Measurements of Thermodynamic Quantities for Molten Ag_2S – Sb_2S_3 and Cu_2S – Ni_3S_2 Systems by Quantitative Thermodynamic Analysis*

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Measurements of thermodynamic quantities for the molten Ag_2S – Sb_2S_3 and Cu_2S – Ni_3S_2 binary mixtures were carried out by using a quantitative thermodynamic analysis method. A double adiabatic wall calorimeter was used as an experimental apparatus to accurately determine heat contents of the sulfide mixtures.

The activities, $a_{\text{Ag}_2\text{S}}$ and $a_{\text{Sb}_2\text{S}_3}$, for the Ag_2S – Sb_2S_3 system at 1123 K presented considerably large, negative deviations from Raoultian behaviour, and the excess stability showed a large maximum in the vicinity of the Sb_2S_3 mole fraction of 0.25, suggesting the influence of a compound of Ag_3SbS_3 . On the other hand, the activities, $a_{\text{Cu}_2\text{S}}$ and $a_{\text{Ni}_3\text{S}_2}$, for the Cu_2S – Ni_3S_2 system at 1423 K presented small deviations from ideal mixing.

(Received November 1, 1983)

Keywords: Ag_2S , Sb_2S_3 , Cu_2S , Ni_3S_2 , heat content, activity, calorimetry

I. Introduction

Matte phases which are composed of molten, mixed sulfides of heavy metals are important intermediate products in the extractions of copper, nickel and lead from their concentrates. A little, however, is known about the thermodynamics of mattes as compared with alloys, slags and fused salts.

The thermodynamic quantities of molten binary systems can be obtained in a calorimetric method by the use of a quantitative thermodynamic analysis method which was developed by Oelsen⁽¹⁾. In the present investigation this method was conducted for the Ag_2S – Sb_2S_3 and Cu_2S – Ni_3S_2 systems using a double adiabatic wall calorimeter as an experimental apparatus.

II. 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 thermodynamics, we can obtain the following equations:

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

By applying eq. (2) to the pure components A, B and a mixture of the mole fraction N of the

component A, the free energy of mixing, $\Delta G_{N,T}^{\text{mix}}$, at T K is given by eq. (3).

$$\Delta G_{N,T}^{\text{mix}} = T \left[\int_{1/\theta}^{1/T} J_T d(1/T) - N \int_{1/\theta}^{1/T} J_A d(1/T) - (1-N) \int_{1/\theta}^{1/T} J_B d(1/T) \right] + \Delta H_{N,\theta}^{\text{mix}} - T \Delta S_{N,\theta}^{\text{mix}}, \quad (3)$$

where $\Delta H_{N,\theta}^{\text{mix}}$ and $\Delta S_{N,\theta}^{\text{mix}}$ are the heat and entropy of mixing at θ K, respectively. Thus, we can derive the free energy of mixing solely from the heat contents of the specimen, J_T , if the values of $\Delta H_{N,\theta}^{\text{mix}}$ and $\Delta S_{N,\theta}^{\text{mix}}$ are known.

The phase diagram of the Cu_2S – Ni_3S_2 binary system represents a simple eutectic

* This paper was originally published in Japanese in J. Japan Inst. Metals, **46** (1982), 1145.

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having a narrow range of primary solid solution, and both $\Delta H_{N,\theta}^{\text{mix}}$ and $\Delta S_{N,\theta}^{\text{mix}}$ are considered to be nearly zero, provided that a temperature below the eutectoid of 808 K is adopted as the reference. Although the $\text{Ag}_2\text{S}-\text{Sb}_2\text{S}_3$ binary system forms stoichiometric compounds of Ag_3SbS_3 and AgSbS_2 , both $\Delta H_{N,\theta}^{\text{mix}}$ and $\Delta S_{N,\theta}^{\text{mix}}$ of these compounds are known⁽²⁾.

III. Experimental Apparatus and Procedures

As the quantitative thermodynamic analysis is applied, a cooling process method has been used in which a specimen is cooled down in a water calorimeter to determine the heat contents⁽³⁾⁻⁽⁵⁾. Although this method is useful for metallic substances, it can't be employed for non-metallic ones of which the thermal conductivities are quite low, due to the lack of temperature uniformity within the specimen. Recently, the authors have noticed that a heating process method using an adiabatic calorimeter might be effective not only for the metallic substances, but also for the non-metallic ones, because the temperature difference within the specimen can be reduced to much extent by using an adiabatic calorimeter⁽⁶⁾. In the present investigation, the heating process method was conducted for the $\text{Ag}_2\text{S}-\text{Sb}_2\text{S}_3$ and $\text{Cu}_2\text{S}-\text{Ni}_3\text{S}_2$ systems.

A double adiabatic wall calorimeter developed by one of the authors was used as an experimental apparatus. The details of the apparatus are described in a separate paper⁽⁷⁾. The construction of a container of the specimen is illustrated in Fig. 1. In order to obtain accurate data for non-metallic substances, a larger surface area and a shorter path for heat transfer are desirable, and the heater is located at the position of about one half of the sample radius. A vacuum-sealed quartz cell was used as a sample container to avoid the experimental difficulties arising from evaporation of the sulfide materials at elevated temperatures. The starting sulfides of Ag_2S , Sb_2S_3 , Cu_2S and Ni_3S_2 were synthesized by reaction between high purity metal and sulfur powders in a vacuum-sealed silica tube and homogenized by melting and slowly cooling. Before the ex-

Fig. 1 Construction of a container of the specimen.

- 1: silica container of the specimen (vacuum-sealed)
- 2: specimen
- 3: nichrome heater (isolated with silica wool)
- 4: thermocouple (alumel-chromel)
- 5: platinum foil

periments, the weighed mixtures of sulfides were melted down in a vacuum-sealed quartz tube, in order to achieve phase equilibrium within the sample during the experiments.

The sample was heated continuously by supplying a constant electric power of 0.4 J/s to the sample heater, and the time taken for elevating the temperature by 1 K was recorded. The experiments were conducted in the temperature range from 623 to 1123 K for the $\text{Ag}_2\text{S}-\text{Sb}_2\text{S}_3$ system and from 773 to 1423 K for the $\text{Cu}_2\text{S}-\text{Ni}_3\text{S}_2$ system.

IV. Experimental Results

The heat contents, J_T , for the $\text{Ag}_2\text{S}-\text{Sb}_2\text{S}_3$ and $\text{Cu}_2\text{S}-\text{Ni}_3\text{S}_2$ systems are illustrated three-dimensionally in Figs. 2 and 3, respectively. Much information concerning the thermochemical properties such as specific heat and

Fig. 2 Heat contents, J_T for the Ag_2S – Sb_2S_3 system. Fig. 3 Heat contents, J_T for the Cu_2S – Ni_3S_2 system.

heat of fusion is involved in these figures. 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. The liquidus and eutectic temperatures for the Ag_2S – Sb_2S_3 system are about 10 K higher than those reported by Jaeger and Klooster⁽⁸⁾. The liquidus and eutectoid temperatures for the Cu_2S – Ni_3S_2 system are 5–10 K lower than those reported by Köster and Multifinger⁽⁹⁾, whereas the eutectic temperatures are 15 K higher than their values. The obtained numerical value for some thermochemical properties are listed in Tables 1 and 2. Concerning the thermochemical properties, there exist no comparable previous data except for the heats of fusion of some compounds. The obtained heat of fusion for Ag_2S agrees with the value of $7.97 \text{ kJ} \cdot \text{mol}^{-1}$ which was reported by Thompson and Flengas⁽¹⁰⁾, whereas that for Sb_2S_3 is 5.7 kJ smaller than the selected value of $46.9 \text{ kJ} \cdot \text{mol}^{-1}$ ⁽¹¹⁾. The heat of fusion for $\text{Ag}_{1.5}\text{Sb}_{0.5}\text{S}_{1.5}$ is 2.4 kJ greater than the

Table 1 Heats of phase change of the Ag_2S – Sb_2S_3 system.

Phase change	Point of phase change		$\Delta H / \text{kJ} \cdot \text{mol}^{-1}$
Fusions	Ag_2S	$1113 \pm 2 \text{ K}$	7.66 ± 0.23
	Sb_2S_3	$824 \pm 2 \text{ K}$	41.21 ± 1.24
	$\text{Ag}_{1.5}\text{Sb}_{0.5}\text{S}_{1.5}$	$756 \pm 2 \text{ K}$	22.05 ± 0.66
	AgSbS_2	$787 \pm 2 \text{ K}$	17.74 ± 0.53
Eutectic reactions	$N_{\text{Sb}_2\text{S}_3} = 0.195$	$736 \pm 2 \text{ K}$	15.86 ± 0.48
	$N_{\text{Sb}_2\text{S}_3} = 0.350$	$735 \pm 2 \text{ K}$	16.95 ± 0.51
	$N_{\text{Sb}_2\text{S}_3} = 0.730$	$733 \pm 2 \text{ K}$	22.38 ± 0.67
Transformations	Ag_2S	$859 \pm 2 \text{ K}$	0.83 ± 0.03
	AgSbS_2	$648 \pm 2 \text{ K}$	13.10 ± 0.39

Table 2 Heats of phase change of the Cu_2S – Ni_3S_2 system.

Phase change	Point of phase change		$\Delta H / \text{kJ} \cdot \text{mol}^{-1}$
Fusions	Cu_2S	$1398 \pm 4 \text{ K}$	9.70 ± 0.49
	Ni_3S_2	$1043\text{--}1063 \pm 2 \text{ K}$	20.84 ± 0.62
Eutectoid reaction	$N_{\text{Ni}_3\text{S}_2} = 0.950$	$803 \pm 2 \text{ K}$	53.56 ± 1.61
Eutectic reaction	$N_{\text{Ni}_3\text{S}_2} = 0.830$	$993 \pm 2 \text{ K}$	17.57 ± 0.53

value reported by Golovei *et al.*⁽¹²⁾. The obtained heats of fusion for Cu_2S and Ni_3S_2 agree well with the values of $9.62 \text{ kJ} \cdot \text{mol}^{-1}$ ⁽¹³⁾ and $19.75 \text{ kJ} \cdot \text{mol}^{-1}$ ⁽¹⁴⁾, respectively.

On the basis of eq. (3), the free energy of mixing can be derived through the integration of J_T over $1/T$. In Fig. 4, the values of $T[\int_{1/0}^{1/T} J_T d(1/T)]$ at 1123 K and $\Delta G_{1123}^{\text{mix}}$ for the Ag_2S – Sb_2S_3 system are plotted. The plots of $T[\int_{1/0}^{1/T} J_T d(1/T)]$ for the Ag_2S – Sb_2S_3 system represent the anomalous behaviour in forming two minima at the compositions of Sb_2S_3 , $N_{\text{Sb}_2\text{S}_3} = 0.25$ and 0.5 , respectively. This arises from the fact that the values of $\Delta H_{623}^{\text{mix}}$ and $\Delta S_{623}^{\text{mix}}$ at the reference temperature of 623 K are not zero because the two compounds of $\text{Ag}_{1.5}\text{Sb}_{0.5}\text{S}_{1.5}$ ($N_{\text{Sb}_2\text{S}_3} = 0.25$) and AgSbS_2 ($N_{\text{Sb}_2\text{S}_3} = 0.5$) are existing at 623 K . The terms, $(\Delta H_{623}^{\text{mix}} - 1123\Delta S_{623}^{\text{mix}})$, on the right hand side of eq. (3) calculated from the published data⁽²⁾ are shown in Fig. 4 (broken line II). The free energy of mixing at 1123 K , $\Delta G_{1123}^{\text{mix}}$ (curve III), was obtained through the addition of these

terms to the difference between curve I and line V. $\Delta G_{1123}^{\text{mix}}$ represents considerably large, negative deviation from ideal mixing, indicated

Fig. 4 $T[f_{1/123}^{1/T} J_T d(1/T)]$ plots and the free energy of mixing for the Ag_2S - Sb_2S_3 system at 1123 K.

Fig. 5 $T[f_{1/1423}^{1/T} J_T d(1/T)]$ plots and the free energy of mixing for the Cu_2S - Ni_3S_2 system at 1423 K.

by curve IV in Fig. 4. The values of $T[f_{1/123}^{1/T} J_T d(1/T)]$ at 1423 K and $\Delta G_{1423}^{\text{mix}}$ for the Cu_2S - Ni_3S_2 system are plotted in Fig. 5. The free energy of mixing at 1423 K, $\Delta G_{1423}^{\text{mix}}$ (curve II), was obtained through the difference between curve I and line IV, because the values of $\Delta H_{773}^{\text{mix}}$ and $\Delta S_{773}^{\text{mix}}$ were considered to be zero. $\Delta G_{1243}^{\text{mix}}$ is slightly positive in the composition range below $N_{\text{Ni}_3\text{S}_2}=0.4$, and shows a very small, negative deviation from ideal mixing (curve III) in the high concentration range of Ni_3S_2 .

V. Discussion

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. The activities of the Ag_2S - Sb_2S_3 system at 1123 K which were obtained by this method are illustrated in Fig. 6. Both $a_{\text{Ag}_2\text{S}}$ and $a_{\text{Sb}_2\text{S}_3}$ show considerably large negative deviations from Raoultian behaviour, suggesting the influence of the compounds of Ag_3SbS_3 and AgSbS_2 . The activities for the Cu_2S - Ni_3S_2 system at 1423 K are illustrated in Fig. 7. Both $a_{\text{Cu}_2\text{S}}$ and $a_{\text{Ni}_3\text{S}_2}$ present small deviations from Raoultian behaviour. Matousek and Samis⁽¹⁵⁾ reported the value of $a_{\text{Cu}_2\text{S}}=0.84$ at $N_{\text{Cu}_2\text{S}}=0.82$ and 1473 K, which is in good agreement with the present one. In Figs. 8 and 9, $\log \gamma_i$ is plotted

Fig. 6 Activities of the Ag_2S - Sb_2S_3 system at 1123 K.

Fig. 7 Activities of the $\text{Cu}_2\text{S}-\text{Ni}_3\text{S}_2$ system at 1423 K. Fig. 8 Activity coefficients of the $\text{Ag}_2\text{S}-\text{Sb}_2\text{S}_3$ system at 1123 K. Fig. 9 Activity coefficients of the $\text{Cu}_2\text{S}-\text{Ni}_3\text{S}_2$ system at 1423 K.

against $(1-N_i)^2$. The activity coefficients become proportional to the values of $(1-N_i)^2$ at the two extreme limits of the composition, because Raoult's and Henry's laws are applicable to the solvent and the solute, respectively. By extrapolation, the activity coefficients at infinite dilution, $\gamma_{\text{Ag}_2\text{S}}^\circ$ and $\gamma_{\text{Sb}_2\text{S}_3}^\circ$, for the $\text{Ag}_2\text{S}-\text{Sb}_2\text{S}_3$ system were estimated at 1123 K to be 0.05 and 1.3×10^{-3} , respectively. Similarly, $\gamma_{\text{Cu}_2\text{S}}^\circ$ and $\gamma_{\text{Ni}_3\text{S}_2}^\circ$ for the $\text{Cu}_2\text{S}-\text{Ni}_3\text{S}_2$ system were estimated at 1423 K to be 0.9 and 1.4, respectively. Darken⁽¹⁶⁾ proposed a thermodynamic function, as follows;

$$\text{excess stability} \equiv \frac{d^2 \Delta G^{\text{ex}}}{dN_i^2} = -\frac{2RT d \ln \gamma_i}{d(1-N_i)^2}. \quad (4)$$

The excess stabilities for the $\text{Ag}_2\text{S}-\text{Sb}_2\text{S}_3$ and $\text{Cu}_2\text{S}-\text{Ni}_3\text{S}_2$ systems can be derived from the slopes of the $\log \gamma_i$ versus $(1-N_i)^2$ plots in Figs. 8 and 9, respectively, and are shown in Fig. 10. The excess stability for the $\text{Ag}_2\text{S}-\text{Sb}_2\text{S}_3$ system represents a large maximum in the vicinity of the mole fraction, $N_{\text{Sb}_2\text{S}_3} = 0.25$, which corresponds to the composition where a stoichiometric compound of Ag_3SbS_3 is located, and the behaviour might be explained by assuming the existence of some complex ions such as SbS_3^{-3} in the melt. On the other hand,

Fig. 10 Excess stabilities of the $\text{Ag}_2\text{S}-\text{Sb}_2\text{S}_3$ system at 1123 K and the $\text{Cu}_2\text{S}-\text{Ni}_3\text{S}_2$ system at 1423 K.

Fig. 11 Activities of the $\text{AgS}_{0.5}$ - $\text{SbS}_{1.5}$ system at 1123 K and the $\text{CuS}_{0.5}$ - $\text{NiS}_{0.667}$ system at 1423 K.

the excess stability for the Cu_2S - Ni_3S_2 system is considerably small, and even the negative values are presented in the high concentration range of Cu_2S , suggesting a tendency to phase separation.

Nagamori⁽¹⁷⁾ conducted a thermodynamic study on Cu-Fe-S and Cu-Ni-S melts and proposed to represent their pseudobinary systems by $\text{FeS-CuS}_{0.5}$ and $\text{CuS}_{0.5}\text{-NiS}_{0.667}$, respectively, whose constituents are sulfides of monatomic metal. The present activity data for the $\text{Ag}_2\text{S-Sb}_2\text{S}_3$ and $\text{Cu}_2\text{S-Ni}_3\text{S}_2$ systems were rearranged for the $\text{AgS}_{0.5}\text{-SbS}_{1.5}$ and $\text{CuS}_{0.5}\text{-NiS}_{0.667}$ systems, and the results are shown in Fig. 11. The activities for these systems deviate considerably from Raoultian behaviours, though the activities for the $\text{CuS}_{0.5}\text{-FeS}$ system nearly obey Raoult's law⁽¹⁸⁾. The activity coefficients at infinite dilution, $\gamma_{\text{AgS}_{0.5}}^\circ$ and $\gamma_{\text{SbS}_{1.5}}^\circ$, for the $\text{AgS}_{0.5}\text{-SbS}_{1.5}$ system were estimated at 1123 K to be 0.44 and 0.36, respectively. Similarly, $\gamma_{\text{CuS}_{0.5}}^\circ$ and $\gamma_{\text{NiS}_{0.667}}^\circ$ for the $\text{CuS}_{0.5}\text{-NiS}_{0.667}$ system were estimated at 1423 K to be 5.6 and 8.3, respectively.

VI. Conclusion

The thermodynamic quantities for the liquid $\text{Ag}_2\text{S-Sb}_2\text{S}_3$ and $\text{Cu}_2\text{S-Ni}_3\text{S}_2$ systems were determined by using a quantitative thermodynamic analysis method. A heating process method

with an adiabatic calorimeter was used to determine heat contents of these systems.

The activities, $a_{\text{Ag}_2\text{S}}$ and $a_{\text{Sb}_2\text{S}_3}$, for the $\text{Ag}_2\text{S-Sb}_2\text{S}_3$ binary melts presented considerably large, negative deviations from Raoultian behaviours, and the excess stability showed a large maximum in the vicinity of the composition, $N_{\text{Sb}_2\text{S}_3}=0.25$, suggesting the influence of a compound of AgSbS_3 . On the other hand, the activities, $a_{\text{Cu}_2\text{S}}$ and $a_{\text{Ni}_3\text{S}_2}$, for the $\text{Cu}_2\text{S-Ni}_3\text{S}_2$ system presented small deviations from ideal mixing.

The accuracy of the thermodynamic quantities obtained by the quantitative thermodynamic analysis method depends basically on the exact determination of the heat content, and it is considered that the present method is not inferior to the conventional methods for activity determinations such as vapour pressure and EMF methods, provided that the heat content can be measured within an accuracy of $\pm 2\text{--}3\%$ as in the present experiments. It can be expected that the heating process method will be employed extensively for determining the thermodynamic quantities of various liquid binary mixtures including the systems of non-metallic substances which are important in the field of physicochemistry and in the fundamental branch of metal extraction.

Acknowledgement

The authors wish to express their thanks to Prof. A. Yazawa of Tohoku University for his valuable discussion.

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