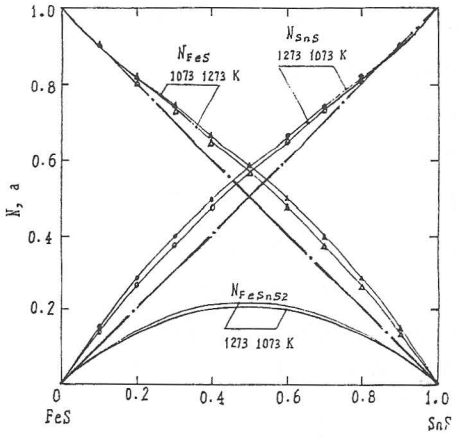

Fig. 3 Comparison of calculated mass action concentrations with measured activities for FeS—SnS mattes

3. 2 Ternary mattes involving eutectic

Using Eqs. (12), (13) and (14) as well as equilibrium constants of corresponding binary mattes at 1473K, the calculated mass action concentrations N_{SnS} are compared with measured activities a_{SnS} in Fig. 4 for different x_{FeS}/x_{Cu_2S} ratios. Good agreement between calculated and measured values indicates that the calculating model for ternary mattes also reflects the structural reality of these mattes.

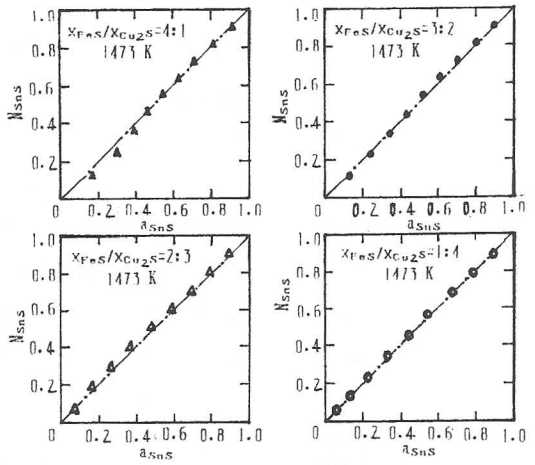

Fig. 4 Comparison of calculated masss action concentrations with measured activities for FeS — Cu_2S — SuS mates at 1473K

For the sake of reference, the calculated mass action concentrations N_{FeS} and N_{Cu_2S} at 1473K for different X_{FeS}/X_{Cu_2S} ratio are also given in Tab. Ⅱ.

Tab. Ⅱ Calculated N_{FeS} and N_{Cu_2S} at 1473K and different X_{FeS}/X_{Cu_2S} ratios for FeS—Cu_2S—SnS ternary mattes

X_{SnS}	X_{FeS}/X_{Cu_2S}	N_{FeS}	N_{Cu_2S}	X_{SnS}	X_{FeS}/X_{Cu_2S}	N_{FeS}	N_{Cu_2S}
0.1	4 : 1	0.708245	0.0788679	0.1	3 : 2	0.478385	0.195359
0.2		0.643199	0.0681760	0.2		0.450445	0.162235
0.3		0.577552	0.0585683	0.3		0.413844	0.135315
0.4		0.510518	0.0497356	0.4		0.371137	0.112238
0.5		0.440859	0.0414233	0.5		0.323408	0.091608
0.6		0.367072	0.0334065	0.6		0.270826	0.072506
0.7		0.287531	0.0254729	0.7		0.212986	0.054268
0.8		0.200642	0.0174094	0.8		0.149140	0.036377
0.9		0.105062	0.0089940	0.9		0.078401	0.018404
0.1	2 : 3	0.250428	0.391925	0.1	1 : 4	0.093758	0.655483
0.2		0.253355	0.311343	0.2		0.096980	0.536925
0.3		0.246014	0.248468	0.3		0.099378	0.425098
0.4		0.229398	0.198283	0.4		0.098744	0.327799
0.5		0.205252	0.156542	0.5		0.093316	0.247660
0.6		0.174938	0.120320	0.6		0.082720	0.182298
0.7		0.139205	0.087674	0.7		0.067511	0.127782
0.8		0.098268	0.057296	0.8		0.048390	0.080726
0.9		0.051976	0.028281	0.9		0.025828	0.038687

4. CONCLUSIONS

(1) Calculating models of mass action concentrations for binary and ternary mattes involving eutectic have been formulated according to the same principle that cations and anions don't separate from each other as in the case of molten salts and binary basic oxide solid solutions.

(2) Good agreement between calculated and measured values shows that aforementioned models can reflect the structural characteristics of corresponding mattes.

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