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THERMODYNAMIC INVESTIGATION OF THE LIQUID Pb-S SYSTEM BY USING A DROP CALORIMETER

K. ITAGAKI[1] and A. YAZAWA[1]

[1]Research Institute of Mineral Dressing and Metallurgy (SENKEN),
Tohoku University, 980 Sendai (Japan)

ABSTRACT

Heat contents of the Pb-S system were measured by a drop calorimeter in the composition range of sulfur X_S= 0 to 0.5 (PbS) and in the temperature range of 560 to 1500 K, and a heat content-temperature-composition ternary diagram was constructed. By using a quantitative thermodynamic analysis method, free energy, heat and entropy of mixing in the liquid Pb-S binary and Pb-PbS pseudo-binary systems were derived from the measured heat contents. The obtained partial molar free energies of mixing (activities) are considerably different from those estimated by the use of a regular solution model.

INTRODUCTION

Thermodynamic data on the liquid Pb-S system are indispensable for establishing equilibrium models for direct smelting of PbS concentrates to Pb (ref. 1). Conventional methods for determining vapor pressure are very difficult to apply to the liquid Pb-S system because of high vapor pressure of PbS and complexity of the vapor species.

The thermodynamic quantities of liquid binary systems can be obtained in a calorimetric method by the use of a quantitative thermodynamic analysis method which was developed by Oelsen (ref.2). In the present study, this method was conducted for the Pb-S binary and Pb-PbS pseudo-binary systems using a drop calorimeter as an experimental apparatus.

METHODS

Theory of quantitative thermodynamic analysis

The theory of quantitative thermodynamic analysis is summarized as follows. The heat content, J_T, is defined as

$$J_T = H_T - H_\theta \quad (1)$$

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 the thermodydynamics, we can obtain the following equations;

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

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

$$\Delta G^{\mathrm{mix}}_{x,T}=T\left\{\int_{1/\theta}^{1/T} J_x\,\mathrm{d}(1/T)-x\int_{1/\theta}^{1/T} J_\mathrm{A}\mathrm{d}(1/T)-(1-x)\int_{1/\theta}^{1/T} J_\mathrm{B}\mathrm{d}(1/T)\right\}+\Delta H^{\mathrm{mix}}_{x,\theta}-T\Delta S^{\mathrm{mix}}_{x,\theta} \tag{3}$$

where $\Delta H^{\mathrm{mix}}_{x,\theta}$ and $\Delta S^{\mathrm{mix}}_{x,\theta}$ are the heat and entropy of mixing at θ K, respectively. The heat and entropy of mixing at T K are given by eqs. (4) and (5), respectively

$$\Delta H^{\mathrm{mix}}_{x,T}=\Delta H^{\mathrm{mix}}_{x,\theta}+J_{x,T}-xJ_{\mathrm{A},T}-(1-x)J_{\mathrm{B},T} \tag{4}$$

$$\Delta S^{\mathrm{mix}}_{x,T}=\Delta S^{\mathrm{mix}}_{x,\theta}+1/T\left[J_{x,T}-xJ_{\mathrm{A},T}-(1-x)J_{\mathrm{B},T}\right]-\left\{\int_{1/\theta}^{1/T} J_x\,\mathrm{d}(1/T)-x\int_{1/\theta}^{1/T} J_\mathrm{A}\mathrm{d}(1/T)-(1-x)\int_{1/\theta}^{1/T} J_\mathrm{B}\,\mathrm{d}(1/T)\right\} \tag{5}$$

Thus, we can derive the free energy, heat and entropy of mixing solely from the heat contents of the specimen, J_T, if the values of $\Delta H^{\mathrm{mix}}_{x,\theta}$ and $\Delta S^{\mathrm{mix}}_{x,\theta}$ at a reference temperature are known. The Pb-S system forms a stoichiometric compound of PbS and has no solid solution, and we can obtain $\Delta H^{\mathrm{mix}}_{x,\theta}$ and $\Delta S^{\mathrm{mix}}_{x,\theta}$ from the heat and entropy of formation of PbS which were well established (ref.3).

Experimental apparatus and procedures

A drop calorimeter was used as an experimental apparatus. The details of the apparatus are described in a separate paper (ref.4). The samples were prepared with lead and lead sulfides which had been synthesized with powders of lead and sulfur (99.99% purity). About 10 g of sample was put into a vacuum-sealed quartz container with an inner diameter of 20 mm and a height of 20 mm to avoid the oxidation and evaporation. The experiments were conducted for ten systems having different ratios of sulfur to lead ($0 \leqq X_S \leqq 0.5$) in the temperature range of 560 to 1500 K. The specimens after the experiments were analyzed by x-ray diffraction and confirmed to be the mixture of crystalline lead and lead sulfide, corresponding to the stable, final states in the phase diagram.

EXPERIMENTAL RESULTS

Heat contents

The enthalpy increments, $H_T - H_{298.15}$, at given temperatures are listed in Table 1. The heat contents, J_T, defined by eq. (1) are illustrated three dimensionally in Fig. 1. The reference temperature, θ, for J_T is 560 K.

Much information concerning the thermochemical properties such as specific

TABLE 1

$H_T - H_{298.15}$ /kJ·mol^{-1} of the Pb-S binary system.

Temp. (K)	atomic fraction of sulfur				
	0	0.048	0.103	0.168	0.229
600	8.7	8.4	8.5	8.6	8.5
700	16.5	15.3	15.2	13.3	13.8
800	19.4	18.1	17.7	16.6	16.4
900	22.3	21.5	20.8	19.8	18.9
1000	25.2	24.9	24.3	23.1	21.8
1100	28.1	29.3	28.3	26.5	25.5
1200	31.3	34.4	36.0	32.8	30.4
1300	34.5	37.3	40.3	44.5	41.3
1400	37.6	40.1	44.4	47.6	51.0
1450	39.2	41.5	46.5	49.1	53.0
1500	40.8	42.9	48.5	50.7	54.9
	0.315	0.344	0.393	0.438	0.500
600	8.6	8.6	8.6	8.3	7.9
700	12.5	11.9	11.1	11.0	10.2
800	14.7	14.1	13.5	13.1	12.9
900	17.3	17.1	16.0	15.3	15.6
1000	20.9	20.4	18.6	18.4	18.3
1100	25.9	24.5	22.4	22.2	21.3
1200	30.3	29.0	26.4	26.1	24.3
1300	39.3	37.1	32.5	32.5	27.2
1400	53.0	52.6	53.5	52.4	30.3
1450	55.0	55.1	55.8	55.1	51.5
1500	57.0	57.5	58.1	57.8	53.5

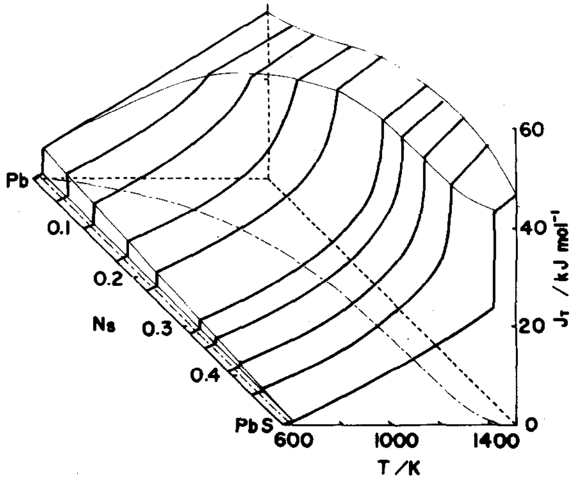

Fig. 1. Heat contents, J_T, of the Pb-S binary system.

heat and heat of phase changes is involved in this figure. The deflection points in the J_T-T curves correspond to the temperatures of phase changes, and we can obtain the phase diagram by projecting these points on the bottom T-N plane, as shown with a dash-dot line in Fig. 1. The liquidus and eutectic temperatures agree well with those by Miller and Komarek (ref.5). The melting point of PbS is 1417 K and considerably higher than reported values. The heat of fusion of PbS is 38.0 ± 0.6 kJ·mol^{-1} and slightly larger than the selected value of 36.4 kJ·mol^{-1} (ref.3).

Thermodynamic quantities of the liquid Pb-S binary system

On the basis of eq. (3), the free energy of mixing can be derived through the integration of J_T over 1/T. The values of $T\int_{1/\theta}^{1/T} J_x d\frac{1}{T}$ at 1473 K for the Pb-S binary system are plotted in Fig. 2 (curve I). The values of $\Delta H_{x,\theta}^{\mathrm{mix}}$ and $\Delta S_{x,\theta}^{\mathrm{mix}}$ at the reference temperature of 560 K are not zero because a compound PbS is existing at 560 K. As illustrated with broken line II in Fig. 2, the terms, ($\Delta H_{x,\theta}^{\mathrm{mix}} - T\Delta S_{x,\theta}^{\mathrm{mix}}$), on the right hand side of eq. (3) could be obtained by the use of the published data on the standard free energy and entropy of the formation of PbS (ref.3) because the Pb-S system is composed of crystalline lead and lead sulfide and has no solid solution at 560 K. The free energy of mixing at 1473 K, (curve III), was obtained through the addition of the term, ($\Delta H_{x,\theta}^{\mathrm{mix}}$-$T\Delta S_{x,\theta}^{\mathrm{mix}}$), to the difference between curve I and a line which ties points a and c in Fig. 2. The standard free energy of formation, ΔG_T° , for the following reaction

$$Pb(l) + \frac{1}{2} S_2(g) = PbS(l) \qquad (6)$$

was obtained on the basis of eq. (7) and is given by eq. (8).

$$\Delta G_T^{\circ} = 2\,\Delta G_{N_S=0.5,T}^{\mathrm{mix}} \qquad (7)$$

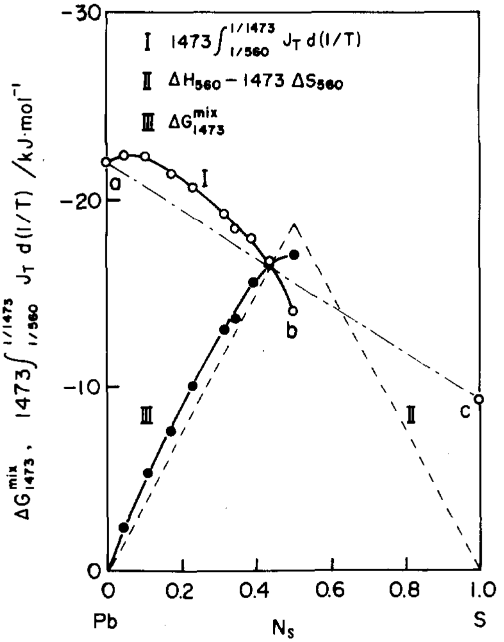

Fig. 2. $T\int_{1/\theta}^{1/T} J_x d\frac{1}{T}$ plots and the free energy of mixing in the liquid Pb-S binary system at 1473 K.

$$\Delta G_T^\circ = -122.50 + 0.060\ T \quad (\mathrm{kJ \cdot mol^{-1}}) \quad (\ T = 1417 \sim 1500\ \mathrm{K}\ ) \qquad (8)$$

The heat and entropy of mixing in the liquid Pb-S binary system were obtained on the basis of eqs. (4) and (5), respectively.

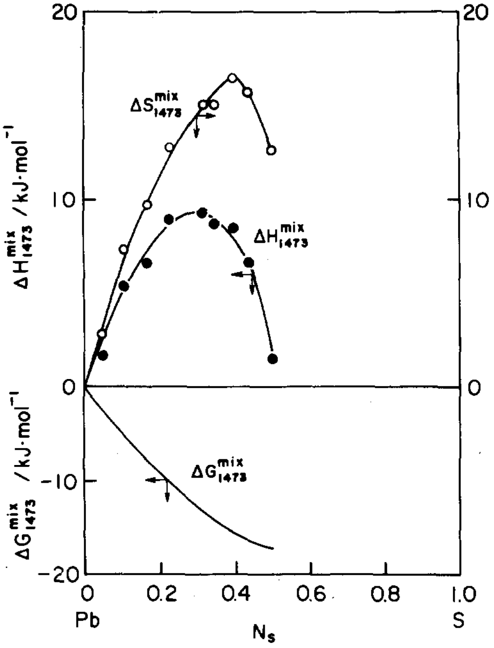

Fig. 3. Free energy, heat and entropy of mixing in the liquid Pb-S binary system at 1473 K.

The free energy, heat and entropy of mixing in the liquid Pb-S binary system at 1473 K are shown in Fig. 3. The standard states are liquid lead and diatomic sulfur gas of 101.325 kPa. It is noticed that the heat and entropy of mixing represent large, positive values but drastically get smaller as the composition approaches $X_S = 0.5$.

By the use of a tangential-intercepts method, partial molar free energies of mixing or activities can be derived from the obtained integral free energy of mixing versus composition plots, and the activities of lead and lead sulfide (a_{Pb} and a_{PbS}) and the partial pressure of diatomic sulfur (p_{S_2}) are shown in Fig. 4. Schuhmann et al. (ref.6) calculated these quantities by using a regular solution model, as illustrated with broken lines in Fig. 4, being considerably different from the present, experimentally determined values.

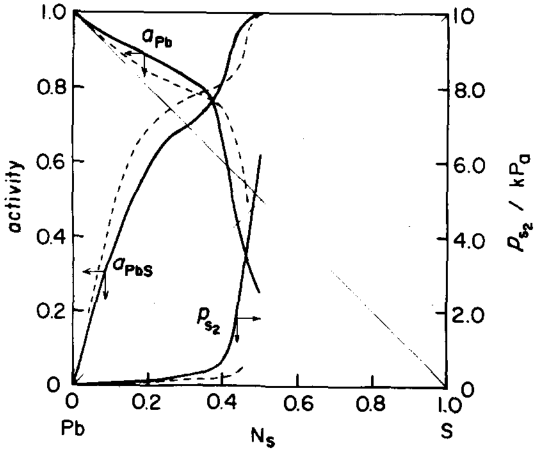

Fig. 4. Activities of the liquid Pb-S binary system at 1473.
----Schuhmann et al., —— This study

Thermodynamic quantities of the liquid Pb-PbS pseudo-binary system

As illustrated in Fig. 1, the Pb-PbS pseudo-binary system presents a simple eutectic having no primary solid solution, and both $\Delta H^{\mathrm{mix}}_{x,\theta}$ and $\Delta S^{\mathrm{mix}}_{x,\theta}$ at the reference temperature of 560 K are zero. Consequently, on the basis of eq. (3), the free energy of mixing at 1473 K for the liquid Pb-PbS pseudo-binary system can be obtained through the difference between curve I and a line which ties points a and b in Fig. 2. The free energy, heat and entropy of mixing in the liquid Pb-PbS pseudo-binary system at 1473 K are shown in Fig. 5. The heat and entropy of mixing represent considerably large, positive values. The excess entropy of mixing, ($\Delta S^{\mathrm{mix}}_{1473}$ — $\Delta S^{\mathrm{mix}}_{\mathrm{ideal}}$), represents a large, positive values, showing that the liquid Pb-PbS does not obey a regular solution.

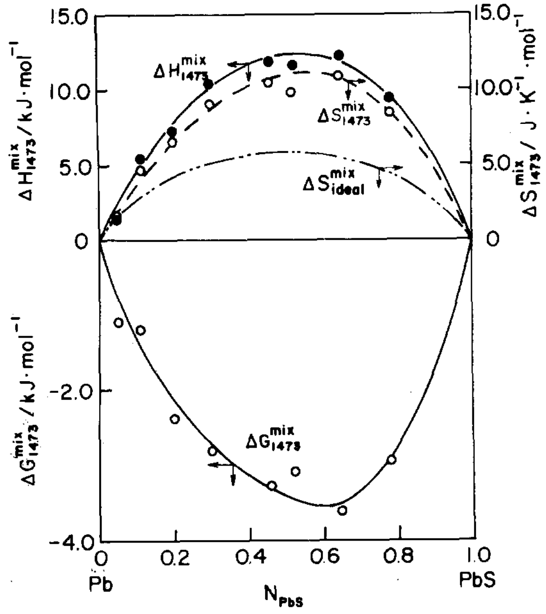

Fig. 5. Free energy, heat and entropy of mixing in the liquid Pb-PbS pseudo-binary system at 1473 K.

SUMMARY

The quantitative thermodynamic analysis method by the use of a drop calorimeter is substantially useful for obtaining not only the heat of mixing but also the free energy and entropy of mixing in liquid binary systems though this method is not so familiar in the field of calorimetry, and we expect that it will be extensively employed.

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