THERMODYNAMIC STUDY OF THE LIQUID Fe–S SYSTEM BY USE OF A DROP CALORIMETER *

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ABSTRACT

Heat contents of the Fe–S system were measured with a drop calorimeter in the sulfur composition range $X_S = 0.380–0.500$ (FeS) and in the temperature range 942–1506 K to construct an $(H_T - H_{298\,15})$–temperature–composition ternary diagram. By use of a thermodynamic analysis method, the mixing free energy, enthalpy and entropy of the liquid Fe–S mixtures were determined at 1473 and 1523 K, based on the measured heat contents. The partial molar free energies (activity of iron and partial pressure of diatomic sulfur) agreed well with the literature values, suggesting the applicability of the thermodynamic analysis method for liquid mixtures with semi-metals or chalcogen.

INTRODUCTION

Matte phases, which are composed of liquid, mixed sulfides of heavy metals, are important intermediate products in the extraction of copper, nickel and lead from their concentrates. The Fe–S system is fundamental to these matte phases, and the knowledge of its physicochemical properties is of practical importance for pyrometallurgy. Little, however, is known about its thermochemical properties at high temperature [1,2], and measurements of heat content, specific heat and enthalpy of phase change in Fe–S mixtures were carried out in this study.

Thermodynamic quantities of liquid mixtures, such as the mixing free energy, enthalpy and entropy, can be obtained calorimetrically by use of the so-called thermodynamic analysis method which was originally developed by

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* Dedicated to Professor Syûzô Seki in honor of his contribution to Calorimetry and Thermal Analysis.
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Oelsen [3]. We consider this method useful for various liquid mixtures with highly volatile semi-metals or chalcogen, whose thermodynamic quantities are not necessarily easy to determine at high temperature by means of conventional methods, such as gas-equilibration, vapour pressure measurement or electromotive force measurement. Hence, this study aims to show the applicability of the thermodynamic analysis method for high temperature, liquid mixtures with volatile elements including sulfur.

METHODS

Experimental apparatus and procedures

A drop calorimeter was used as the experimental apparatus, details of which are given in a separate paper [4]. The samples were prepared with iron (99.99% purity) and a stoichiometric compound of FeS which was synthesized with iron chips and sulfur (99.999% purity) in a vacuum-sealed silica container at high temperature. About 8 g of sample was put into a vacuum-sealed silica ampoule (3 g in weight) with an inner diameter of 20 mm and a height of 20 mm to avoid oxidation and evaporation of the sample. The experiments were conducted for eight mixtures having different mole fractions of sulfur ($0.380 \leqslant X_S \leqslant 0.500$) in the temperature range 942–1506 K, as illustrated by the shaded area in the phase diagram of the Fe–S binary system (Fig. 1) [5]. The experiments were limited to temperatures less than 1550 K due to the collapse of the vacuum-sealed sample container. After the experiments the specimens were analyzed by X-ray diffraction and it was confirmed that crystalline iron and iron sulfide with an equi-atomic composition coexisted, in accordance with the stable phase relation at ambient temperature, as shown in Fig. 1.
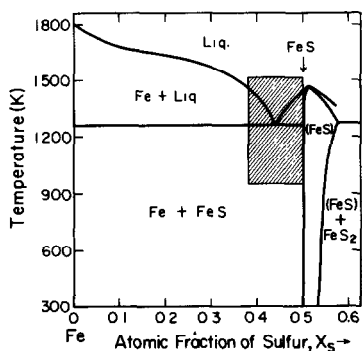

Fig. 1. Phase diagram of the Fe–S binary system [5].

Derivation of thermodynamic quantities

The integral molar mixing free energy of the liquid Fe–S system can be obtained by a thermodynamic analysis method, based on enthalpy increments, $H_T - H_{298.15}$, as follows. The heat content, J_T, is defined as

$$J_T = H_T - H_\theta \tag{1}$$

where H_T and H_θ are the enthalpies of a specimen at T K and a specified reference temperature, θ K, respectively. On the basis of the second law of thermodynamics, we can obtain the following equation:

$$T\int_{1/\theta}^{1/T} J_T \, d(1/T) + H_\theta - TS_\theta = H_T - TS_T \tag{2}$$

By applying eqn. (2) to the pure components A, B and a mixture of mole fraction X of component B, the mixing free energy, $\Delta G_{X,T}^{mix}$, at T K is given by eqn. (3):

$$\Delta G_{X,T}^{mix} = T\left[\int_{1/\theta}^{1/T} J_T \, d(1/T) - (1-X)\int_{1/\theta}^{1/T} J_A \, d(1/T)\right.$$

$$\left. - X\int_{1/\theta}^{1/T} J_B \, d(1/T)\right] + \Delta H_{X,\theta}^{mix} - T\Delta S_{X,\theta}^{mix} \tag{3}$$

where $\Delta H_{X,\theta}^{mix}$ and $\Delta S_{X,\theta}^{mix}$ are the mixing enthalpy and entropy at θ K, respectively. Thus, we can derive the mixing energy solely from the heat contents of the specimens, J_T, provided that the values of $\Delta H_{X,\theta}^{mix}$ and $\Delta S_{X,\theta}^{mix}$ are known. The phase diagram of the Fe–S binary system, as shown in Fig. 1, represents a simple eutectic having a very narrow range of primary solid solution of iron in the range of sulfur content less than $X_S = 0.5$, and almost-pure iron and an equi-atomic compound of FeS coexist below 1261 K. Hence, the term $(\Delta H_{X,\theta}^{mix} - T\Delta S_{X,\theta}^{mix})$, of eqn. (3) is given by eqn. (4) for mixtures in the range of sulfur content less than $X_S = 0.5$, provided that a temperature below the eutectic of 1261 K is adopted as the reference:

$$\Delta H_{X,\theta}^{mix} - T\Delta S_{X,\theta}^{mix} = 1/2\, X_S \Delta H_{FeS,\theta}^{f} - 1/2TX_S\Delta S_{FeS,\theta}^{f} \tag{4}$$

where $\Delta H_{FeS,\theta}^{f}$ and $\Delta S_{FeS,\theta}^{f}$ are the molar enthalpy and entropy of formation of FeS at θ K, respectively, and both were well established at moderate temperatures [6].

The integral molar mixing enthalpy of the liquid Fe–S system is given by eqn. (5):

$$\Delta H_{X,T}^{mix} = \Delta H_{X,\theta}^{mix} + J_{X,T} - (1-X)J_{A,T} - XJ_{B,T} \tag{5}$$

The integral molar mixing entropy can also be derived by a combination of eqns. (3) and (5).

RESULTS AND DISCUSSIONS

Heat contents

The enthalpy increments were measured for eight different mixtures of the Fe–S binary system in the solid, solid + liquid, and liquid states, and the results are listed in Table 1. The values for solid FeS reported by Borne-mann and Hengstenberg [1] and Coughlin [2] agree with the present results within the uncertainty of the present experiments ($\pm 2\%$). No literature values were found for the enthalpy increments of the Fe–S mixtures in the solid + liquid or liquid regions. As suggested in Fig. 1, the equi-atomic compound of FeS represents an incongruent melting point. The present results at $X_S = 0.500$ show that the temperature range of the incongruent melting is considerably wide: $T_b < 1265$ and $1469 < T_e$, where T_b and T_e are the temperatures at the beginning and end of incongruent melting, respec-tively, and T_e was estimated to be 1473 ± 4 K. The enthalpy of fusion at a hypothetical melting point of 1473 K was evaluated to be 15.10 ± 0.26 kJ mol^{-1} by extrapolating the present results for solid FeS to 1473 K. The eutectic temperature and composition are 1273 K and $X_S = 0.440$, respec-tively, and the enthalpy of eutectic reaction is 16.30 ± 0.28 kJ mol^{-1}.

The average heat capacities of the liquid Fe–S mixtures were obtained from the tangents of ($H_T - H_{298.15}$) versus temperature plots, and are listed in Table 2. The C_p of the liquid Fe–S mixtures has a tendency to decrease with increasing sulfur content, but in the composition range above the eutectic point it is almost constant at 40 J mol^{-1} K^{-1} within an uncertainty of 1 J mol^{-1} K^{-1}. The value of C_p reported by Coughlin [2] for a liquid mixture corresponding to FeS is 37.2 J mol^{-1} K^{-1}, which is 7% lower than the present results.

Thermodynamic quantities of the liquid Fe–S binary system

On the basis of eqn. (3), the integral molar mixing free energy can be derived through the integration of J_T over $1/T$. Diatomic sulfur gas at 1 atm pressure was chosen as the standard state of sulfur. Hence, $\int_{1/\theta}^{1/T} J_B$ d($1/T$) in eqn. (3) is equal to $\int_{1/\theta}^{1/T} 1/2 J_{S_2}$ d($1/T$), and J_{S_2} was calculated by using the C_p value for diatomic sulfur gas [6]. The results at 1473 K are shown in Fig. 2 together with the integral molar mixing enthalpy and entropy which were derived on the basis of eqn. (5) and by a combination of eqns. (3) and (5), respectively. $\Delta G^{mix}_{X,1473}$ represents a rather simple behaviour against the sulfur compositions, but ΔH^{mix}_{1473} and ΔS^{mix}_{1473} of the liquid mixtures decrease drastically with increasing sulfur content. Nagamori et al. [7] determined ΔH^{mix} and ΔS^{mix} from the temperature dependence of the iron activity and the partial pressure of diatomic sulfur gas which were obtained by means of a gas-equilibration method. Their results are lower

TABLE 1

Enthalpy increment, $H_T - H_{298.15}$, of the Fe–S binary mixtures

Phase	Temp. (K)	$H_T - H_{298.15}$ (kJ mol^{-1})
$X_S = 0.380$		
solid	1005	24.09
	1038	26.80
	1086	27.38
	1128	29.23
	1179	31.06
	1224	33.69
	1268	34.15
solid +	1310	50.28
liquid	1347	52.37
	1396	54.73
	1433	56.52
	1440	57.42
	1452	58.83
liquid	1466	58.98
	1477	59.24
	1494	60.31
	1506	60.75
$X_S = 0.400$		
solid	978	21.99
	1027	23.95
	1065	25.18
	1111	27.04
	1171	29.32
	1224	32.10
	1244	32.28
solid +	1295	48.71
liquid	1318	49.47
	1339	50.44
	1353	52.05
	1401	54.68
	1436	55.79
	1452	57.95
liquid	1464	59.40
	1479	60.21
	1488	60.60
	1503	61.19

TABLE 1 (continued)

Phase	Temp. (K)	$H_T - H_{298.15}$ (kJ mol^{-1})
$X_S = 0.420$		
solid	1057	25.65
	1112	27.20
	1164	30.24
	1180	31.36
	1222	32.20
	1238	34.01
solid +	1286	49.11
liquid	1312	51.45
	1323	52.03
	1367	53.70
	1402	55.40
liquid	1410	56.95
	1425	57.84
	1458	58.62
	1470	59.82
	1482	59.90
	1487	60.56
$X_S = 0.440$		
solid	942	20.57
	981	23.05
	1071	26.17
	1125	27.56
	1174	30.08
	1218	30.72
	1254	32.30
	1273	33.85
liquid	1309	51.18
	1313	51.22
	1360	53.14
	1376	54.75
	1440	57.13
	1487	58.87
$X_S = 0.455$		
solid	1010	24.46
	1053	26.45
	1106	27.35
	1145	29.15
	1199	30.22
	1246	32.74

TABLE 1 (continued)

Phase	Temp. (K)	$H_T - H_{298\,15}$ (kJ mol^{-1})
solid +	1299	48.05
liquid	1314	50.37
	1323	52.63
liquid	1357	53.98
	1373	54.76
	1393	55.56
	1429	56.32
	1459	57.85
	1476	59.21
$X_S = 0.470$		
solid	954	20.75
	1044	23.61
	1106	25.24
	1153	28.50
	1230	30.88
	1255	31.97
solid +	1282	42.73
liquid	1320	43.85
	1356	47.44
	1385	51.42
liquid	1400	53.30
	1420	54.51
	1446	55.87
	1470	56.03
	1498	57.46
$X_S = 0.485$		
solid	1018	24.99
	1106	28.51
	1201	31.42
	1228	32.60
	1261	33.88
solid +	1313	39.43
liquid	1372	35.94
	1396	49.28
	1401	53.57
liquid	1406	55.76
	1435	56.95
	1480	58.67
	1488	59.32
	1496	59.72

TABLE 1 (continued)

Phase	Temp. (K)	$H_T - H_{298\,15}$ (kJ mol^{-1})
$X_S = 0.500$		
solid	981	21.76
	1018	23.06
	1105	25.90
	1158	27.84
	1196	29.74
solid +	1265	31.79
liquid	1286	32.46
	1359	34.53
	1391	38.69
	1441	44.65
	1454	48.76
	1465	52.41
	1469	53.92
liquid	1482	55.02
	1493	55.15
	1509	56.07
	1512	56.15

than the present ones, and the maximum discrepancies in ΔH^{mix} and ΔS^{mix} are 11 and 35%, respectively.

By the use of a tangential-intercepts method, the partial molar mixing free energies or activities can be derived from the integral molar mixing energy versus composition plots shown in Fig. 2, and the activities of iron and iron sulfide as well as the partial pressure of diatomic sulfur at 1473 K are shown in Fig. 3. The International Copper Research Association, INCRA [8], selected values of iron activity and the partial pressure of diatomic sulfur from literature values which were determined by gas-equilibration methods, and the selected values are shown with broken lines in Fig. 3. Both a_{Fe} and

TABLE 2

Average heat capacity of the liquid Fe–S mixtures

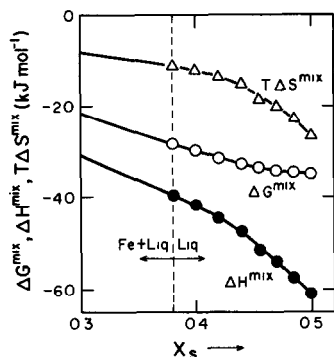| X_S	Temperature range (K)	C_p (J mol^{-1} K^{-1})
0.380	1460–1506	46 ± 2
0.400	1455–1503	45 ± 2
0.420	1405–1487	45 ± 1.5
0.440	1273–1487	44 ± 1.5
0.455	1355–1476	40 ± 1
0.470	1390–1498	40 ± 1
0.485	1405–1496	40 ± 1
0.500	1473–1512	40 ± 1

Fig. 2. Integral molar mixing free energy, enthalpy and entropy of the liquid Fe–S mixtures at 1473 K (standard state, Fe: solid iron, S: $1/2$ S_2 (g)).

p_{S_2} obtained in this study agreed satisfactorily with the selected values, and it is suggested that the thermodynamic analysis method based on calorimetry is a useful method for determining thermodynamic quantities at high temperature.

The standard free energy of the equi-atomic FeS compound for the following reaction,

$$Fe(s) + 1/2S_2(g) = FeS(l) \tag{6}$$

is given by eqn. (7):

$$\Delta G_T^0 = 2\Delta G_{X_S=0.5,T}^{mix} \tag{7}$$

By the use of $\Delta G_{X_S=0.5}^{mix}$ at 1473 and 1523 K, which were determined in this study, ΔG_T^0 was obtained as

$$\Delta G_T^0 = -119.22 + 3.33 \times 10^{-2}T \text{ (kJ mol}^{-1}) \tag{8}$$

and is shown in Fig. 4 together with other literature values [6–10]. Although appreciable discrepancies are observed between the literature values, the present results are closest to those of Bale and Toguri [9] who used TGA as
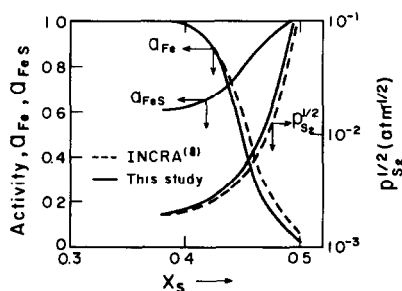

Fig. 3. Activities of iron and iron sulfide and partial pressure of diatomic sulfur at 1473 K.
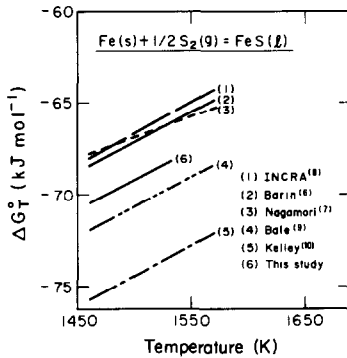
Fig. 4. Standard free energy of formation of FeS.

a method to determine the sulfur composition of a liquid specimen after equilibration and avoided problems associated with the conventional chemical analysis method for determining sulfur content from a sample of $BaSO_4$.

CONCLUSIONS

The thermodynamic analysis method was applied to the liquid Fe–S mixtures to determine the integral molar mixing free energy, enthalpy and entropy as well as the partial molar mixing free energies. The results agreed satisfactorily with the selected literature values, predicting that this method might be useful for obtaining the thermodynamic quantities of high temperature, liquid mixtures with the highly volatile semi-metals or chalcogen, including sulfur whose thermodynamic investigations are becoming increasingly important in the field of electronic materials.

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